

Atomic scale modelling of transition metal dichalcogenide electrocatalysts for the electrocatalytic CO_2 reduction reaction

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Atomic scale modelling of transition metal dichalcogenide electrocatalysts for the electrocatalytic CO_2 reduction reaction

PhD Thesis Pernille Dalsgaard Pedersen

Atomic scale modelling of transition metal dichalcogenide electrocatalysts for the electrocatalytic CO_2 reduction reaction

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Approval

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Pernille Dalsgaard Pedersen

Hersen

Signature

31/07-2023

Date

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Abstract

Electrocatalytic CO_2 reduction (CO2RR) utilizing renewable energy and captured CO_2 from hard-to-abate sectors offers a promising solution for generating net zero fuels and chemicals while serving as an energy storage technology. Existing catalysts suffer from low efficiency and selectivity. One of the main challenges to be overcome in the process of designing new and improved catalysts is the competition with the Hydorgen Evolution Reaction (HER). Among the transition metals copper (Cu) stands out due to its unique ability to reduce CO_2 to highly reduced products, thanks to its intermediate adsorption strength of both CO and H.

The Transition Metal Dichalcogenides (TMDCs) are a group of promising candidate materials. In this thesis the catalytic activity and stability of 2H TMDC edges has been investigated. It is found that the favored edge termination is very dependent on the potential and pH under relevant operating conditions. Also the stability regions of different terminations are significantly different for different TMDCs. The study shows interesting trends in the adsorption energies of H and CO, crucial for the CO2RR selectivity. Larger anion size is found to lead to a shift toward stronger CO adsorption and weaker H adsorption, indicating the possibility of producing "beyond CO" products.

Furthermore, the potential dependence of CO2RR and HER mechanisms on MoTe₂ using Grand Canonical DFT (GC-DFT) is investigated. It is found, that while a purely thermodynamic analysis suggests that the HER is favored, including also kinetics, which is possible only because of the explicit inclusion of potential, CO2RR is in fact favored, in agreement with previous experimental studies. This highlights the necessity of going beyond the Computational Hydrogen Electrode (CHE) model to fully comprehend electrocatalytic activity. Additionally, different intermediate steps exhibit varying potential behaviors, influencing the the balance between HER and CO2RR as well as CO desorption and further reduction.

Resumé

Elektrokatalytisk CO_2 -reduktion (CO2RR) ved hjælp af vedvarende energi og CO_2 opsamlet fra sektorer, der er svære at decarbonisere, kan generere CO_2 -neutrale brændstoffer og kemikalier, og fungerer samtidig som energilagringsteknologi. Eksisterende katalysatorer lider under lav effektivitet og selektivitet. En af de vigtigste udfordringer, der skal overvindes i processen med at designe nye og forbedrede katalysatorer, er konkurrencen med Hydorgen Evolution Reaction (HER). Blandt overgangsmetallerne skiller kobber (Cu) sig ud på grund af dets unikke evne til at reducere CO_2 til stærkt reducerede produkter, takket være dets mellemstærke adsorption af både CO og H.

Overgangsmetal Dichalcogeniderne (TMDC'er) er en gruppe af lovende katalysatormaterialermaterialer. I denne afhandling er den katalytiske aktivitet og stabilitet af 2H TMDC-kanter blevet undersøgt. Det har vist sig, at den foretrukne kantafslutning er meget afhængig af potentialet og pH under relevante driftsbetingelser. Ydermere er stabiliteten for forskellige afslutninger signifikant forskellige for forskellige TMDC'er. Undersøgelsen viser interessante tendenser i adsorptionsenergierne af H og CO, afgørende for CO2RR-selektiviteten. Større anionstørrelse viser sig at føre til et skift mod stærkere CO-adsorption og svagere H-adsorption, hvilket indikerer muligheden for at producere "ud over CO"-produkter.

Desuden undersøges potentiale afhængigheded af CO2RR- og HER-mekanismer af MoTe₂ ved brug af Grand Canonical DFT (GC-DFT). Det har vist sig, at mens en rent termodynamisk analyse antyder, at HER er favorabel, viser en analyse der også inkluderer kinetik, hvilket kun er muligt på grund af den eksplicitte inklusion af potentiale, at CO2RR faktisk er begunstiget, i overensstemmelse med tidligere eksperimentelle undersøgelser. Dette understreger nødvendigheden af at gå ud over Computational Hydrogen Electrode (CHE)-modellen for fuldt ud at forstå den elektrokatalytisk aktivitet. Derudover udviser forskellige mellemtrin varierende potentiale afhængighed, hvilket påvirker balancen mellem HER og CO2RR samt COdesorption og yderligere reduktion.

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List of Publications

Paper I

Trends in CO₂ **reduction on Transition Metal Dichalcogenide Edges** <u>Pernille D. Pedersen</u>, Tejs Vegge, Thomas Bligaard and Heine A. Hansen ACS Catalysis (2023), 13, 4, 2341–2350

Paper II

A Grand Canonical DFT investigation of the CO2RR and HER reaction mechanisms on MoTe $_2$ edges

<u>Pernille D. Pedersen</u>, Marko M. Melander, Thomas Bligaard, Tejs Vegge, Karoliina Honkala and Heine A. Hansen

Submitted to Journal of Physical Chemistry C.

List of Abbreviations

CCUS	Carbon capture, utilization and storage
CO2RR	CO_2 Reduction Reaction
OER	Oxygen evolution Reaction
HER	Hydrogen evolution Reaction
TMDC	Transition metal dichalcogenide
DFT	Density Functional Theory
KS	Kohn-Sham
XC	Exchange-correlation
LDA	Local density approximation
GGA	Generalized gradient approximation
vdW	Van der Waals
BZ	Brillouin zone
PW	Plane wave
PES	Potential energy surface
MEP	Minimum energy path
NEB	Nudged elastic band
CI	Climbing-image
SHE	Standard hydrogen electrode
RHE	Reversible hydrogen electrode
abs	absolute electrode potential
ET	Electron transfer
PCET	Proton coupled electron transfer
CHE	Computational hydrogen electrode
GCE	Grand canonical ensemble
GC-DFT	Grand canonical density functional theory
TS	Transition state
QN	Quasi-Newton
FE	Faradaic efficiency
SJM	Solvated jellium model
scf	Selc consistent fiels
MD	Molecular dynamics
NRR	Nitrogen reduction reaction
RDS	Rate determining step
LCAO	Linear combination of atomic orbitals
PDOS	Projected density of states

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1 Introduction

1.1 Carbon capture, utilization and storage

The urgent need to transition from fossil energy to renewable energy sources is now widely acknowledged due to the already evident consequences of climate change on human societies and natural ecosystems. However, as of 2021, fossil fuels still accounted for 83% of the global energy consumption, while it is estimated that renewable energy production needs to increase six to eight times to eliminate fossil energy consumption by 2050 [1]. The intermittent nature of renewable energy sources, such as wind and solar power, poses a fundamental challenge to a society fully reliant on renewable energy; we need energy also when the sun is not shining and the wind is not blowing. Therefore, implementation of large-scale energy conversion and storage is required, to ensure a constant energy supply [2]. A variety of conversion technologies, including electro-chemical, electro-mechanical, electrical, thermal and chemical methods show great potential in this regard [3].



Figure 1.1: Schematic showing the Carbon Capture and Utilization principle. Reprinted with permission from [4]. Electricity from renewable source and carbon captured from point sources or ambient air is utilized in an electrolyzer to produce net zero fuels or chemicals.

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Another main objective is the decarbonization of industry, which collectively account for an estimated >30 % of global CO₂ emissions [5]. Apart from energy consumption, these also includes carbon emissions from non-combustion processes from hard-to-abate sectors such as steel and cement production, fertilizer production or chemical industries. Point source carbon capture is highlighted as a key requisite in these sectors [6]. Heavy transport, such as aviation, shipping and road freight are likewise hard-to-abate sectors, as direct electrification would require unfeasible battery size and charging time using existing battery technology.

Carbon Capture, Utilization and Storage (CCUS) introduces an intriguing solution bridging together all of these important objectives; carbon captured from industrial point sources or even ambient air is converted and either stored (e.g geologically) or utilized as fuels or chemical feedstock for hard-to-abate sectors. The International Energy Agengy (IEA) emphasizes that reaching net zero emissions will be "virtually impossible" without CCUS, hence, a substantial acceleration of CCUS deployment is necessary in the next decade [7]. Figure 1.1 shows a simple schematic of the CCU principle [4].

1.2 Electrocatalytic CO₂ Reduction Reaction

 CO_2 is the most oxidized form of carbon, making its conversion a reduction reaction known as the CO_2 reduction reaction (CO2RR). However, reducing the inert CO_2 molecule requires a strategy to lower the high kinetic barrier [8]. In nature, this process is famously accomplished during photosynthesis by chlorophyll molecules, which utilize solar energy to produce carbohydrates [9]. Unfortunately, a corresponding link in the anthropogenic carbon cycle has been largely absent since the beginning of industrialization. Nevertheless, various technological conversion methods are now being developed, including thermochemical [10], photochemical [11], and biological approaches [12].

Electrocatalytic CO₂ reduction in particular offers several advantages including mild operating conditions, the possibility of combining the technology with various renewable energy sources and controllability through the electrode potential [13]. Specifically, electrocatalysis combines electrochemistry and (mostly heterogeneous) catalysis to improve the kinetics of a chemical reaction, utilizing the electrode surface not only as the electron conductor, but also as the catalyst for the reaction. An external electric circuit facilitates the non-spontaneous transfer of electrons between anodic and cathodic electrodes, submerged in an ion conducting medium (electrolyte) and separated by a membrane to keep the products apart. The CO2RR is a reduction reaction, hence it takes place at the cathode. The anodic counter reaction is here the oxygen evolution reaction (OER)[14]. The CO₂ reduction reaction (CO2RR) mechanism is extremely complex involving a large number of different possible pathways yielding a range of different final products [15, 16]. The most commonly observed products include the C1 products carbon monoxide (CO) and formate/formic acid (HCOO⁻/ HCOOH), which are produced in the first two reduction steps of the CO2RR mechanism:

$$* + \mathrm{CO}_2 + (\mathrm{H}^+ + \mathrm{e}^-) \rightarrow \mathrm{^*COOH}$$
(1.1)

$$^{*}COOH + (H^{+} + e^{-}) \rightarrow ^{*}CO + H_{2}O$$
 (1.2)

Here * denotes a surface site. Further reduction beyond CO to obtain two-, four-, six-, eightor even more electron products can also be achieved. Of the transition metals Copper (Cu) is famously the only one to produce so called "beyond CO products", including C_2 and C_{2+} products, in a notable amount [17], however, this process is inefficient and unselective, with high overpotentials and as much as 16 different products being produced [18]. In fact improving the selectivity, overpotential and long term stability of the CO2RR catalyst are identified among the key objectives to speed up the large scale deployment [4, 19].

The mechanism of the further reduction of CO is extremely complex and still not completely understood, but is believed to involve enol-like surface intermediates [18]. Countless of strategies to enhance the production of high value products has been proposed, the majority of which include altering the intrinsic characteristics, e.g. surface structure, particle size and chemical composition, of various Cu based nanostructures [15, 20–27], however a wide range of alternative catalyst candidates have also been proposed including alloys [28], 2D materials, e.g N-doped graphene [29], metal-organic frameworks [30], molecular catalysts [31] and single-atom catalysts [32].

1.3 The competing Hydrogen Evolution Reaction

The Hydrogen Evolution Reaction (HER) is an electrocatalytic process in which water is reduced to produce molecular hydrogen, H_2 . The similar equilibrium potential between the HER and CO2RR products introduces a competition that limits the selectivity of CO2RR in aqueous environments [34]. Achieving a higher Faradaic efficiency for CO2RR requires adjusting the catalyst selectivity. The ideal scenario involves a catalyst that weakly binds HER intermediates while strongly binding desired CO2RR intermediates. However, this presents a challenge due to the scaling relationship between the adsorption strengths of different adsorbates [35]



Figure 1.2: H adsorption energy vs CO adsorption energy for the transition metals. The solid black lines indicate $\Delta G_{bind} = 0$ and nicely classifies the materials according to their major CO2RR products. Reprinted with permission from [33].

In the case of CO2RR on transition metals, it has been observed that the bonding between hydrogen (H) and carbon monoxide (CO) is indeed correlated. Plotting the adsorption energies against each other identifies copper (Cu) as the only material with intermediate bonding strengths for both, which explains why copper is the only transition metal capable of producing products beyond CO as shown in Figure 1.2 [33]. One group of transition metals bind CO strongly, however because of the similarly strong bonding of H, the metals are only active for HER. On the other hand, there is a group of metals that exhibit weak H bonding, but this comes at the expense of weak CO bonding, resulting in the reduction reaction not proceeding beyond CO or formic acid.

Additionally, the selectivity for products beyond CO is further complicated by a strong scaling relationship among CO2RR intermediates. While these intermediates need to have sufficiently strong bonding to avoid early product desorption, excessively strong adsorption can hinder further reduction and potentially lead to catalyst poisoning, in accordance with the Sabatier principle [36]. Various strategies to circumvent the linear scaling relations for improved tuneability has been proposed, including engineering of the catalyst geometry, e.g. introduction of bifunctionality through different adsorption sites or sterically hindering adsorption of molecules of different sizes [37, 38].

1.4 Transition Metal Dichalcogenides in electrocatalysis

Transition metal dichalcogenides (TMDCs) are layered materials composed of transition metal atoms sandwiched between two layers of chalcogen atoms (MX_2 , X=(S, Se, Te)). The most common polymorphs are the trigonal prismatic 2H phase and the octahedral 1T phase [39]. While sulfides and selenides typically adopt the 2H phase, the stable phase of tellurides varies across different transition metals, exhibiting diverse phases [40–44].

These materials can be obtained as single or few-layered 2D nanostructures through methods such as mechanical or chemical exfoliation or chemical vapor deposition, leading to intriguing properties, including high catalytic activity [45, 46]. TMDCs hold significant promise for various processes in energy applications [47–52]. Extensive research has focused on the Hydrogen Evolution Reaction (HER), with MoS₂ being a particularly well-studied catalyst [46, 53–55], but high activities have also been reported for the Oxygen Evolution and Oxygen Reduction reactions [56] as well as Nitrogen Reduction Reaction (NRR) [57–59]

Regarding the CO2RR, numerous TMDCs have been investigated [60–66]. For instance, nanostructured sulfides and selenides of group VI elements (M=(Mo, W)) have shown high activity for CO production in an ionic liquid electrolyte [67]. While transition metal ditellurides have received less attention compared to sulfides and selenides in general, thin film $MoTe_2$ has demonstrated a predominant production of methane in an ionic liquid (FE=83 ± 3%) [68]. Moreover, even in an aqueous electrolyte (0.1 M KHCO₃), a methane Faradaic efficiency of approximately 15% was observed.

1.5 Atomic scale modelling in material design

The rapid advancement of computing power in recent decades has elevated the significance of computational modeling tools in catalyst design and materials science as a whole. Atomic scale modelling (Density Functional Theory (DFT) in particular) is one of the most utilized approaches in this field and is also the method of choice in this study. Here, a quantum mechanical description of atomic nuclei and electrons is utilized, enabling the investigation of fundamental chemical and physical properties at the atomic scale in molecules or solids. Its primary advantage lies in its capacity to predict properties and provide explanations for experimentally observed phenomena.

When searching for new catalyst materials, the possibilities for envisioning various material compositions are virtually limitless. However, the conventional process of designing, synthesizing, characterizing, and testing a single material can span several years. Alternatively, computational screening of a broad range of candidates can be performed to identify the most promising ones for subsequent experimental investigations. This approach not only expedites the design process but also limits costs and potential environmental hazards.

Moreover, atomic scale modelling often offers insights at the atomic level that may not be experimentally accessible. These insights can contribute to a deeper understanding of observed phenomena, such as providing mechanistic explanations

1.6 Outline of the thesis

This thesis is organized as follows. In Chapter 2, a brief overview of the theoretical concepts and methods used in in this thesis will be presented, which is followed in Chapter 3 by an introduction to the electrochemical interface and the computational methods employed herein to model it. The remaining chapters will be dedicated to presenting the results of the two studies included. In Chapter 4 the results obtained in the first study are presented; a computational screening, addressing the edge termination, adsorption energies and aqueous stabilities of a range of TMDC materials. These results were also presented in Paper I, which is published in ACS Catalysis and included in Appendix A1. The potential dependent thermodynamics and kinetics of the CO2RR and HER mechanisms on MoTe₂ are presented in Chapter 5 and Paper II, which is submitted to Journal of Physical Chemistry C. and attached in Appendix A2. Finally, a brief summary and outlook is presented in Chapter 6.

2 Theoretical background

2.1 Electronic structure theory

The time-independent Schrödinger equation is the fundamental basis for all electronic structure methods. In its simplest form, it can be expressed as [69]:

$$\hat{H}\psi(\mathbf{r},\mathbf{R}) = E\psi(\mathbf{r},\mathbf{R})$$
(2.1)

Here, $\psi(\mathbf{r}, \mathbf{R})$ represents the total wave function of the electrons (their coordinates denoted as \mathbf{r}) and nuclei (\mathbf{R}), while E denotes the corresponding energy. The Hamiltonian operator, \hat{H} , for an atomistic system can be written as:

$$\hat{H} = \hat{T}_{elec}(\mathbf{r}) + \hat{T}_{nuc}(\mathbf{R}) + \hat{V}_{ext}(\mathbf{r}, \mathbf{R}) + \hat{V}_{elec}(\mathbf{r}) + \hat{V}_{nuc}(\mathbf{R})$$
(2.2)

The terms $\hat{T}_{elec}(\mathbf{r})$ and $\hat{T}_{nuc}(\mathbf{R})$ represent the kinetic energy of the electrons and nuclei respectively, while the $\hat{V}_{ext}(\mathbf{r}, \mathbf{R})$, $\hat{V}_{elec}(\mathbf{r})$ and $\hat{V}_{nuc}(\mathbf{R})$ terms account for the Coulomb interactions among electrons, between electrons and nuclei, and among nuclei, respectively. Solving the Schrödinger equation presents a complex problem. To simplify the calculations, the Born-Oppenheimer approximation [70] is employed, which treats the nuclei as stationary and thus decouples the Hamiltonian and the wave function into nuclear and electronic parts. However, the electronic Schrödinger equations are necessary before the theory can be applied to most systems of scientific interest.

2.2 Density Functional Theory

Density Functional Theory (DFT) is built upon the groundbreaking theorems established by Hohenberg and Kohn [71], stating that 1) The ground state energy obtained from Schrödinger's Equation is a unique functional of the electron density, and 2) the electron density that minimizes the overall functional represents the true electron density, thereby adhering to the variational principle. Furthermore, the theory is extended by the Kohn-Sham (KS) theorem [72], which states that the problem of determining the minimum energy wave function can be expressed as a set of equations, each of which only involves a single electron, the Kohn-Sham equations:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) + V_H(\mathbf{r}) + V_{XC}(\mathbf{r})\right]\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r})$$
(2.3)

The solutions to the KS-equations are single electron wavefuntions, $\psi_i(\mathbf{r})$, and their corresponding energies, ϵ_i . The left hand side of the equation contains a kinetic energy contribution, $\frac{\hbar^2}{2m}\nabla^2$ and three potentials. $V(\mathbf{r})$ describes the coulomb interactions between the ith electron and the nuclei, $V_H(\mathbf{r})$ represents the Hartree potential that accounts for the Coulomb repulsion between the ith electron and the total electron density. This creates an undesired scenario where the electron experiences repulsion from itself, as it is also part of the total electron density. A correction for this self-interaction is included, among other effects, in the exchange-correlation (XC) potential, $V_{XC}(\mathbf{r})$. Assuming that the form of the XC-functional, E_{XC} , is known, the KS-equations can be solved iteratively to obtain the lowest energy wave function. As the energy follows the variational principle, and thus can be minimized in a self-consistent field (scf) cycle. Unfortunately, the exact form of the XC-functional is in most cases not known and must be approximated.

2.2.1 The exchange-correlation functional

The exact form of the exchange-correlation functional is known for a uniform electron gas, where the electron density remains constant throughout space [73, 74]. This provides a straight-forward initial approximation known as the local density approximation (LDA) for the exchange-correlation functional in the KS equations. Building upon the LDA, a ladder of approximations with increasing complexity has been developed. Advancing up this hierarchy holds the potential for improved accuracy, although it is never guaranteed. The first step up the ladder involves incorporating the local gradient of the electron density, leading to a class of functionals known as generalized gradient approximations (GGAs), which encompass numerous variations. In the meta-GGA approximation, the second-order gradient is also included. Additionally, hybrid functionals incorporate a portion of the exact exchange-energy.

The functional employed throughout this thesis, the BEEF-vdW functional [75, 76], is an example of a so-called parametrized functional, which is constructed by fitting a range of test data sets of various physical and chemical properties to Legendre polynomials. A special feature of this functional, that makes it particularly suitable for the surface reactions, is that Van der Waals (vdW) dispersion interactions are included.

2.2.2 Solid state DFT

The wave function in DFT is expressed in a basis set of functions. These can be spatially localized which is convenient for molecules, where a linear combination of atomic orbital (LCAO) approach is often employed, using either Gaussian or Slater type orbitals. For bulk materials the more popular approach is to use a set of periodic functions. In this approach, the wave function is expressed in so-called plane waves, a type of periodic functions in reciprocal space obeying Bloch's theorem, which states that the wave function can be expressed as a sum of terms in the form [77]:

$$\phi_k(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r})\mu_{\mathbf{k}}(\mathbf{r}) \tag{2.4}$$

where $\exp(i\mathbf{k} \cdot \mathbf{r})$ are plane waves. The space of vector \mathbf{r} is real space and vector \mathbf{k} is in reciprocal space (k space). $\mu_k(\mathbf{r})$ has the same periodicity as the supercell and can be expanded in plane waves (PW), so that they can be interpreted as solutions to the Schrödinger equation with kinetic energy. Typically, only solutions with kinetic energies lower than a specified cutoff energy, E_{cut} , are included in the calculations. However, core electron wave functions are associated with high kinetic energies. Therefore, achieving an accurate description necessitates a high cutoff energy, which can be inconvenient since the core electrons are chemically and physically less relevant than the valence electrons, which govern most of the important properties. To mitigate the computational cost, the frozen core approximation can be employed. This approach replaces the core electron densities with smoothed densities, known as pseudopotentials

K space is a central concept in plane wave DFT. In particular, evaluation of integrals over possible values of k in the Brillouin zone (BZ), the primitive cell in k space, is of great importance in practical DFT calculations. Most often the k points are chosen based on the method developed by Monkhorst and Pack [78]. This method involves specifying a certain number of k points along the x, y, and z directions. Generally, increasing the number of k points leads to higher accuracy in the calculation.

In the case of metals, the BZ can be divided into regions that are occupied or unoccupied by electrons, separated in k space by the Fermi surface. This introduces a discontinuity in the functions which greatly complicates the evaluation of integrals. To avoid a slow convergence in k points, smearing methods can be applied. The idea is basically to enforce continuity by replacing the step function with a continuous function than can be integrated. Some popular smearing functions include the Fermi-Dirac function or Gaussian smearing.

An alternative approach to expanding the wave function in plane waves, is the Finite Difference approach, where the wave functions are expanded onto a real-space grid in 3 dimensions. Provided with a grid point spacing, the wavefuntions are evaluated numerically at each point. As for the PW approach, an improved accuracy can usually be expected for an increasing number of grid points.

2.3 The Nudged Elastic Band method

Thermodynamics can predict whether a reaction is favorable or not, however the kinetics of the reaction can only be adressed considering the shape of the potential energy surface (PES). The Nudged Elastic Band (NEB) is a method for optimising the minimum energy path (MEP) on the PES between the final and initial states of a reaction step [79]. The energy barrier of the reaction can be obtained from the Transition State (TS), which is the saddlepoint of the MEP. The NEB is initialized from a provided initial guess of a number of images, corresponding to structures along the path, often obtained from linear interpolation. Adjacent images are connected by a harmonic spring potentials, which gives rise to the name of the method. Two force components therefore act on each image, spring forces parallel to the band, $\mathbf{F}_i^s|_{||}$ and structural forces perpendicular to the band, $\mathbf{F}_i|_{\perp}$. The total forces acting on each image, i, are given by Equation 2.5:

$$\mathbf{F}_{i}^{NEB} = \mathbf{F}_{i}^{s}|_{||} + \mathbf{F}_{i}|_{\perp}$$
(2.5)

where the individual components are given by Equation 2.6 and 2.7:

$$\mathbf{F}_{i}^{s}|_{\parallel} = k(|\mathbf{R}_{i+1} - \mathbf{R}_{i}| - |\mathbf{R}_{i} - \mathbf{R}_{i-1}|)\tau_{i}$$
(2.6)

$$\mathbf{F}_i|_{\perp} = \mathbf{F}_i - \mathbf{F}_i|_{||} = \mathbf{F}_i - \mathbf{F}_i \tau_i \tau_i$$
(2.7)

Here, k is the spring constant, τ is the normalized tangent along the band and \mathbf{R}_i is the position of the *i*th image. During the optimization, the spring forces ensure an equidistant spacing of the images and the structural forces push the path towards the MEP.

The climbing-image (CI) NEB can be utilized to obtain a more accurate description of the TS region [80]. In this method, the forces of the highest energy image are modified by removing the spring forces and inverting the structural forces to make this particular image climb up in energy, to more easily reach the saddle point. The total forces are then given by Equation 2.8:

$$\mathbf{F}_{i,max} = \mathbf{F}_{i,max}|_{\perp} - \mathbf{F}_{i,max}|_{\parallel} = \mathbf{F}_{i,max} - 2\mathbf{F}_{i,max}|_{\parallel}$$
(2.8)

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2.4 Bader charge analysis

The Bader charge analysis algorithm is used to analyse the charge localization on individual atoms [81]. In this method, the individual atoms in a system are separated by planes, so called zero flux surfaces, where the charge density perpendicular to the plane is a local minimum. Integrating the electron density over the regions corresponding to each atom yields the Bader charges, which can be utilized to quantify charge transfer between atoms.

3 Atomic scale modelling of electrochemical systems

A number of variables are used to describe the system when considering a conventional gas phase reaction, such as the number of particles, N, the temperature, the pressure and the volume (T, p and V respectively), the total energy of the system, E, and the chemical potential of the particles, μ . In an electrochemical reaction, an additional variable is introduced, i.e. the electric potential, ϕ , defined as the potential energy required to move one unit of charge from a reference point to a specific point against the electric field. Choosing some reference electrode potential as the reference point, the electric potential can be accounted for in the chemical potential of particle *i*:

$$\mu_i = \mu_{i,0} + z_i e \phi \tag{3.1}$$

where μ_i is now the electrochemical potential, $\mu_{i,0}$ is the chemical potential, corresponding to the electrochemical potential at $\phi = 0$ V, e is the elementary charge, and z_i is the unit charge of particle i. Some of the most common reference electrode potentials are briefly outlined in the following section.

3.1 Reference electrodes

A number of common reference potentials exist. Here, we briefly summarize the three potential scales used in this thesis.

- The Standard Hydrogen Electrode (SHE) is conventionally the most commonly used reference electrode. It is defined as a platinum electrode over which 1 atm H₂ gas is passed in a 1M H⁺ solution.
- The **Reversible Hydrogen Electrode (RHE)** is closely related to the SHE, the main difference being that its potential is dependent on the pH through Equation 3.2:

$$U_{RHE} = U_{SHE} + k_B T \cdot p H \cdot \ln(10) \tag{3.2}$$

This reference potential is more experimentally practical compared to SHE as the electrode in this case is submerged directly in the electrolyte used. • The **Absolute electrode potential (abs)** is by definition the difference in electronic energy between a point inside the metal (Fermi level) of an electrode and a point outside the electrolyte in which the electrode is submerged [82]. The experimentally determined correlation between the absolute potential, Φ_e , and the potential vs SHE, U_{SHE} , is given by equation 3.3

$$U_{SHE} = \Phi_e - 4.44V \tag{3.3}$$

3.2 Electrochemical reaction energetics

Electrocatalytic reactions take place at the electrified solid-liquid interface between an electrode and an electrolyte. Here, charge is transferred between the solid and liquid phases in electron transfer (ET) reactions and proton coupled electron transfer (PCET) reactions. The reaction thermodynamics and kinetics are controlled by electrode material and reaction conditions such as temperature and pressure as in any catalytic process, but the potential will also drive the reaction in an electrochemical experiment. Simulation of reactions at the electrochemical interface is greatly complicated by the potential dependency of the reaction energetics as well as the complexity of the interface with e.g. the formation of the electric double layer. Various approaches to describe electrochemical systems have been proposed and are continuously being developed [83]. In the following sections, two commonly applied approaches, the Computational Hydrogen Electrode model and Grand Canonical Ensemble DFT, will be presented.

3.2.1 Computational Hydrogen Electrode

The computational hydrogen electrode (CHE) is a simple method to implicitly account for electrode potential in the calculation of thermodynamics of proton-coupled electron transfers [84]. In this method, it is utilized that molecular hydrogen, H_2 , in the gas phase is in equilibrium with solvated protons and electrons defining 0 V vs SHE at standard conditions (pH = 0, T = 298 K, p = 1 bar)::

$$\mathsf{H}_2(g) \rightleftharpoons 2(\mathsf{H}^+(\mathsf{aq}) + \mathsf{e}^-(\mathsf{aq})) \tag{3.4}$$

hence, the chemical potential of an electron-proton pair, $\mu(H^+ + e^-)$, can be substituted by that of 0.5 H₂ molecule, $\mu(H_2)$ which is much less complicated to calculate:

$$\mu(\mathsf{H}^{+} + \mathsf{e}^{-}) = 0.5\mu(\mathsf{H}_{2}) \tag{3.5}$$

The reaction free energy then varies linearly with electrode potential, as the chemical potential of the electron is shifted by -neU at potentials different from 0 V vs RHE, where e is the elementary charge and n is the number of transferred electrons, as given in Equation 3.6:

$$\Delta G_i(U) = \Delta G_i(U=0) + neU_{SHE} + ln(10)k_bTpH$$
(3.6)

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The Gibbs free energy of the reaction can now be obtained without the implicit inclusion of any charged species. Shifting from the SHE to RHE scale, the equilibrium potential of reaction 3.4 is 0 V at any pH, hence Equation 3.6 simplifies to:

$$\Delta G_i(U) = \Delta G_i(U=0) + neU_{RHE} \tag{3.7}$$

CHE is widely used in electrocatalysis due to its simplicity and success in calculating accurate thermodynamic properties. However, the method has several limitations, including the inability to account for explicit potential effects. It is furthermore only possible to consider proton coupled electron transfers, whereas decoupled reactions are neglected. In its basic form, the CHE model is not suitable for calculation of kinetic barriers, hence the thermodynamic barriers of the elementary reaction steps are usually considered as a substitute for the overall reaction barrier. This approach, however, only gives an estimate of the lower limit of the reaction energy required to drive the reaction.

3.2.2 Grand canonical ensemble DFT

In conventional DFT the internal energy $E(S, V, N)[\rho]$ is a functional of the density, ρ , at a fixed entropy, S, volume, V, and number of particles, N. In thermal DFT, this is modified by performing a Legendre tranformation replacing S with temperature, T, so that the Helmholtz energy, $A(T, V, N)[\hat{\rho}]$, a functional of the thermal density, $\hat{\rho}$, is obtained. This corresponds to the canonical ensemble. Within both ensembles, the number of particles is fixed, which is in most cases a reasonable assumption, however, in reactions taking place at the electrochemical interface, charge is transferred to an from the electrode. While the Fermi level is kept constant by an external circuit in a real life experiment, in a canonical simulation the Fermi level will change notably when electrons are transferred to or from the electrode in a simulation cell of limited size.

From the canonical ensemble another Legendre transformation can be performed replacing the number of particles with a fixed chemical potential, μ . This leads to the Grand Canonical Ensemble (GCE) and the corresponding grand free energy, $\Omega(T, V, \mu)[\hat{\rho}_{gce}]$, which is a functional of the grand canonical density, $\hat{\rho}_{gce}$. Within this description, the number of particles is allowed to change, while the chemical potential, hence also the electrode potential, is fixed.

The grand canonical formulation of DFT (GC-DFT) thereby enables simulation of electrochemical reactions mimicking experimental conditions [85, 86]. In this way problems that are not easily addressed by the CHE model, such as explicit pH and potential dependencies and reaction kinetics can be investigated. However, several new problems arises with the introduction of the fluctuating number of electrons, e.g. the divergent Coulomb energy of a charged periodic system needs to be neutralized and the solvent (often the proton donor) needs to be properly described. In the following section the Solvated Jellium Model (SJM), which is the approach employed here is introduced.

3.3 Solvated Jellium Model

The excess electrons introduced to accomplish a constant electrode potential introduces a charge to the simulation cell, which can be difficult to handle computationally for periodic systems. In the Solvated Jellim Model (SJM) [87], [88], which is implemented in the GPAW electronic structure code, charged "jellium-slab" is introduced to the vacuum region of the system. This consists of a smeared-out background charge in a fixed region of the simulation cell along with a compensating number of electrons, that are allowed to move freely in the simulation cell during the scf-cycle to enforce an overall neutral charge of the cell.

A dipole correction is added between the jellium slab and the reverse of the periodic cell, to ensure that the countercharge is isolated at the reactive side of the electrode. This approach allows for a simple way of changing the number of electrons over the course of the simulation. In order to screen the electrode from the large electric field caused by the dipole between the jellium and the slab, the region above the molecular system is filled with a dielectric continuum (implicit solvent). Often an explicit/ implicit solvation is employed, where a number of explicit water molecules, serving as proton donors for the surface reactions, are included between the surface and the implicit solvent region.

With the countercharge and solvent model in place a charging workflow is initiated. Supplied with an initial guess for the number of electrons and the atomic positions, a DFT calculation is performed. The resulting potential is measured against the target potential and the number of electrons is adjusted accordingly. Rather than guessing randomly, the adjustment is done by exploiting the linear relationship between charge and potential, so that the new potential can be estimated by the slope of the previous charges and potentials. This part is referred to as the computational potentiostat, and continues until the desired target potential is reached. At this point, the forces on the atoms are passed to the optimizing algorithm to adjust the atomic structure performing a new DFT calculation without changing the number of electrons. The resulting structure is then passed to the computational potentiostat to check and possibly adjust the number of electrons, in case the geometry change induced a change in potential. This continues until convergence of the optimization algorithm and the potentiostat. .

Three factors significantly limit the computational cost of the computational potentiostat. First, the ionic steps are usually so small in a structural optimization that the impact on the potential is very limited. Hence, in practice several ionic steps can be taken before the number of electrons need to be adjusted. Moreover, the linear relationship between charge and potential transfers well between geometric steps, hence the number of electrons is updated usually within just one (or a few) DFT iteration. Finally, the wave functions are reused as the starting point for the changed value of electrons, which results in fast convergence of the SCF cycle.

3.3.1 Implicit solvation model

Continuum models of solvation rely on the statistical nature of the solvent, averaging out the solvent molecules to create a homogeneous continuum embedding the solvated species. In SJM, the employed solvation model is based on the effective potential cavity method [89]. This type of solvation model is generally based on solving the generalized Poisson equation:

$$\nabla(\epsilon(\mathbf{r})\nabla\Phi(\mathbf{r})) = -4\pi\rho(\mathbf{r}) \tag{3.8}$$

Where, ρ (r) is the charge density of the system, Φ is the electrostatic potential and ϵ (r) is the permittivity function, describing the cavity of the solvated species and the screening. The permittivity is specifically described by an effective potential, based on the repulsive branch of the Lennard-Jones potential:

$$u_{eff}(\mathbf{r}) = u_0 \sum_{a} \left(\frac{R_a^{vdW}}{|\mathbf{r} - \mathbf{R}_a|} \right)^{12}$$
(3.9)

where where R_a^{vdW} and R_a are the vdW radius and atomic position of atom a and u_0 is an empirical scaling parameter. $u_{eff}(\mathbf{r})$ then relates to the permittivity, $\epsilon(\mathbf{r})$, via:

$$\epsilon(\mathbf{r}) = 1 + (\epsilon_{\infty} - 1) \exp\left(-\frac{u_{eff}(\mathbf{r})}{k_B T}\right)$$
(3.10)

where ϵ_{∞} is the macroscopic dielectric constant of the solvent. In SJM, an additional extension to the charge density, $\rho(\mathbf{r})$, is made to include the charge density of the jellium slab:

$$\rho(\mathbf{r}) = \rho_{explicit}(\mathbf{r}) + \rho_{jellium}(\mathbf{r})$$
(3.11)

Where the explicit part contains the contributions from electrons and ions of the explicit system and the jellium part accounting for the added electrons and the countercharge. In order to realistically model an electrode, the solvent is usually excluded from the backside of the slab. This side should correspond to the bulk electrode, which should be indifferent to the varying potential.

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Figure 3.1: The minima hopping principle. Molecular dynamics (MD) steps are taken to jump out of the current minimum when the barrier between basins, E_B is lower than a continuously adjusted kinetic energy threshold, E_{kin} . These are followed by Quasi-Newton (QN) calculations to decide the energy of the new minimum. A minimum is accepted if the energy of the new minimum (E_2) is lower than the sum of the energy of the current minimum (E_1) and a continuously adjusted threshold E_{dif} .

The implicit solvation approach, however, can not account for specific interactions between solvent and solute, such as hydrogen bonding or proton transfers. An alternative approach to modelling the liquid phase is to explicitly model each water molecule, allowing for an accurate description of interactions between solvent molecules and solute however greatly increasing computational cost of the simulation. Hybrid approaches in which a number of solvent atoms are explicitly embedded in an otherwise implicit continuum based simulation have proven successful in accurately describing the interface[90].

3.4 Global optimization using the minima hopping method

Selecting a representative geometry of the explicit solvation layer presents another challenge. The number of local minima on the PES increases exponentially with the number of atoms in the system, hence a common geometry optimization is not likely to localize the global minimum.

A basin, which is a central concept in global optimization, is by definition a part of configurational space around a local minimum on the potential energy surface, which contains all configurations that will relax into this minimum using small step downhill optimization. In a regular local optimization of the molecular geometry, the result will depend heavily on the initial guess of the structure, as the obtained relaxed structure will be the minimum of the nearest basin.

The minima hopping algorithm is one among many existing global optimization methods to identify the overall lowest energy structure. [91]. As opposed to many other approaches one advantage of this method is that it is not based on thermodynamic principles, hence the jumping between different basins is not limited by the Boltzmanns distribution. The idea behind the minima hopping is instead to take alternating steps of Quasi-Newton (QN) relaxation and molecular dynamics (MD), respectively. In the molecular dynamics steps, jumps are performed to pass barriers between basins. In the subsequent QN, step the structure is relaxed to the local minimum. The step is accepted if the new energy, E_2 , is less than some threshold, E_{dif} , higher in energy than the current minimum energy, E_1 . E_{dif} , is defined such that exactly half of the steps are accepted and is continuously adjusted. In this way, steps that are downhill in energy are preferred, but after sufficiently many rejected steps, the threshold is increased to include uphill steps. The atoms in the system posses an amount of kinetic energy, E_{kin} , initially specified by the MD temperature. In an MD step, the system can cross over a barrier of a magnitude that is lower than E_{kin} . If E_{kin} is small, the system is likely to relax back into the same minimum. In this case E_{kin} is increased. Likewise, if the new minimum is a previously accepted minimum, is increased until the system gains enough energy to jump to unexplored regions. In this way, repeated visits to the same minima is limited, while still allowing crossings through transition basins are.

3.5 Pourbaix diagrams

The thermodynamic stability of an aqueous electrochemical system as function of potential and pH at equilibrium is plotted in a Pourbaix diagram. Solid lines indicate the boundaries between the most stable phases, which can be solvated ions or solids. The potential and pH dependence is governed by the Nernst equation:

$$E_{SHE} = E^0 - \frac{RT}{nF} \ln K - \frac{RTh}{nF} pH$$
(3.12)

where, E_{SHE} is the reduction potential of the considered reaction, E^0 is the standard reduction potential, R is the universal gas constant, n is the number of electrons transferred, F is the Faraday constant, K is the equilibrium constant of the reaction and h is the number of protons transferred in the reaction. E^0 is defined relative to the standard Gibbs free energy change, ΔG^0 , by:

$$E^0 = -\Delta G^0 / nF \tag{3.13}$$

Three types of boundary lines arise in the diagram:

- 1. horizontal lines correspond to purely electrochemical reactions, where no pH dependence is present.
- 2. vertical lines correspond to acid-base reactions, purely depending on pH.
- 3. sloped lines correspond to reactions that depend both on pH and potential.

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4 Trends in CO₂ reduction on Transition Metal Dichalcogenide Edges

MoS₂ is a widely studied material for numerous applications in energy research, however, much less attention has been paid to its more exotic cousins within the transition metal dichalcogenide (TMDC) material class. In particular the transition metal ditellurides are not often included in computational or experimental studies. In this study we set out to unravel catalytic trends among the TMDCs, including sulfides, selenides and tellurides and present suggestions for future catalyst selection. Three properties of the materials are addressed. First, the relative stability of different structural edge terminations will be assessed, then the adsorption geometries and energies for important intermediates will be discussed and finally a short discussion about the aqueous stability is presented. Based on these parameters, interesting catalyst candidates are suggested. The results in this section and Figures 4.1-4.6, 4.7, 4.8, 4.10 and 4.11 were reprinted with permission from [92]. the full paper is included in Appendix A1.

4.1 Computational Methods

In this part, the DFT calculations have been carried out using the Vienna Ab Initio Simulation Package (VASP 5.4.4) [93, 94] integrated with the Atomic Simulation Environment (ASE) [95]. The task and workflow scheduling system MyQueue is used to handle the large number of calculation tasks [96].

The exchange-correlation functional used herein is the BEEF-vdW functional [75, 76]. A plane wave basis set with a cut off energy of 450 eV is used along with $N_{\text{k-points}} \cdot a \geq 30 \text{ Å}$ ($N_{k-points}$ is the number of k points and a is the length of the unit cell) in the periodic directions and 1 k-point in non-periodic directions. Gaussian smearing ($\sigma = 0.03 \text{ eV}$) is employed. The atomic positions are relaxed until all residual forces are below 0.03 eV/Å.

Preoptimized 2D periodic TMDC sheet structures are obtained from the Computational2D materials database (C2DB) [97, 98]. While the structures are periodic in x and y directions, 7.5 Å of vaccum at each side of the structure in the z-direction is added to obtain the 2 dimen-


Figure 4.1: Visual representation of the computational workflow followed to evaluate expected catalytic activity of TMDC materials.

sionality. Pre-defined C2DB stability criteria [97, 98] are adapted as initial selection criteria. According to these, the dynamic and thermodynamic stabilites of materials are classified as low, medium or high. The overall stability is decided based on the lowest of these. In this work only materials with a high overall stability (heat of formation >convex hull + 0.2 eV/atom, minimum eigenvalue of the Hessian > $-0.01 \text{ meV}/\text{Å}^2$ and minimum stiffness tensor eigenvalue >0) are considered, which according to the C2DB criteria are likely to be synthesizable based on comparison with experimental data.

The overall workflow describing the calculation tasks is shown in Figure 4.1. To obtain the lattice constants of the 2D sheets, the atomic positions and cell shape of 2×4 supercells (8 metal atoms and 16 chalcogen atoms) are relaxed. Nanoribbons are constructed by adding an additional 7.5 Å of vacuum at each side of the sheet in the x direction, while the edge configuration is constructed by adding or removing atoms at the edge. Subsequently all atomic positions are reoptimized.

In the final task, all ontop an bridge adsorption edge sites are identified and different adsorbates are added. The edge is defined as the outermost row of X and M atoms. Holding all atoms but the edge atoms and one additional row of X atoms fixed, the atomic positions of each adsorption structure are relaxed. The lowest energy structure is then identified, excluding structures where the adsorbate and/or a surface atom is considered to "fly off" the surface. The structures are furthermore excluded if the TMDC layer is curved as defined by a displacement in the z direction of one or more metal atoms by more than 10%.

The minimum adsorption free energies are calculated with reference to the pristine nanoribbon and the gas phase reference molecule by:

$$\Delta G_{adsorption} = E_{*ads} + ZPE_{*ads} - E_{*} - (E_{mol} - TS_{mol} + ZPE_{mol})$$
(4.1)

where, * indicates a free site, *ads indicates an adsorbed species and "mol" indicates a gas phase molecular species. The surface entropy (S) and the zero point vibrational energies (*ZPE*) are assumed unaffected by adsorption, hence neglected, whereas they are included for molecular species. MoS₂ is used as the model system to calculate ZPE correction terms for adsorbed species.

Pourbaix diagrams are constructed for each material using the ASE Phase diagrams package, adding additional reference energies from The Atlas of Electrochemical Equilibria in Aqueous Solutions [99]. Bulk metal reference energies are calculated from their preferred crystal lattice. Bulk sulfur (mp-96), selenide (mp-570481) and tellurium (mp-19) structures are obtained from the Materials Project [100].

4.2 Results and discussion

For the 2H phase, the catalytic activity is exclusively ascribed the undercoordinated "edges", whereas the basal plane is found to be inactive in the pristine form [101–103]. Therefore, the structure of the edges will determine the possible adsorption sites and energies. In the first part of this chapter the termination of the metal (M) and chalcogen (X) edges are investigated using the Computational Hydrogen Electrode (CHE). In the subsequent part, the adsorption geometries and energies of CO, H and COOH will be addressed. These are important intermediates of the CO2RR and the competing HER and are therefore key descriptors in determining the overall CO2RR reactivity and product formation. Finally, the aqueous stability under reaction conditions, which is a prerequisite for any aqueous phase catalytic reaction, is discussed. A potential range from 0 V vs RHE to -1 V vs RHE is considered throughout the chapter. Based on experimental results, we expect that the most realistic reaction conditions for CO2RR is from -0.3 to -1 V vs RHE [67, 68].

4.2.1 Edge configuration

Cutting out a nanoribbon from a periodic slab in in the "zig-zag" direction results in the formation of two distinct edges. One is stoichiometrically terminated by chalchogen atoms (X edge) and the other one by exposed metal atoms (M edge). Assuming some availability of chalchogen (X) atoms, the M edge could possibly obtain a more favorable coordination by adsorption of X atoms, e.g. resulting from the removal of X atoms from the X edge, which by stoichiometry upholds a full 6-fold coordination of the metal atoms. Figure 4.2 shows the possible combinations of edge coverages of the two edges, assuming two basic structural motifs, the monomer and dimer terminations, which has an edge coverage of 0.5 and 1 respectively, assuming that a full coverage of 1 corresponds to $2 \cdot n_M$ X atoms [104, 105]. The fully exposed edges are not included in this study, as they are found to subtract to expose the first layer of X



Figure 4.2: a) MoS_22D sheet top view (center left), sheet side view (center right) and side views of the chalcogen edge (top) and metal edge (bottom). Edge terminations at the M edge (b) and X edge (c) with different X coverages. Edge atoms are indicated with black. The examples shown are optimised MoS_2 structures (Mo=blue, S=yellow, O=red, H=white).

atoms during the geometry optimization, so that the lattice is not retained. This is in agreement with previous studies finding that this termination is unstable [104]. For the M edge, the opposite edge is in all calculations terminated by the stoichiometric configuration, while in case of the X edge calculations, the M edge is terminated by the monomer termination, as the stoichiometric configuration is not stable. For the stoichiometric X edge termination, it is found that a staggered dimerization of the X-pairs is more stable than retaining the lattice configuration. Likewise, for the X edge monomer termination, it is found that a staggered configuration is more favorable than the symmetric configuration.

Within the framework of the CHE, the transformation from the fully covered dimer edge to the fully exposed edge in steps removing one X atom at the time, is described by the following reaction:

$$S^* + H_2 \rightarrow * + H_2 S \tag{4.2}$$

In aqueous solutions, adsorption of hydroxyl groups (OH), which have been shown to influence CO2RR, could be favorable [106, 107]:

* +
$$H_2O \rightarrow 0.5H_2 + *OH$$
 (4.3)

Here, three different terminations involving adsorbed OH groups are considered for each of the edges $OH_{0.25}$ and $OH_{0.5}$ and $X_{0.25}OH_{0.25}$ which are shown in Figure 4.2

Figure 4.3 c (M edge) and d (X edge) summarizes the most stable terminations as a function of

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Figure 4.3: Edge terminations stability as a function of U vs RHE relative to the X_1 termination calculated by the Computational Hydrogen Electrode (CHE) model. Relative stabilities at the M edge exemplified for MoS_2 M edge (a) and X edge (b). The results for all materials studied are summarized by plotting the most stable termination as a function of U vs RHE at the M edge (c) and the X edge (d).

potential for all the materials. For clarity, the full CHE diagrams are shown for MoS_2 in Figure 4.3 a and b. Notably, there is a large variation in the relative stability comparing the different materials, signifying that simply using the widely studied MoS_2 as a model system does not give a correct description of a given TMDC material. Inspecting both the M and X edges, it is observed that the affinity for hydroxyl adsorption is increased in the order of sulfide > selenide > telluride, whereas the X edge in general is more prone to OH adsorption. This observation is in agreement with previous observations for MoS_2 [55], suggesting that the M edge is more catalytically relevant.

Going towards increasing applied potentials, the more reduced terminations become domi-



Figure 4.4: Calculated adsorption Gibbs free energies of H and CO calculated at the $X_{0.5}$ (left) and the $X_{0.25}$ (right) M edges. Inserts show top and side views of the relevant edge configuration. The black lines at $\Delta G_{ads} = 0$ indicate expected product regions (H₂, CO/HCOOH and Beyond CO).

nant. Generally, in the relevant potential range for CO2RR, the $X_{0.25}$ termination is the most stable M edge termination, while the $X_{0.5}$ termination in some cases could also have some significance. At the X edge, the intercepts are shifted to higher potentials, so that the $X_{0.5}$ termination and even the $X_{0.75}$ termination are stable in a larger part of the relevant potential range.

4.2.2 Adsorption

In heterogeneous catalysis, linear scaling relations among the adsorption energies of reaction intermediates is a fundamental limiting factor. In a simple picture, a surface that binds one intermediate strongly will in most cases also bind intermediates of other reaction steps or even competing reactions strongly. In the case of CO2RR on transition metal catalysts, it is well known that such scaling relations exist between *CO₂, *COOH, *CO and *COH, which all bind through the carbon atom. Furthermore, a linear scaling with hydrogen (*H), the first intermediate of HER, is observed. In fact, the CO and H adsorption energies can be used to classify the main products of the different transition metal catalysts [33]. At strong H and CO bonding, CO2RR cannot compete with HER and H₂ is the only observed product, while metals that bind CO and H weakly will stop the reaction at formate or carbon monoxide. Only in the case of Cu, an intermediate bonding of both intermediates is observed, so that reaction products "beyond CO" are produced.

To investigate likely CO2RR products of the 2H TMDC catalysts, CO and H adsorption energies are presented for the $X_{0.25}$ and $X_{0.5}$ edges in Figures 4.4 (M edge) and 4.5 (X edge). These were found to be the most stable terminations under relevant conditions, excluding the OH



Figure 4.5: Calculated adsorption Gibbs free energies of H and CO calculated at the $X_{0.5}$ (left) and the $X_{0.25}$ (right) X edges. Inserts show top and side views of the relevant edge configuration. The black lines at $\Delta G_{ads} = 0$ indicate expected product regions (H₂, CO/HCOOH and Beyond CO).

terminated edges. Comparing the adsorption energies at the different edges show some interesting trends. Due to more significant edge reconstructions, the X edge data is generally associated with more uncertainty, visible as noise in Figure 4.5. Notably, the CO adsorption energy is significantly increased going from the $X_{0.5}$ termination to the $X_{0.25}$ for both the M and X edges.

Interestingly, whereas a positive linear scaling among each group of TMDCs is observed for both M edges and the $X_{0.5}$ X edge the opposite trend is observed going from S to Se to Te, that is a shift towards weaker H bonding and stronger CO bonding is observed. Assuming that the classification boundaries (see Figure 1.2) established for the pure transition metals are valid also for TMDCs, this correspond to a shift towards beyond CO products. This highlights the transition metal tellurides as interesting candidates for CO2RR to highly reduced products, in agreement with methane being a major product of MoTe₂ [68].

The trend can be rationalized considering the ligand properties of CO and H. Whereas H can act as a σ -donor or acceptor, CO binds partly as a strong π^* -backbonding ligand. The TMDC M-X bond is polar with a partial negative charge on X and a partial positive charge on M. The polarity is decreased with decreasing electronegativity of the X atoms as shown in Figure 4.6. The strength of the sigma bonds of both H and CO is therefore decreased in the order S>Se>Te in agreement with the trend observed for the purely sigma-bonding H adsorbate. π^* -backbond of CO, on the other hand, is strengthened for the less positively charged metal site, where a larger electron density is available for back-donation. Hence, the CO adsorption is increased in the order of S<Se<Te. A simple indicator for the strength of the π -back-bonding is the length of the C-O bond length, which is increased for increased backbonding strength, as illustrated



Figure 4.6: CO bonding to the metal site via σ -bonding (left) and π^* -backbonding (middle). The right Panel shows how the polarity of the M-X bond is decreased with size of X increasing the electron density on the M site, leading to stronger π^* -backbonding.

in Figure 4.7.

The basic assumption for deciding the expected final product based on the H/CO scaling is that the classification boundaries observed for transition metals are also valid for the TMDCs. One prerequisite for this is that the COOH adsorption is favorable. For the transition metals a linear scaling is observed between CO and COOH, ensuring that for strong CO bonding, strong COOH bonding is also observed. However, for the TMDCs it has previously been found that the linear scaling between the two is broken, due to different CO and COOH adsorption sites [108]. The COOH/CO scaling calculated in this study is shown in Figure 4.8.

For the $X_{0.5}$ termination we likewise find that while CO is adsorbed on the metal site, COOH is adsorbed ontop the X atom. This results in a similar adsorption trend as observed for H and CO: a linear scaling is observed within each group of chalcogenides and the trend is shifted towards weaker COOH adsorption going from S to Se to Te (Figure 4.8 left), however, for the $X_{0.25}$ edge, where both adsorbates are adsorbed at the metal site, this trend is significantly less pronounced. It should be noticed that whereas the most feasible adsorption geometry for the majority of the materials is a bidentate bonding, where C and O are both coordinating to a metal atom. For the Fe, Co and Mn tellurides, the small size of the metal atom prevents this behaviour, and only the C atom is binding to the site as illustrated in the right subfigure in Figure 4.11. This leads to a significantly decreased COOH adsorption strength for these materials.



Figure 4.7: Calculated CO bond length after adsorption for the $X_{0.5}$ and $X_{0.25}$ M edges.

4.2.3 Aqueous stability

The stability of a material when subjected to reaction conditions is central in determining the suitability of a potential catalyst material, as this will largely influence the durability. In fact, long term stability is considered one of the key objectives in the future development of CO2RR catalysts [4, 19]. As a relatively simple measure of the stability of the TMDCs in an aqueous medium under reducing conditions, Pourbaix diagrams are constructed for each of the materials as examplified for MoTe₂ and VTe₂ in Figure 4.10. For most of the materials, a delicate pH and potential dependence, with many possible Pourbaix phases is found, as clearly seen in the case of VTe₂, which is in case not the Pourbaix stable phase under any conditions included in the diagram. MoTe₂ on the other hand is stable in a large part of the diagram.

In order to simplify the analysis, the Gibbs energy required to convert the TMDC to its stable phase under realistic operating conditions (here -0.6 V vs RHE and pH=7) is calculated and illustrated in the heatmap shown in Figure 4.10 for each mateiral. Note that materials not meeting the initial selection criteria have also been included in this figure for a better overview.

At negative potentials, most TMDCs are not in their Pourbaix stable phase. However, several, such as MoS₂, MoSe₂, MoTe₂, WS₂, and WSe₂, have been successfully synthesized and utilized for CO₂RR, despite not being the stable phase. This suggests that materials with similar stabilities might still be kinetically stable (meta-stable) under the specified conditions. This assumption is supported by a previous study, which suggested that materials with ΔG_{pbx} values up to 0.5 eV per atom could be meta-stable in aqueous media [109].



Figure 4.8: Calculated adsorption Gibbs free energies of COOH and CO calculated at the $X_{0.5}$ (left) and $X_{0.25}$ (right) M edges. Structures were a bidentate bonding is sterically hindered are labelled by star-shaped markers. Inserts show top and side views of the relevant edge configuration.



Figure 4.9: Calculated Pourbaix diagrams for $MoTe_2$ (left) and VTe_2 (right)

Applying the stability criterion of $\Delta G_{pbx} < 0.5$ eV, ten new materials are classified as metastable at -0.6 V versus RHE. These materials are TiTe₂, VTe₂, NbSe₂, NbTe₂, TaS₂, WTe₂, MnTe₂, FeTe₂, CoTe₂, and NiTe₂, besides the already known materials. Interestingly, the tellurides, seem to generally have a higher aqueous stability than the corresponding sulfides and selenides, however it should be noted, that a number of the tellurides are in fact more stable as other TMDC polymorphs, which are not included in this analysis.

Whereas the Pourbaix analysis provides a useful starting point for the discussion of the catalyst stabilities, many factors that may influence the actual stability have been excluded from the discussion in this section. For example, the cyclic stability of MoS_2 "nano flowers" is found to be very dependent on the electrolyte composition (1 M H₂SO₄, 1 M Na₂SO₄, and 2 M KOH) [110]. The results presented in Section 4.2.1 showed that to a large extend the TMDC edges

				1 /
SC	1.3	1.2	0.79	1.4
Έ	0.79	0.73	0.36	1 0
N.	0.96	0.93	0.6	·1.2
ΗĻ	0.93	0.94	0.66	1 0
>-	0.65	0.61	0.23	1.0
٩N	0.36	0.34	0	0 0 2
Tal	0.48	0.53	0.25	e/8.0
۲.	0.69	0.67	0.28	Gpb
9	0.43	0.42	0.044	10.0⊲
Š	0.48	0.55	0.26	0.4
- L	1.1	0.98	0.38	0.4
E -	0.89	0.71	0.11	0.2
0.	1.1	0.89	0.19	-0.Z
ïZ	1.2	0.99	0.22	0.0
	Ś	Se	Te	0.0

Figure 4.10: Pourbaix stabilities calculated at -0.6 V vs RHE and pH=7. Numbers marked with purple indicate pourbaix energies below the 0.5 eV stability threshold. White numbers are above the threshold, while materials that do not fulfill the initial stability criteria are marked with black and only included for overview.

are expected to be covered by OH, which may inhibit the degradation, even in pure water. Likewise, adsorption of hydrogen or CO2RR intermediates could possibly have a similar effect. Under operating conditions a2D-catalyst would often be supported by some other material, which has been previously found to influence the catalytic properties of MoS_2 [111], and is likely to also improve the aqueous stability.

4.2.4 Reaction diagrams

Reaction diagrams for CO2RR are shown for selected materials in Figure 4.11. It is observed that CO desorption is generally less favorable for the tellurides compared to MoS_2 and $MoSe_2$. Moreover, COH is stabilized relative to CO for, in particular, MoTe2 and FeTe2 compared with the sulfide and selenide. This indicates that from *CO, further reduction is more favorable for the tellurides. COOH adsorption is generally energetically unfavorable at equilibrium potential, however as previously discussed it is significantly less favorable for materials where bidentate bonding is hindered. Hence, a significant (> 0.7 V) increase in the CO2RR overpo-



Figure 4.11: Reaction energy diagrams for CHE CO2RR reaction steps on the $X_{0.25}$ M edge at CO /CO₂ equilibrium potential (-0.3 V vs RHE) (left). Adsorption geometries for the CO2RR intermediates for MoTe₂ and CoTe₂ (right).

tential for $FeTe_2$ and $CoTe_2$ compared to $MoTe_2$ is expected.

4.3 The 1T phase

The discussion so far has been limited to the 2H-phase which is the most stable e.g for MoS_2 , however for some materials such as $NiTe_2$ and VTe_2 have been synthesized only in the 1T phase [112, 113]. In this section the termination and adsorption energies of 1T-edges is briefly touched upon.

The 1T edge differs fundamentally from the 2H-phase in the sense a stoichiometric cut creates two identical edges, edge covered by two X atoms, this is denoted $X_{0.5}$. An additional three different edge terminations were compared, which are comparable to the OH free terminations considered for the 2H phase; X_1 , $X_{0.75}$ and $X_{0.25}$. The terminations are shown in Figure 4.12 (right) and their relative stability is compared in Figure 4.12 (left). The dominant terminations in the potential range are, as for the 2H phase, the $X_{0.25}$ and $X_{0.5}$, with the higher X-coverages having only a small stability window at low applied potentials for the tellurides. Note that OH adsorption adsorption is not considered in this case, but is likely to be favorable in some potential range.

The adsorption energies for CO and H at the $X_{0.5}$ and $X_{0.25}$ edges are calculated and shown in Figure 4.13. The $X_{0.25}$ is very prone to edge reconstruction upon adsorption, hence a large amount of noise is present while also many data points are excluded from the plot. However,



Figure 4.12: Edge terminations stability for the 1T edges as a function of U vs RHE relative to the X_1 termination calculated by the Computational Hydrogen Electrode (CHE) model (left). Structures showing the different edge terminations (right).

at the $X_{0.5}$ edge, a trend similar to that observed for the 2H phase is observed, that is the CO adsorption strength is decreased in the order of S<Se<Te. Meanwhile the H adsorption energy is generally decreased. Platinum (Pt) stands out in that regard as the CO adsorption strength is approximately constant, while the H adsorption strength is significantly decreased. On the other hand, the trend within each group of chalcogenide, the positive linear scaling observed for the 2H phase is not observed, rather a flat, or even negative trend is observed, however, the large amount of noise in the data result in a high uncertainty associated with the linear fits.

4.4 Conclusion

The findings presented in this chapter indicate that transition metal ditellurides exhibit promising adsorption properties for CO_2 reduction beyond CO, while simultaneously limiting the competing hydrogen evolution reaction (HER). This observation aligns with experimental results showing that ultrathin $MoTe_2$ layers predominantly produce methane as a CO2RR product in ionic liquid (and to some extent in an aqueous electrolyte), while the corresponding sulfide and selenide act as efficient CO catalysts in an ionic liquid [67, 68]. The tellurides are moreover found to have high aqueous stability under relevant operating conditions compared to the sulfide and selenide counterparts.



Figure 4.13: Adsorption free energies of CO and H at the $X_{0.5}$ (left) and $X_{0.25}$ 1T edges. The black lines at $\Delta G_{ads} = 0$ indicate expected product regions (H₂, CO/HCOOH and Beyond CO).

Furthermore, it is demonstrated that the termination of the edges in these materials significantly influences the binding strengths of CO2RR intermediates and hydrogen. By selectively targeting a specific termination through choice of reaction conditions and material, it may be possible to direct the formation of different reaction products. However, it is crucial to acknowledge that the relative stability of edge terminations is highly dependent on the applied potential and might be affected by other reaction conditions, such as pH, which is not accounted for by the Computational Hydrogen Electrode (CHE) model used in this study. The explicit potential and pH dependence is investigated in more detail in Chapter 5.

Notably, the study also reveals that hydroxyl adsorption is favorable for many materials and is likely to have an impact on the reaction in aqueous electrolyte. Further studies investigating the influence of OH edge adsorption on the aqueous stability and adsorption of CO2RR and HER intermediates would be of interest. Initial studies of the co-adsorption of OH and other adsorbates show that this analysis is greatly complicated by the OH edge atom reorganization upon adsorption of the second adsorbate. The 1T phase show promising catalytic activity, which is mainly ascribed to the high basal plane activity and high conductivity of the semimetallic 1T phase [66, 101]. Here, the 1T edges were briefly studied, however more in depth investigations of the stability and adsorption properties would be of interest, including consideration of the basal plane adsorption.

5 Grand canonical ensemble studies of the CO2RR and HER mechanisms on MoTe₂ edges

In the previous chapter, it was found, using the CHE model, that the transition metal ditellurides show promising adsorption thermodynamics with respect to CO2RR. In agreement with this, an experimental study have shown that $MoTe_2$ nanoflakes produce methane as a major product [44]. However, the thermodynamics do not provide a full understanding of the reaction as kinetics will significantly contribute to deciding the selectivity and overpotential of the reaction. Furthermore, the CHE model does not consider direct potential dependency.

As outlined in Chapter 3, the explicit inclusion of potential is required in order to calculate kinetics of electrochemical reactions, and requires careful consideration [114–117]. In this chapter, a grand canonical ensemble approach is employed using the Solvated Jellium Model (SJM) [87] to study the reaction pathways of CO2RR and the competing HER at explicitly treated potentials [85, 86]. Several electrochemical reactions have previously been investigated using GC-DFT, e.g. the NRR/ HER on Ru-N₄[118], Glycerol Electro-oxidation catalyzed by Au, [119] and HER at MoS₂ and MoTe₂ basal planes [120]. Also, CO2RR on various catalysts has been the subject of multiple GC-DFT investigations [121–124].

The results presented in this chapter are presented in Paper II which is submitted to the Journal of Physical Chemistry C., included in Appendix A2.

5.1 Computational methods

In this part, all DFT calculations have been performed in a projector augmented wave (PAW) formalism in GPAW 21.6.0 [75, 88] integrated with the Atomic Simulation Environment (ASE) [95]. The calculations, unless otherwise stated, were performed on a real space grid using a grid spacing of 0.16 Å with the BEEF-vdW functional [76] and a Fermi Dirac smearing with a width of σ =0.05 eV. Atomic positions are allowed to relax until all residual forces are below



Figure 5.1: The computational setup used in the SJM calculations

0.06 eV/ Å.

The model system is constructed as a nanoribbon similarly to the method described in the Chapter 4, however the nanoribbon is here turned around so that the edge is pointing towards the z-direction (Figure 5.1). To make room for the water layer and jellium region, slightly more empty space is added, that is 8 and 10 Å in the y and z directions respectively (each side), while the structure is shifted in the z direction to make more space on the reactive side. The system is periodic in the x- and y- directions, while the z-direction, where the solid-liquid interface is located, is non-periodic.

The electrochemical solid-liquid interface is modelled by an implicit/explicit hybrid solvent approach. Four explicit water molecules are added, acting as electrolyte and proton-donor for the reactions. This is combined with an implicit Simple Continuum Model based on Volumetric Data (SCMVD) dielectric continuum model [89] defined within a box-shaped region ranging from 1 Å above the outermost atom in the cell in the z-direction and 1 Å below the top of the simulation cell. This is chosen to avoid the leaking of implicit solvent between the layers in the y-direction that could arise using a cavity shaped implicit solvent region. For Mo, a vdW-radius of 2.1 Å is employed in the SCMVD model[125], while for the remaining atoms default values are adapted from the GPAW database.

To optimize the locations and orientations of the explicit water molecules, The minima hopping method as implemented in ASE is employed [126]. These calculations are performed in LCAO mode with a double zeta plus polarization functions (DZP) basis set to minimize the computational cost. The obtained minimas are subsequently reoptimized using the parameters outlined above.

To obtain grand canonical energies at different fixed potentials, the Solvated Jellium Model (SJM) method as implemented in GPAW is used [87, 127]. The foundation of this approach is

the inclusion of a homogeneous counter charge (a jellium slab) positioned within the implicit solvent region. In this way, the system is kept overall charge neutral, even though the number of electrons in the cell is iteratively adjusted to reach the target potential (Φ_e) within a selected tolerance of 0.025 V. Rather than mainly simulating the electrolyte, the purpose of the implicit solvent is to screen the system from the high potential field originating from the excess electrons and counter charge. To allow for a potential difference across the system, a dipole correction is applied in the periodic xy direction.

The energies employed are the grand canonical energies, Ω :

$$\Omega = E_{tot} + \Phi_e N_e \tag{5.1}$$

with E_{tot} being the DFT energy, N_e the number of excess electrons and Φ_e being the absolute potential, which is converted to the SHE scale (U_{SHE}) by Equation 3.3 and subsequently to RHE scale by Equation 3.2.

The gas phase Gibbs free energies including zero point vibrational energy and entropy contributions are used for molecular reference species. Similarly to the approach employed in the CHE, the Gibbs free energy of reactant H^+ + e^- is calculated by:

$$G_{H^++e^-} = 0.5G_{H2} - eU_{RHE}$$
(5.2)

where G_{H2} is the Gibbs free energy of a gas phase dihydrogen molecule.

Reaction barriers are obtained by the Nudged Elastic Band (NEB) method with the climbing image (CI) modification as implemented in ASE (Chapter 2) [79, 80, 128]. Initial and final states are relaxed, letting the three outermost rows of edge atoms (Te, Mo, Te) as well as the adsorbate and explicit water molecules move, while the additional surface atoms are fixed. When required for the calculations to converge, the bond length between the adsorbate and the Mo reaction site is additionally constrained to ensure, e.g. to shorten the NEB path, without enabling reaction of the reactants in the initial state. Here, an intermediate image from a non-converged NEB calculation is utilized as the initial geometry guess before restarting the relaxation of the entire path. The initial guesses for the NEB paths are constructed by linear interpolation.

The Bader charge analysis scheme is used to compute he atomic charges as outlined in Chapter 2 [81, 129–131]. Charge differences between final and initial images are calculated by Equation 5.3:

$$\Delta q = q_f - q_i \tag{5.3}$$

where q is the Bader charge of an atom, i and f indicating initial and final states, respectively.

Atomic scale modelling of transition metal dichalcogenide electrocatalysts for the electrocatalytic CO_2 37 reduction reaction



Figure 5.2: Variation of the Grand free energy, Ω , as a function of potential, U vs RHE, for six different terminations of the MoTe₂ M edge (structures shown as inserts). The solid lines show polynomial fits to the datapoints, each corresponding to a GCE-DFT calculation at different potentials.

5.2 Edge termination

The edge termination of the nanoribbons were studied using the CHE model in Chapter 4, however explicit potential effects could influence the stabilities of the edge terminations. Here, the most favorable edge terminations found by the CHE model are re-investigated using GC-DFT. Figure 5.2 shows the grand free energies as a function of potential for each of these terminations along with inserts showing the edge configuration. The data is fitted to second order polynomials in accordance with the expected potential dependence [119, 132, 133]. Note the change in notation from Chapter 4, where the the monomer termination is now considered the fully saturated termination, as the terminations with higher X coverages were found to have low stabilities under relevant conditions. The terminations are here furthermore denoted according to the number of tellurium atoms at the edge of width 2 Mo atoms, so that e.g. the monomer termination is denoted Mo₂, and the previously denoted X_{0.25} edge here is Te₁.

The polynomial fits are subsequently used to construct Pourbaix diagrams showing the edge



Figure 5.3: Heatmaps showing the relative stabilities of different edge termination relative to the Te₂ termination. $\Delta\Omega$ has been normalized to the number of electrons transferred.

stabilities as functions of potential and pH according to Equation 3.2 as shown in Figure 5.3, omitting the OH_2 termination which is highly unstable in the considered region. The potential dependence is generally in agreement with the results obtained in Chapter 4 presented in Figure 4.3; lower Te coverage as well as OH coverage is increasingly favored for more negative potentials.

The pH dependence, which was not investigated by the CHE model show some interesting trends. Whereas only a very slight shift towards lower Te coverage is observed for increasing pH, a very significant shift towards OH relative to Te coverage is observed for decreasing pH. This is attributed to the stronger dipole-field interaction of the polar OH group. Due to this strong pH dependence, the Te₁OH₁ termination in particular gains a significant stability at low pH, which could be relevant under experimental conditions using an acidic electrolyte. Here, we assume neutral conditions and a potential below -0.6 V vs RHE, as expected from the study by Liu et al., where activity was measured under neutral conditions in a 0.1 M KHCO₃ electrolyte [68]. At these conditions, the Te₁ termination is expected to dominate. Upon adsorption of CO₂ in the expected most favorable adsorption site, the relative stabilities of Te₁ and Te₂ is not significantly altered, implying that the adsorption of CO₂, which is the initial step of CO2RR, is thermodynamically feasible.

Reaction	Step		Additional constraints
CO2RR	CO_2 adsorption	CO_2 + * $ ightarrow$ * CO_2	r_{Mo-C} fixed in IS
	H transfer 1	$H_2O \texttt{+}^*CO_2 \rightarrow \texttt{^*COOH}\texttt{+} OH^-$	
	H transfer 2	$H_2O \texttt{+} \texttt{*}COOH {\rightarrow} \texttt{*}CO \texttt{+} OH^-$	
	CO desorption	$*CO \rightarrow CO + *$	

Table 5.1: CO2RR reaction steps. Additional constraints indicate if a bond length in the final state (FS) or initial state (IS) was necessary to converge the NEB calculation.

Table 5.2: Evolution of excess electrons for different CO2RR elementary steps at -1.23 V vs RHE.

Elementary step	Initial state	Transition state	Final state
CO_2 adsorption	2.61	2.82	3.10
H transfer 1	2.87	3.22	3.31
H transfer 2	2.54	2.89	3.71
CO desorption	2.89	2.65	2.57

5.3 Potential dependency of thermodynamics and reaction barriers

The selectivity of CO2RR compared to HER could be dependent on chemical kinetics. In this section the reaction barriers of intermediate steps of CO2RR and HER are calculated and compared. Furthermore, the explicit potential dependence of all steps is considered to obtain a better understanding of the selectivity under experimental conditions. Many of the reaction steps of the two reactions involve the transfer of protons from the electrolyte to the surface, hence an explicit treatment of the solvent is here required. This is done by including a layer of four explicit water molecules above the active edge. Under neutral condition in aqueous solution, water rather than H_3O^+ is expected to be the main proton donor.

The water layers considered for CO2RR and HER are constructed for $*CO_2$ and for the pristine surface, respectively. The water layers are optimized using the minima hopping global optimization method. The initial and final states for the NEB calculations are constructed based on the initial water layer, and are subsequently reoptimized. Upon transfer of an proton from water, an OH⁻ ion is formed in the water layer. It is assumed that a proton is subsequently immediately transferred from the bulk reservoir reforming the water layer, so that each NEB final state is considered a short-lived intermediate state.



Figure 5.4: Reaction pathways for the CO2RR reaction steps calculated at different potentials. The forward grand canonical energy barriers, Ω_{\pm} , are given in the legends.

5.3.1 CO2RR

The CO2RR reaction mechanism is considered starting from the CO₂ adsorption step and up to the CO desorption step. The considered reactions are tabulated in Table 5.1. The NEB method is employed to obtain reaction barriers of each intermediate step at three different potentials. The resulting minimum energy paths are shown in Figure 5.4.

The adsorption of CO₂ is exergonic with a barrier ranging from 0.15 eV at -1.23 V vs RHE to 0.29 eV at -0.43 V. A decreasing barrier height is found for increasing potentials, indicating that charge is transferred from the electrode. The observed potential-dependency is rationalized by the charge analysis given in Figure 5.5 showing that the adsorbed CO₂ gains $\sim 0.8e$ charge. Table 5.2 furthermore displays that a total of 0.5 additional electrons are added to the system during the adsorption to maintain a fixed electrode potential at -1.23 V vs RHE.

The first proton transfer reaction resulting in the formation of *COOH, is significantly uphill in energy, however a significant amount of energy is gained when replacing the OH⁻ ion with



Figure 5.5: Bader harge difference defined as $charge_{final}$ -charge_{initial} calculated by the Bader charge analysis scheme for adsorbate C and O, the adsorption site Mo and the neighboring Te atom. CO₂ adsorption (left) and CO desorption (right).

a water molecule from the reservoir. The barriers of both H transfer reactions are decreased with increasing applied potentials indicating that charge is transferred along with the proton transfer as is also evident from Table 5.2. The CO desorption reaction, which is the final elementary step considered here, is found to be highly endergonic and associated with a substantial barrier of more than 1.4 eV at all the potentials considered, indicating that CO desorption is unfavorable. This is likely to explain the observation of methane, a "beyond CO"-product, as the major product of CO2RR on MoTe₂ nanoflakes [68].

Interestingly, the CO desorption barrier increases with increasing applied potential, which is expected to push the overall selectivity towards further reduction. This is indicative of charge transfer from the CO molecular orbitals to the surface upon desorption, which is expected if π -backbonding is involved in the bonding. Figure 5.6, showing the projected density of states (PDOS) before and after desorption, displays how the bonding and antibonding π -orbitals of CO(g) are observed as sharp lines in the spectrum. After adsorption, additional C and O (C+O) p-peaks arise within the Mo d-band (Mo(d)) showing clearly the π^* -backbonding. Furthermore, a small peak at the highest occupied molecular orbital (HOMO) from the p-orbitals of the CO (CO(p)) arises in the Mo(d) demonstrating the corresponding σ -bond. A very similar bonding behaviour is exhibited by CO₂ as seen in Figure 5.7, however here the arising π -backbonding states are more pronounced implying a larger degree of electron transfer in agreement with the actual observed number of transferred electrons (see Figure 5.5)



Figure 5.6: Projected density of states for the C and O orbitals of CO and the adsorption site Mo d-orbital after (left) desorption and before (right). The energy, E is plotted relative to the Fermi level, Ef.

Comparing the barrier heights of the three first reactions, the first H transfer is expected to be the rate determining step (RDS) assuming that CO desorption will not take place. The experimentally measured Tafel slope in an ionic liquid is 68 mV/dec [68]. Under certain restrictive assumptions, a simple equation for the overall Tafel slope of the entire reaction can be derived [134]:

$$slope_{Tafel} = \frac{60 \text{mV/dec}}{n+q/2}$$
 (5.4)

where n is the number of electrons transferred up until the RDS and q is the number of electrons transferred in the RDS. this gives rise to the so-called cardinal Tafel slopes corresponding to certain (n, q) pairs. E.g (1, 0), which is the RDS is a chemical step following an electron transfer event, corresponds to a Tafel slope of 60, which is close to the observed 68 mV/dec observed. From CO₂ to *CO two electrons are transferred in total. Given the smaller amount of charge transferred in the first H transfer compared to the CO₂ adsorption step, the first H transfer step could approximately be considered a chemical step and would therefore be considered the RDS. As this is the step with the highest calculated barrier, this interpretation is in agreement with the results. However there are several uncertainties, e.g. further reaction barriers are not considered, the barriers of H transfer 1 and 2 are similar in magnitude, and the Tafel slope was measured in an ionic liquid, and do not necessarily transfer directly to an aqueous medium.

The size and structure of the explicit water layer is likely to impact the computed thermodynamics and barriers. This effect was investigated by calculation of selected NEB paths (H transfer 1 and CO desorption) for two additional minima structures for the water layers resulting from minima hopping calculations for 4 and 5 water molecules in the layer respectively (4wb



Figure 5.7: Projected density of states for the C and O orbitals of CO_2 and the adsorption site Mo d-orbital before (left) and after (right) adsorption. The energy, E is plotted relative to the Fermi level, Ef.

and 5wa) as shown in Figure 5.8 and 5.9. The influence of the water layer structure on these two reaction barriers is found to be relatively minor, i.e within 0.04eV (6%) for H transfer 1 and 0.19 eV (12%) for CO desorption. Whereas these deviations are small, the difference between some of the barriers is similarly small, e.g H transfer 1 and H transfer 2.

5.3.2 HER

In aqueous medium, HER is the main competing reaction for CO2RR. HER is usually considered to take place via either the Volmer-Heyrovsky or the Volmer-Tafel mechanism. Both mechanisms are initiated by the Volmer step, where a H atom is adsorbed from the solvent water. This step is followed either by the Heyrovsky step, the reaction of H* with an additional solvent H atom, or another Volmer step followed by a subsequent Tafel step, which is the combination of two adsorbed H atoms. Both mechanisms are terminated by H_2 desorption. Table 5.3 shows the 5 elementary reactions involved in these two mechanisms and any additional constraints that were necessary to converge the NEB calculations.

The computed NEB paths at three different applied potentials are shown in Figure 5.10. The reaction barriers for the Volmer and Heyrovsky steps are rather high (1.07 eV, 1.20 eV and 0.84 eV at -1.23 V vs RHE) and all three reactions are furthermore endergonic. A large amount of energy is gained so that the reactions become exergonic upon reformation of the charge-neutral water layer (Figure 4.11). Comparing with the barrier observed for CO_2 adsorption (0.29 eV at -1.23 V vs RHE), the barrier for the first Volmer step is larger by more than 0.8 eV, indicating that CO2RR is favored.



Figure 5.8: Atomic structures for water layers 4wa, 4wb and 5wa. Top view (left) and side view(right). Turquise=Mo, brown=Te, gray=C, red=O, white=H.

As was observed for CO2RR, the charge monotonously changes over the course of the reaction in the case of Volmer 1, Volmer 2, Heyrovsky and H_2 desorption as seen in Table 5.4. Oppositely, for the Tafel reaction, a slight non-linear charge evolution is found. That is, the charge decreases from the initial to the transition state and subsequently increases from the transition to the final state, implying a higher potential sensitivity of the reaction barrier than the reaction energy [118]. However, the charge evolution through the reaction is minor for the Tafel step, hence the observed trend is associated with a high degree of uncertainty.

Comparing the barriers for the Heyrovsky step and the second Volmer step (the second step in the Volmer-Heyrovsky and Volmer-Tafel mechanism respectively) shown in Figure 5.10, the dominating HER pathway is expected to be the Volmer-Heyrovsky at the electrode potentials considered here. The reaction barriers of the Volmer1, Volmer2, and Heyrovsky steps decrease with increasing applied potential, implying that the proton transfer reactions are coupled with



Figure 5.9: Reaction pathways for the CO2RR reaction steps calculated at -0.8 V vs RHE for different water layer configurations and sizes. The forward grand free energy, Ω_{\ddagger} , barriers are given in the legends.

Table 5.3: HER reaction steps.	Additional constraints indicate if a bond	length in the initial
state (IS) or final state (FS) was	necessary to converge the NEB calculation	۱.

Reaction	Step		Additional constraints
HER	Volmer 1	* + H ₂ O \rightarrow * H+ OH $^-$	r _{Mo-O} fixed in FS
	Heyrovsky	$^{*}\text{H} + \text{H}_{2}\text{O} \rightarrow ^{*}\text{H}_{2} + \text{OH}^{-}$	
	Volmer 2	$^{*}\mathrm{H}+\mathrm{H}_{2}\mathrm{O}$ $ ightarrow$ 2 $^{*}\mathrm{H}+\mathrm{OH}^{-}$	r _{Mo-O} fixed in FS
	Tafel	$2^*H \rightarrow^*H_2$	
	H_2 desorption	$^*H_2 \rightarrow H_2$	

charge transfer. Both mechanisms are terminated by the desorption of $\mathsf{H}_2.$

Two different *H₂ structures are identified (*H₂^a and (*H₂^b)) both of which are adsorbed flat on the Mo-site, rather than stacked on top of each other. The H-H distances are 1.86 Å (*H₂^a) and 0.82 Å (*H₂^b), with *H₂^a being energetically favorable by 0.26 eV. Interestingly, it is found that whereas the Tafel reaction has *H₂^a as the final state, the barrier for the Heyrovsky step is lower for the *H₂^b final state than using *H₂^a as the final state. The desorption barrier for the more stable *H₂^a is 0.30 eV larger than for *H₂^b. Furthermore, the desorption of H₂^a is found to proceed via the initial formation of *H₂^b (observed as a shoulder in the NEB path in Figure 5.10 bottom center). However, only at low negative potentials, this initial step is found to have a significant barrier.



Figure 5.10: Reaction pathways for the HER reaction steps calculated at different potentials. The forward grand canonical energy barriers, Ω_{\pm} , are given in the legends.

5.3.3 Potential trends

Figure 5.11 summarizes the potential dependency of the grand free energy barriers of the CO2RR and HER elementary steps. Notably, the potential-dependency for the first Volmer step is stronger than that of the CO₂ adsorption step, which results in HER becoming relatively more favorable with increasing applied potential. However, at experimentally relevant potentials, CO2RR is expected to be preferred, e.g the barrier for the first Volmer step is more than 1 eV larger than for the CO₂ adsorption at -0.8 V vs RHE. Comparing the trends for Heyrovsky step and the second Volmer step, a slightly more sensitive potential dependency is found for the

Table 5.4: Evolution of excess electrons of the DFT region for different HER elementary st	eps
at -1.23 V vs RHE.	

Elementary step	Initial state	Transition state	Final state
Volmer 1	2.68	3.14	3.37
Volmer 2	2.81	3.18	3.42
Heyrovsky	2.80	3.18	3.40
Tafel	2.84	2.75	2.83
H_2 desorption a	2.83	2.63	2.59
H_2 desorption b	2.80	2.62	2.59



Figure 5.11: Forward grand canocnical energy barrier, Ω_{\ddagger} as a function of potential. Linear fits for each CO2RR (left) and HER (right) step are given in the plots.

second Volmer step, indicative of a shift towards the Volmer-Tafel mechanism compared to the Volmer-Herovsky at highly negative potentials. Finally, the two H transfer steps in CO2RR show significantly different potential dependency with the second step being more potential dependent. As the barriers for these two reactions are similar in magnitude, this is likely to result in the RDS being potential dependent.

The energy diagrams for the full CO2RR and HER mechanisms at -0.8 V vs RHE are shown in Figure 5.12. Comparison of the reaction pathways shows that, although HER is thermodynamically favored, CO2RR is kinetically preferred, as all CO2RR barriers to *CO are smaller than the barrier for the first Volmer step. The sluggish HER kinetics compared to CO2RR at the MoTe₂ edge are likely to explain the experimentally observed CO2RR activity in aqueous electrolytes [68]. These results furthermore emphasize that the inclusion of reaction kinetics as a function of the electrode potential is crucial, as the CHE approach, which only considers thermodynamics, would fail in predicting the preference for CO2RR over HER.

5.4 Conclusion

In this chapter, the reaction thermodynamics and kinetics of the CO₂ reduction reaction (CO2RR) as well as the competing Hydrogen Evolution Reaction (HER) at MoTe₂ edges in the 2H were investigated. To implicitly account for the effect of the electrode potential, a grand canonical



Figure 5.12: Full energy diagram showing the reaction pathways for CO2RR and HER at -0.8 V vs RHE. (H^++e^-) is abbreviated "H". Grey text denote shared levels for the Volmer-Heyrovsky and Volmer-Tafel mechanisms. TS denotes a transition state.

ensemble DFT approach was employed using an implicit/explicit hybrid solvent model. It is found that while HER is thermodynamically more favorable, CO2RR is kinetically preferred at the experimentally relevant potentials due to the high reaction barriers of the initial HER steps. This finding aligns well with with previous experimental findings demonstrating a relatively high aqueous electrolyte CO2RR activity on MoTe₂ [68].

Fundamentally different potential dependencies are found for the different elementary steps. Most notably, the barrier for CO_2 adsorption is decreased for increasing applied potentials, while the opposite is observed for CO desorption. This implies that reduction beyond CO is becoming increasingly favorable for more negative potentials compared to CO desorption. On the other hand, the potential dependence of the first Volmer step initiating the HER mechanism is more sensitive than those of the CO2RR elementary steps. Hence, HER competition is expected to become more and more problematic with the increasing potential. The findings in this section emphasize, that a thermodynamic description, as e.g. provided by the CHE model, is insufficient as including the kinetic barriers here result in a qualitatively different conclusion. Furthermore, it is demonstrated that the different potential dependence of different reactions significantly impacts the overall reaction path. This could be utilized to target different reaction products.

The CO2RR mechanism was studied up until the point where CO is potentially desorpbed from the surface. The further mechanism towards CH_4 is significantly more complicated. Further studies of interest include investigations of the further reduction of CO^{*} to CHO^{*} or COH^{*}, which are believed to be possible pathways.

6 Summary

The reduction of CO_2 provides the missing link in the anthropogenic carbon cycle, where increasing emissions of CO_2 from fossil fuel burning has lead to highly increased concentrations of CO_2 in the atmosphere. Using renewable energy and CO_2 captured from emmissions from hard to abate sectors, the electrcatalytic CO2 reduction (CO2RR) provides us with net zero fuels and chemicals, while serving as a energy storage technology.

The search for new electrocatalysts for the reaction has become a hot topic in the field of heterogeneous catalysis, with countless of different materials being proposed. So far copper (Cu) has been unique in its ability to reduce CO_2 to highly reduced products, due to its not too strong, not too weak adsorption of CO and H, an intermediate of the infamous competing Hydrogen Evolution Reaction (HER). Among the many promising candidate materials are the Transition Metal Dichalcogenides (TMDCs), which have been the topic of this thesis.

The TMDCs as a group was investigated in a screening study in Chapter 4, where it was found that the edge termination is highly dependent on which TMDC material is being investigated, clearly demonstrating that MoS_2 , an extensively studied material, will not serve well as a model structure for the remaining members of this family. It was also shown that the adsorption energies of H and CO, which for the transition metals are neat descriptors for the CO2RR selectivity, show some interesting trends. Within each group of TMDC (S, Se, Te), a linear scaling is observed between the two adsorbates, however a shift towards stronger CO adsorption and weaker H adsorption is observed with increasing size of the anion. Assuming that the trend observed for the transition metals is valid also for the TMDCs, this corresponds to a shift towards the much desired "beyond CO" products. Furthermore, the edge terminations is found to have a large effect on the adsorption energies.

The explicit potential dependence of the CO2RR and HER mechanisms on $MoTe_2$ was investigated in Chapter 5 using a Grand Canonical DFT (GC-DFT) approach. Here, it was found that whereas a purely thermodynamic description of the reactions would predict that the catalyst was selective for HER, the kinetics were found to favor CO2RR. This illustrates the need for going beyond the Computational Hydrogen Electrode (CHE) model in order to fully understand the activity. The different intermediate steps are found to show very different potential behaviour, an effect that could e.g. result in HER being increasingly problematic for increasingly negative potentials. Meanwhile, it is also found that beyond CO production could become increasingly favorable compared to CO desorption.

The results presented in this thesis provide new insights that may aid future design of TMDC electrocatalysts for CO2RR, but also for other catalytic reactions, as the edge termination an stability data provided are fundamental for any process. The results explain existing experimentally observed trends and will guide in the selection of new candidate materials, e.g. for future experimental studies.

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A Included publications

A.1 Paper I

Trends in CO₂ **reduction on Transition Metal Dichalcogenide Edges** <u>Pernille D. Pedersen</u>, Tejs Vegge, Thomas Bligaard and Heine A. Hansen ACS Catalysis (2023), 13, 4, 2341–2350

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Trends in CO₂ Reduction on Transition Metal Dichalcogenide Edges

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ABSTRACT: Electrocatalytic CO_2 reduction is a promising solution to close the anthropogenic carbon cycle. However, linear scaling relations among reaction intermediates of the CO_2 reduction reaction (CO2RR) and the competing hydrogen evolution reaction (HER) limits the Faradaic efficiencies and selectivities of traditional transition metal catalysts. The two-dimensional transition metal dichalcogenides (TMDCs) is a promising class of catalysts for the reaction. Selected transition metal dichalcogenides have been shown experimentally to effectively reduce CO_2 and in some cases produce "beyond CO"products. The majority of theoretical investigations have focused on



 MoS_2 and WS_2 , materials that have been widely studied for various applications, e.g desulfurization, HER, Li metal batteries and optical devices. In this computational study, we go beyond Mo and W and study the edge configurations, adsorption properties and aqueous stability of a range of TMDC materials in the 2H phase. We show that the most stable edge configuration is highly dependent on the specific composition of the material, while adsorption properties of H, CO, and COOH vary significantly with edge configuration. We furthermore find that, while a linear scaling among H and CO adsorbates is observed within each group of the sulfides, selenides, and tellurides, respectively, the scaling is shifted toward weaker H bonding and stronger CO bonding going from sulfides to selenides to tellurides. A similar trend is observed for CO/COOH for some edge configurations. The results indicate that the transition metal ditellurides are a promising class of materials with the potential of reducing CO_2 further than CO while limiting HER.

KEYWORDS: electrocatalytic CO₂ reduction, density functional theory, transition metal dichalcogenides, adsorption energies, edge termination, aqueous stability

INTRODUCTION

The global transition from fossil to renewable energy requires the implementation of large-scale energy conversion and storage due to the intermittent nature of most renewable energy sources. In this regard, the conversion of CO_2 to fuels and chemicals using electrocatalytic CO_2 reduction is an intriguing solution.^{1,2} Provided with CO_2 , e.g., from direct air or point source carbon capture, this technology closes the anthropogenic carbon cycle, thereby providing net-zero fuel solutions for applications where electrification is not feasible.

The complex mechanism of the CO_2 reduction reaction (CO2RR) is still debated.^{3,4} The simplest possible products involve transfer of 2 e⁻ to yield either formate/formic acid (HCOO⁻/HCOOH) or carbon monoxide (CO). The formation of further reduced products is believed to proceed via reaction of CO.

The electrocatalytic activity toward the CO2RR of the transition metals has been widely studied, and it is wellestablished that they can be grouped based on their major CO2RR products.⁵ Fe, Ni, Pd, and Pt are not active for CO2RR and produce only hydrogen from the competing Hydrogen Evolution Reaction (HER); Cd, In, Sn, Hg, Ti, and Pb produce formate; and Zn, Ag, and Au produce CO. Of the transition metals, Cu is the only pure metal which produces (unselectively and at a high overpotential) a range of products beyond $\text{CO.}^{3,6,7}$

It has been shown that the H and CO adsorption energies can be used to classify the transition metals based on their major products.⁸ The HER-active materials have a sufficiently strong H bonding that the CO2RR cannot compete. The COand formate-producing metals have weak hydrogen bonding; hence, due to the linear scaling between the adsorption energies,⁹ also a weak CO bonding so that CO or formate is released from the surface before reacting further. Among the transition metals, only Cu has intermediate bonding of both intermediates; hence, the reduction is allowed to proceed beyond CO.

Transition metal dichalcogenides (MX_2 , X = (S, Se, Te)), are promising catalyst materials for a range of processes in energy applications.^{10–13} Most of the research in catalytic applications has been carried out in relation to the HER, where

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Figure 1. Visual representation of the computational workflow followed to evaluate expected catalytic activity of TMDC materials from the Computational 2D Materials Database (C2DB).

MoS₂ in particular is extensively studied.^{14,15} High activities toward both the Oxygen Evolution and the Oxygen Reduction has been observed for a range of TMDCs, with MoS₂, NbS₂, VS₂, and VSe₂ being the most promising candidates.¹⁶ Finally, a range of different TMDCs have been studied for the CO2RR. Nanostructured MoS₂, MoSe₂, WS₂ and WSe₂ catalysts have been shown to have high activity for CO production in an ionic liquid electrolyte.¹⁷ In another study, 1-propanol was observed as the major CO2RR product (FE= 1-3.5%) from single-crystal and ultrathin MoS₂ in an aqueous electrolyte, most likely produced by a semicatalytic mechanism involving desulfurization of the surface.¹⁸ In yet another study using an aqueous electrolyte, the only observed product was hydrogen.¹⁹ TiS₂ has been shown to have high efficiency toward CO and formate formation, which is attributed to the high conductivity of the semimetallic 1T phase.²⁰ The transition metal ditellurides are generally less explored than the sulfides and selenides; however, thin film MoTe, is interestingly found to produce methane as the major product in ionic liquid (FE = $83 \pm 3\%$).²¹ Notably, the authors report also a Faradaic efficiency for methane of around 15% in an aqueous electrolyte $(0.1 \text{ M KHCO}_3).$

2D TMDCs are usually obtained from mechanical or chemical exfoliation or chemical vapor deposition.^{14,22} The TMDCs are commonly found in three different phases: 2H, 1T, and 1T'. MoS₂ is found in the stable 2H phase and metastable 1T phase, which has very different catalytic properties. The 2H edges and 1T basal planes are widely believed to be the active sites for catalysis.^{23–25} Hence, in the 2H phase, the catalytic activity is highly dependent on the structure of the edge. Doping MoS₂ with 5% Nb has been shown to increase the turnover frequency for CO by an order of magnitude.²⁶ While the sulfides and selenides are usually only stable in the 2H phase, the more exotic tellurides are found in a variety of phases.^{27–31}

The atomic-scale edge structure of 2D Mo and W TMDCs (MoS_2 in particular) in the 2H phase has been the subject of a range of density functional theory (DFT) studies;^{32–35} however, other TMDCs are much less investigated. Computational studies of the adsorption properties of MoS_2 and $MoSe_2$ 2H edges show that CO and COOH are adsorbed on different sites, thereby breaking the scaling relation observed for transition metals.^{36,37} The basal chalcogenide vacancy on the 2H and 1T/1T' phase group V, VI, and X sulfides and selenides was furthermore systematically investigated, and it was found that most are only active toward HER or prone to OH poisoning.³⁸

With the decreasing cost of computational resources, computational screening studies addressing catalytically relevant properties, such as stability and adsorption energies, have become more common in energy research to explore the vast chemical space of potential material candidates for various processes. 2D materials have been the subject of screening studies, e.g., for photocatalytic and electrocatalytic $\rm CO_2$ reduction.^{39–41}

In this study, we perform a systematic screening of edges of 2D TMDC materials in the 2H phase, addressing the configuration of the edge, the adsorption energy of H, CO, and COOH, as well as aqueous stability of the materials in order to unravel trends and suggest potential novel candidates for the CO2RR.

COMPUTATIONAL METHODS

All DFT calculations have been carried out in the Vienna Ab Initio Simulation Package (VASP 5.4.4)^{42,43} integrated with the Atomic Simulation Environment (ASE).⁴⁴ The BEEF-vdW exchange-correlation functional has been employed^{45,46} with a plane wave basis set with a cut off energy of 450 eV and a $N_{k\text{-points}} \cdot a \geq 30$ Å in the periodic directions and 1 k-point in nonperiodic directions. Gaussian smearing with a smearing width of 0.03 eV is employed. The atomic positions are allowed to relax until residual forces in all directions are less than 0.03 eV/Å.

A single layer of TMDC in the 2H phase consists of a hexagonal lattice of transition metal atoms sandwiched by two chalcogen atom layers. Each metal atom is coordinated by six chalcogen atoms in a trigonal prismatic lattice. 2D periodic sheet structures are taken from the Computational 2D Materials Database (C2DB).^{47,48} The structures are periodic in x and y directions, while an added vacuum of 7.5 Å at each side of the structure ensures nonperiodicity in the z direction. The materials are selected according to the predefined C2DB stability criteria.47,48 Materials are classified as having low, medium, or high thermodynamic and dynamic stability, with the lower value deciding the overall stability. Based on a comparison with a data set of experimentally synthesized 2D materials, the authors consider materials with a "high" overall stability likely to be stable and thus potentially synthesizable. In this work, we include only materials classified with "high" overall stability. Specifically, this corresponds to materials with a tabulated heat of formation > convex hull + 0.2 eV/atom, a minimum eigenvalue of the Hessian > $-0.01 \text{ meV/}\text{Å}^2$, and a minimum stiffness tensor eigenvalue > 0.

To handle the large number of calculations performed, an automatic workflow structure is set up within the framework of



Figure 2. a) MoS_2 2D sheet top view (center left), sheet side view (center right) and side views of the chalcogen edge (top) and metal edge (bottom). Edge terminations at the M edge (b) and X edge (c) with different X coverages. Edge atoms are indicated with black. The examples shown are optimized MoS_2 structures (Mo = blue, S = yellow, O = red, H = white).

the task and workflow scheduling system MyQueue.⁴⁹ The overall workflow describing the calculation steps of this study is visualized in Figure 1, and the individual steps are described below.

As a first step, the atomic positions and cell shape of 2×4 supercells (8 metal atoms and 16 chalcogen atoms) for the bulk 2D materials, selected according to the criteria described above, are relaxed.

From the relaxed sheet structures, nanoribbons are constructed by adding an additional 7.5 Å of vacuum at each side of the structure in the x direction. In this way, two opposite zigzag edges are obtained: the M edge and the X edge as shown in Figure 2. These edges have a number of possible terminations which will be further discussed in Section 4.1. The atomic positions of the nanoribbons are relaxed with the lattice parameters fixed in the sheet configuration.

Adsorption configurations and energies are obtained by placing the adsorbate in all on-top and bridge adsorption sites involving edge atoms of the nanoribbons, while fixing the additional three rows of atoms so that only the outermost row of X and M atoms, as well as the next row of X atoms, are allowed to relax. The relaxed structures are then passed through a sorting scheme to exclude structures undergoing major reorganizations. This includes curved structures, defined as structures where one or more of the metal atoms are displaced in the z direction by more that 10% compared to the average z position. Furthermore, structures where an edge X atom has been subtracted from the surface by the adsorbate and structures where the adsorbate-surface distance > 2.9 Å, where the adsorbates are assumed to no longer be adsorbed, are excluded. Of the remaining structures, those for which the maximum residual forces did not reach 0.03 eV/Å in the first relaxation are allowed to start a rerelaxation from the last point of the first relaxation. From the final relaxed structures, the adsorption site with the lowest total energy is then selected and the adsorption energy is calculated with reference to the clean nanoribbon and the gas phase reference molecule. The entropy (S) and the zero point vibrational energies (ZPE) are included for molecular species at T = 293 K but neglected for surfaces, as these quantities are expected to be largely unchanged upon adsorption. A ZPE correction is calculated for adsorbed species on the MoS₂ edge. Assuming furthermore that the surface composition has a minor impact on the adsorbate vibrations, the MoS₂ values are used as correction terms for the remaining

surfaces. The adsorption Gibbs free energies are then calculated by

$$\Delta G_{\text{adsorption}} = E_{*_{\text{ads}}} + ZPE_{*_{\text{ads}}} - E_{*}$$
$$- (E_{\text{mol}} - TS_{\text{mol}} + ZPE_{\text{mol}})$$
(1)

where, * indicates a surface site, *ads indicates the adsorbed species on the surface, and "mol" indicates the free adsorbate. The computational hydrogen electrode (CHE) model has been used to compare the stability of different edge terminations of the nanoribbons.⁵⁰ In this model, the chemical potential of an electron—proton pair is equal to that of one-half hydrogen molecule in gas phase at standard pressure, i.e., μ (H⁺ + e^-) = 0.5 μ (H₂), to calculate the free energies at 0 V vs the Reversible Hydrogen Electrode (RHE) The reaction free energy varies linearly with electrode potential (RHE), *U*, as the chemical potential of the electron is shifted by — eU at potentials different from 0 V (RHE), where *e* is the elementary charge.

$$\Delta G_{\rm i}(U) = \Delta G_{\rm i}(U=0) + eU \tag{2}$$

Stability under reaction conditions is a fundamental prerequisite for a successful candidate material. Here, the aqueous stability of the materials is considered using Pourbaix diagrams as implemented in ASE. Additional solid and solvated reference energies are adapted from The Atlas of Electrochemical Equilibria in Aqueous Solutions.⁵¹ Bulk metal references are calculated in their preferred crystal lattice using the same computational methods as described above. Bulk sulfur (mp-96), selenide (mp-570481) and tellurium (mp-19) structures are adapted from the Materials Project and reoptimized using the details outlined above.⁵²

RESULTS AND DISCUSSION

In this section, we first discuss the edge configurations of the M and X edges. Then, CO, H and COOH adsorption energies will be presented before addressing the aqueous stability. Finally, we will suggest candidate materials, taking into account the findings from the previous sections. Throughout the section, we consider a potential range from 0 V vs RHE to -1 V vs RHE. Based on experimental results, we expect that the relevant potential range for CO2RR is -0.3 to -1.^{17,21}

Edge Configuration. The catalytic activity of the TMDC catalysts will depend on the atomic structure of the edges, which are expected to contain the active sites for catalysis. In



Figure 3. Edge terminations stability as a function of U vs RHE relative to the X₁ termination calculated by the Computational Hydrogen Electrode (CHE) model. Relative stabilities at the M edge exemplified for MoS₂ M edge (a) and X edge (b). The results for all materials studied are summarized by plotting the most stable termination as a function of U vs RHE at the M edge (c) and the X edge (d).

this section, the thermodynamic stability of the edge structures under reducing conditions in the absence of CO_2 is investigated.

M Edge. The M edges of the nanoribbon structures are stoichiometrically terminated by a row of exposed metal atoms, which are undercoordinated by two chalcogen atoms (Figure 2a). Previous studies have shown that the fully exposed M edge in MoS_2 is unstable relative to terminations, where additional sulfur atoms are adsorbed on the edge.³³

In agreement with this, our initial calculations show that these exposed surfaces in many cases are inclined to contract the outermost metal atoms to regain an outer layer of chalcogen atoms because retaining the undercoordinated metal edge atoms is highly unfavorable. Hence, this termination is not considered any further herein.

Two different edge configurations upholding a full six-fold coordination of each M atom at the M edge have previously been reported.^{32,33} In the dimer termination, four additional X atoms are adsorbed at the edge following the same crystal lattice as the remaining atoms, giving a coverage of 1 (X₁). For the monomer termination, the adsorption site is shifted by half a lattice constant in order to ensure coordination to six X atoms for each M atom, giving a total coverage of 0.5 (X_{0.5}). As the edges studied here have a width of two metal atoms, it is furthermore possible to construct terminations in between the fully coordinated terminations with coverages of 0.25 (X_{0.25})

and 0.75 $(X_{0.75})$ as illustrated in Figure 2b. In all cases, the opposite X edge is terminated by the stoichiometric configuration of four X atoms organized in the same lattice as the remaining X atoms.

The stepwise transformation from the fully covered dimer edge to the fully exposed edge can be described by the following reaction:

$$S^* + 2(H^+ + e^-) \to {}^* + H_2S$$
 (3)

Surface hydroxyl groups have been shown to significantly influence the CO2RR for various materials.^{53,54} In aqueous solutions, OH can be adsorbed on the surface through the following oxidation reaction:

$$^{*} + H_{2}O \rightarrow ^{*}OH + (H^{+} + e^{-})$$
 (4)

At the M edge, we consider the edge terminations with 0.25 $(OH_{0.25})$ and 0.5 $(OH_{0.5})$ OH coverage, as well as mixed terminations with the 0.25 S and OH coverage $(X_{0.25}OH_{0.25})$.

The relative thermodynamic stability of all the considered terminations is plotted for MoS_2 in Figure 3a. In agreement with previous studies,^{32,33} the intermediate $X_{0.75}$ termination is not the most stable at any relevant potential. Of the two fully coordinated terminations, i.e., the monomer and dimer, the monomer termination is favorable at all negative potentials; however, the undercoordinated $X_{0.25}$ edge is found to be more stable below -0.1 V vs the RHE. OH-terminated config-



Figure 4. Calculated adsorption Gibbs free energies of H and CO calculated at the $X_{0.5}$ (left) and $X_{0.25}$ (right) M edges. Inserts show top and side views of the relevant edge configurations. The black lines at $\Delta G_{ads} = 0$ indicate expected product regions (H₂, CO/HCOOH, and Beyond CO).

urations are found to be unfavorable at potentials between -0.6 and -1 V vs RHE. A similar analysis is performed for each of the materials, and the results are summarized in Figure 3c, which shows the most stable termination as a function of the potential. Here, we find that, generally, the $X_{0.25}$ termination is the most stable of the OH-free terminations at high negative potentials, while the monomer termination is found to be stable at intermediate potentials for some selenides and tellurides. The affinity for hydroxyl adsorption is observed to decrease in the order of sulfide > selenide > telluride for the three metals for which all three transition metals are considered (Cr, Mo, and W). A similar trend is observed going from the selenide to the telluride for V, Ti, Nb, and Hf.

X Edge. The chalcogen-terminated edge in the stoichiometrically cut surface exposes a row of four X atoms. For practical reasons, the opposite M edge is here terminated by the monomer (0.5) termination, as the stoichiometric exposed M atoms row is not stable. Removing gradually X atoms from the X edge, coverages of 0.75, 0.5, and 0.25 are obtained. In agreement with previous studies, we find it is more favorable for the stoichiometric termination to dimerize such that every other X-pair is pointing either up or down rather than retaining the lattice configuration. Likewise, for the monomer termination, it is found that displacing the edge atoms, so that one atom is pointing up and one is pointing down, is more favorable than the symmetric configuration. OH-terminated edges with coverages of 0.25 and 0.5, as well as the mixed 0.25 S/OH edge, are furthermore considered. The relative stabilites of the edge terminations are plotted for MoS₂ in Figure 3b and summarized for all of the materials in Figure 2c. Similarly to the metal edge, the 0.25 and 0.5 coverages are generally the most stable of the OH-free terminations at high negative potentials as shown in Figure 3d. At low and intermediate negative potentials, the X_{0.75} and dimer terminations have a larger stability window than was seen for the M edge. Interestingly, the OH adsorption is found to be significantly more favorable at the X edge, which is in good agreement with the observation for MoS_2 ,³⁴ suggesting that the M edge is the more important edge for catalysis.

Adsorption. Adsorption of CO2RR intermediates and intermediates of competing reactions is a key factor determining the catalytic activity. In a previous study, it was found that the CO and H adsorption energies are excellent descriptors determining the major products of the CO2RR on

transition metal catalysts.⁸ If hydrogen is bonded strongly, the HER is expected to dominate, while a weak CO and H adsorption is an indicator of CO or formate being the major product. In the case of sufficiently weak hydrogen adsorption and sufficiently strong CO adsorption, it becomes possible to further reduce CO to "beyond CO" products, as is only observed for Cu among the transition metals. In this section, the adsorption energies of CO and H on selected edge terminations are investigated. We also present adsorption energies of COOH, the first intermediate of CO2RR. Database files containing all adsorption geometries, as well as R² values for the linear fits presented in this section, are provided in SI.

M Edge. We showed above that in most cases, the $X_{0.25}$ and X_{0.5} edges are the most stable of the OH-free edge configurations in the relevant potential range. We find that for X_{0.5}, CO adsorption in all cases is energetically most favorable in the on-top M position. H is in most cases adsorbed in the on-top X position, whereas for four of the tellurides the on-top M site is slightly favored. This behavior can be rationalized by the ability of the hydrogen atom to bind as a σ acceptor or donor. For X_{0.25}, the most favorable adsorption site for CO is the on-top M position, with the CO molecule rotated toward the X vacancy. This is in most cases also the favorable H adsorption site, but in some cases various other sites are favored. As the H adsorption is generally weak, there is a minor difference between the adsorption energies at the different sites. Adsorption energies of CO and H in the most favorable adsorption sites are plotted in Figure 4 for each edge configuration. On the plot is furthermore indicated ΔG_{H^*} = 0 and ΔG_{CO^*} = 0 (black lines), which have previously been shown to separate the transition metals into groups based on their major products (H₂, CO/HCOOH, and Beyond CO).⁸

Within each group of TMDCs, a positive linear scaling relation is observed between H and CO bonding. However, a clear trend going from the sulfides to the selenides to the tellurides is observed for both terminations; hydrogen adsorption is weakened while CO adsorption is enhanced on agreement with previous calculations for Mo and W dichalcogenides.³⁵ According to the classification boundary this would correspond to a shift toward the "beyond CO" region. This unusual observation can be rationalized considering the ligand bonding properties of CO and H. Going from S to Se to Te, the polarity of the M-X bond is decreased, thereby decreasing the partial positive and negative



Figure 5. Calculated adsorption Gibbs free energies of H and CO calculated at the $X_{0.5}$ (left) and $X_{0.25}$ (right) X edges. Inserts show top and side views of the relevant edge configurations. The black lines at $\Delta G_{ads} = 0$ indicate expected product regions (H₂, CO/HCOOH, and Beyond CO).



Figure 6. Calculated adsorption Gibbs free energies of COOH and CO calculated at the $X_{0.5}$ (left) and $X_{0.25}$ (right) M edges. Structures were a bidentate bonding is sterically hindered are labeled by star-shaped markers. Inserts show top and side views of the relevant edge configuration.

charges on the metal and chalcogen sites. Whereas H, as a purely σ -bonding ligand, will bind more weakly to the less charged sites, CO, which is an efficient π -backbonding ligand, binds more strongly to the less positively charged metal site due to the increased electron density available for backbonding. Supporting this interpretation, the C–O bond length is generally increased in the order of S < Se < Te, indicating a weakening of the CO triple bond (Figure S.2). However, more insight into this relationship could possibly be obtained by careful investigation of the electronic structure.

In agreement with this observation, $MoTe_2$ in ultrathin layers is the only Mo dichalcogenide which has been found experimentally to produce methane as a major product in an ionic liquid electrolyte and to a lesser extent in an aqueous electrolyte,²¹ whereas MoS_2 and $MoSe_2$ nanoflakes yield CO as a major product in an ionic liquid electrolyte.¹⁷ Interestingly, the edge termination is also found to influence the adsorption energies, as it is observed that the creation of a vacancy going from a coverage of 0.5 to 0.25 results in the CO adsorption energies being shifted toward stronger binding. Hence, targeting a specific edge configuration by choice of reaction conditions (e.g., potential) could potentially be a mean for targeting different CO2RR products.

X Edge. For the X edge adsorption, the $X_{0.5}$ and $X_{0.25}$ edges are investigated. As previously discussed, $X_{0.5}$ is ordered so that

the X atoms, to varying extents, are shifted up and down. In order to limit the number of adsorption sites, the adsorbates are added to the initially symmetric surface. This perturbation is in most cases sufficient to shift the X atoms. The adsorption energies are plotted in Figure 5. Comparing the X edge X_{0.5} termination with the corresponding M edge termination, an overall shift toward stronger CO bonding is observed. The identified minimum adsorption site for CO is generally either the on-top metal atom site or the bridging site between the two outermost metal atoms, where H is in most cases adsorbed in the metal bridge site. Generally, the trend for going from S over Se to Te is less clear than what was observed at the M edge. This is attributed the larger tendency for small displacements of the X edge atoms upon adsorption, causing larger spread of the adsorption energies. The trend for the X_{0.25} edge is significantly different from those of any of the other edges, as there is one common scaling relation for all the chalcogen atoms. At this edge configuration, the dominating adsorption site for both CO and H is the X vacancy. This site also corresponds to a bridge position between the outermost M atoms. The distance between these two atoms is found to vary a lot, ranging from 1.9 Å (MnTe₂) to 5.2 Å (CrTe₂). The CO adsorption energy is found to increase linearly with this distance (Figure S.3). It is furthermore observed that for each



Figure 7. Calculated adsorption Gibbs free energies of COOH and CO calculated at the $X_{0.5}$ (left) and $X_{0.25}$ (right) X edges. Inserts show top and side views of the relevant edge configurations.



Figure 8. Reaction energy diagrams for CO2RR reaction steps on the $X_{0.25}$ M edge at CO/CO₂ equilibrium potential (0.3 V vs RHE) (left). Adsorption geometries for the CO2RR intermediates for MoTe₂ and CoTe₂ (right).

chalcogen within each group of the periodic table, the H adsorption energy is decreased with atomic number.

COOH Adsorption. The first reduction step of the CO2RR path is the reduction of CO₂ to COOH; hence, the COOH adsorption energy is an important factor in determining the overall product and overpotential of the reaction.^{4,36,55} Figures 6 and 7 show the COOH adsorption energies plotted against the CO adsorption energies at the M and X edges, respectively. Generally, COOH is found to adsorb in the same sites as CO. Only for the $X_{0.5}$ M edge, the favorable site for COOH adsorption is found to be on top of the X atom, whereas CO was found to adsorb in the on-top M position. Generally, the large amount of degrees of freedom of COOH and the edge reorganizations caused by the adsorption cause a relatively large amount of scatter in Figures 6 and 7. For the $X_{0.5}$ termination of both edges, there is a similar trend to what was observed for CO and H; that is, within each group of chalcogenides, a positive linear scaling is observed between COOH and CO, while going from S to Se to Te, there is a shift toward weaker COOH bonding with stronger CO bonding. For the $X_{0.25}$ terminations, the trend for COOH is less pronounced, with the S, Se, and Te chalchogenides seemingly following a common scaling relation. For the X_{0.25} M edge, it is interesting to note that, whereas the majority of adsorption geometries involve a bidentate binding through C and O to both of the edge M atoms, for Fe, Mn, Co, and Ni chalcogenides, this bonding fashion is prevented by the small

ionic radius of these metal atoms, resulting in these having weak COOH bonding (marked with star-shaped markers in Figure 6 (right)). Examples of the two adsorption geometries are shown in Figure 8.

Aqueous Stability. The stability of a material under reaction conditions is a key factor determining whether it can be a viable electrocatalyst. Here, Pourbaix diagrams have been constructed for each of the selected TMDC 2D sheets to study the aqueous stability. The Gibbs energy for converting the TMDC to the Pourbaix stable phase at realistic operating conditions (pH = 7 and U = -0.6 V vs RHE) are shown in the heatmap in Figure 9. For completeness, the materials that do not fulfill the initial selection criteria and have not been studied in the previous sections are included in this figure. In most cases, the TMDC is not the Pourbaix stable phase at negative potentials. Nevertheless, a range of them have been successfully synthesized and used for CO2RR including MoS_{2} , $MoSe_{2}$, $MoTe_{2}$, WS_{2} and WSe_{2} . Hence it is reasonable to assume that materials of similar stabilities can be kinetically stable (metastable) under the given conditions. Supporting this assumption, a previous study concluded that materials with $\Delta G_{\rm pbx}$ up to 0.5 eV could be metastable in aqueous media.⁵⁶ Using the stability criteria that $\Delta G_{\rm pbx}$ < 0.5 eV, 11 new materials are classified as metastable at -0.6 V vs RHE: TiTe₂, VTe₂, NbSe₂, NbTe₂, TaS₂, WTe₂, MnTe₂, FeTe₂, CoTe₂, and NiTe₂. We note that the aqueous stability of a number of these materials is lower at U = 0 V vs RHE, which could also

				1 /
SC.	1.3	1.2	0.79	1.4
٣	0.79		0.36	1 2
л.	0.96	0.93		1.2
Η	0.93	0.94		1.0
>			0.23	1.0
٩N	0.36	0.34	0	0.02
Tal	0.48	0.53	0.25	-0.8 e
۲.			0.28	G _{pb}
10	0.43	0.42	0.044	-0.6⊲
Š	0.48		0.26	0.4
٦ ا	1.1	0.98	0.38	-0.4
Fe P	0.89	0.71	0.11	0.0
0	1.1	0.89	0.19	-0.2
ïZ	1.2	0.99	0.22	0.0
	Ś	Se	Т́е	-0.0

Figure 9. Aqueous stability at pH 7 and -0.6 V vs RHE. Materials that do not fulfill the initial stability selection criteria (heat of formation < convex hull + 0.2 eV/atom, a minimum eigenvalue of the Hessian > $-0.01 \text{ meV}/\text{Å}^2$, and a minimum stiffness tensor eigenvalue > 0) are marked with black. Materials with aqueous stability lower than 0.5 eV are marked with white. Materials with $\Delta G_{\text{pbx}} < 0.5$ eV are marked with purple.

influence the suitability of the catalyst material. The aqueous stabilities at 0 V vs RHE can be found in Supporting Information.

Candidate Selection. In order to select the most interesting candidate materials out of the 26 materials fulfilling the initial stability criteria, a set of selection criteria has been established as shown in Figure 10. First, the materials should



 $FeTe_2$, NiTe₂, MoS_2 , MoS_2 , $MoSe_2$ $MoTe_2$

Figure 10. Graphic representation of the selection scheme for identifying the most promising candidates for CO2RR.

have aqueous stability defined according to the Pourbaix calculations as $\Delta G_{\text{pbx}} < 0.5$ eV at pH = 7 and U = -0.6 V, as shown in Figure 9. Fifteen materials fulfill these criteria, including eleven new materials, which, to the best of our knowledge, have not been investigated for CO2RR before. Furthermore, OH-free edge terminations should be favorable at either the M or X edge in the majority of the relevant potential range -0.3 to -1.0 V vs RHE. Ten materials fulfill this criteria including seven new materials. Finally, to limit the HER, the calculated hydrogen adsorption energy at the stable

OH-free edge should be larger than 0.0 eV; this is the case for all of the already identified materials as the $X_{0.25}$ M edge is stable in the majority of the potential range for all of the candidates but MoTe2. The seven new material candidates include: VTe₂, NbTe₂, CrTe₂, MnTe₂, CoTe₂, FeTe₂, and NiTe₂. As we do not specifically target one particular CO2RR product, we have not included a selection criteria for the CO and COOH adsorption energies; however, our adsorption energy calculations indicate that beyond CO products may be favored for the tellurides, including the new material candidates. It should be noted that NiTe₂ is computationally very difficult to handle, with adsorption in many cases causing major reconstructions of the surface, resulting in large uncertainties of the adsorption energies and missing data points. To the best of our knowledge, there are no previous studies of any of these materials as electrocatalysts for CO2RR. Whereas nanostructures of these materials have been reported in different phases (e.g., NbTe₂ in the 1T or distorted 1T phases,²⁸⁻³¹ orthorhombic marcasite structured $CoTe_2$,⁵⁷ $FeTe_2$ in a hexagonal crystal structure,⁵⁸ and NiTe₂ and VTe₂ in the 1T phase^{59,60}), to the best of our knowledge, only CrTe₂ has been reported experimentally in the 2H phase,⁶¹ although in theory all of the identified candidates should fulfill the thermodynamic and dynamic stability criteria used in this work.47,48

Reaction Energy Diagrams. The findings in this study highlight the transition metal ditellurides as a promising class of CO2RR electrocatalysts due to the favorable adsorption energies of H and CO, potentially favoring beyond CO products. Energy diagrams showing the reaction pathway for the first three steps in the likely reaction mechanism of CO2RR are shown in Figure 8. For comparison, energy diagrams are shown for MoS₂, MoSe₂, and MoTe₂, as well as FeTe₂ and CoTe₂, which were selected as promising candidates. The $X_{0.25}$ M edge was found to be the most energetically favorable at relevant potentials. Furthermore, this edge has the most promising adsorption energies for beyond CO product formation, hence we choose this edge as the model system. CO and COOH adsorption energies are generally decreased for the tellurides relative to MoS2 and MoSe₂, indicating that desorption of CO is less favorable. As previously discussed, COOH adsorption is found to be significantly stronger on the Mo chalcogenides than for FeTe₂ and CoTe₂ due to the difference in possible adsorption geometries. While a bidentate bonding to both Mo edge atoms is increasing the adsorption strength for MoS₂, MoSe₂, and MoTe₂ as exemplified for MoTe₂ in Figure 8, this geometry is not possible for FeTe₂ and CoTe₂ due to the smaller ionic radius of these metal atoms. The free energy diagram suggests a significant (> 0.7 V) increase in the CO2RR overpotential for FeTe₂ and CoTe₂ compared to MoTe₂.

CONCLUSIONS

Various nanostructured transition metal dichalcogenides (TMDCs) have been demonstrated experimentally to be efficient catalysts for the CO_2 reduction reaction. We have performed a computational DFT-level screening study of the zigzag edges of 2D TMDC materials in the 2H phase in order to understand trends in adsorption energies and identify potential new candidates for further exploration. We find that, in general, the tellurides have the highest aqueous stability and are less prone to OH poisoning. The trend in H and CO adsorption energies shows that there is a shift going from

sulfides to selenides to tellurides toward weaker hydrogen bonding and stronger CO bonding, corresponding to a shift toward adsorption properties favoring products beyond CO. We propose that this trend could be explained based on the π backbonding properties of CO. For some edge configurations, a similar trend is observed comparing CO and COOH adsorption. We furthermore find that the structural configuration of the edge has a significant influence on the adsorption energies. Additional investigations of the electronic structure of the edges would be of interest to understand this behavior. As the edge configuration is dependent on reaction conditions, such as applied potential, this could possibly be used to tune the process toward a desired product.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.2c04825.

Information about availability of data, R² values, energy convergence with respect to vacuum, and short discussions about the C–O distance and metal–metal distance (PDF)

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Notes

The authors declare no competing financial interest.

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Supporting Information: Trends in CO₂ reduction on Transition Metal Dichalcogenide Edges

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Figure 1: Adsorption sites at the $X_{0.5}$ and $X_{0.25}$ M and X edges

Adsorption sites

Edge atoms are defined as the outermost row of M and X atoms. All ontop and bridge sites involving these atoms are identified and symmetrically equivalent sites are excluded. The resulting adsorption sites are shown for each considered termination in Figure S1. In the relaxation calculations, three rows of atoms are fixed. To verify that this constraint has limited affect on the energy, Figure 2 show relaxed minimum adsorption configurations



Figure 2: Optimized adsorption structures for H and CO on $MoS_2 X_{0.25} X$ edge holding 2 and 3 rows of atoms fixed

for H and CO at the $X_{0.25}$ X edge constraining 2 and 3 rows of atoms. The energy difference is 0.012 eV and 0.013 eV for CO and H respectively. The lowest energy converged adsorption sites for each material are made available as ASE database files from data.dtu.dk (DOI:10.11583/DTU.21155521)¹



Figure 3: Calculated energies for CO on MoS_2 as a function of vacuum in the y and z directions

H/CO	M 0.25	M 0.5	X 0.25	X 0.5
S	0.20	0.53	0.88	0.52
Se	0.40	0.44	0.83	0.17
Те	0.651	0.80	0.79	0.01

Table 1: \mathbb{R}^2 values for the linear fits in Figure 4 and 5 in the main text

Table 2: \mathbb{R}^2 values for the linear fits in Figure 6 and 7 in the main text

COOH/CO	M 0.25	M 0.5	X 0.25	X 0.5
S	0.68	0.36	0.99	0.84
Se	0.49	0.50	0.67	0.01
Te	0.01	0.75	0.70	0.1

Vacuum convergence

In order to ensure no interaction of adsorbates or sheets with neighboring periodic images the energy convergence for added vacuum was investigated. As an example, MoS_2 with CO adsorbed in the minimum energy adsorption site was chosen. The amount of vacuum is varied from 3.0 to 10.0 Å at each side of the sheet in the y and z directions respectively. In the other direction 7.5 Å of vacuum is added at each side of the structure. Figure 3 shows the energy as a function of vacuum. The figure shows, that the energy is well converged to within 0.01 eV at a value of 7.5 Å in both directions which is the value applied in the main manuscript.

Coefficients of determination

In Table 1 and 2 the \mathbb{R}^2 coefficients of the fits in Figures 4-7 in the main text are given.

Pourbaix stability

Aqueous stabilities are calculated using the Pourbaix module as implemented in the atomic simulation environment (ASE). Additional solid and aqueous references are manually added from the Atlas of electrochemical equilibria in aqueous solutions and made available as a



pH=7, U= -0 V vs RHE

Figure 4: Aqueous stability at pH 7 and 0 V vs. RHE. Materials that do not fulfill the initial stability selection criteria (heat of formation < convex hull + 0.2 eV/atom, a minimum eigenvalue of the Hessian $> -0.01 \text{ meV}/\text{Å}^2$ and a minimum stiffness tensor eigenvalue > 0) are marked with black. Materials with aqueous stability lower than 0.5 eV are marked with white, while materials with aqueous stability larger that WSe₂ are marked with purple

Python dictionary in data.dtu.dk (DOI: 10.11583/DTU.20631648).²

The Pourbaix stabilities at pH=7 and U=0 V vs. RHE is shown in Figure 4

Adsorption distance

The adsorbed CO bond length is plotted in Figure 5. It is observed that the CO bond length is increased with increasing atomic number of the X atom and hence increasing with increasing CO adsorbtion strength. This implies a weakening of the CO triple bond as a consequence of the enhanced π backbonding.



Figure 5: CO bond length after adsorption

$\mathbf{X}_{0.25}$ X edge metal- metal distance

At the $X_{0.25}$ X edge The most favorable adsorption site is in most cases the M-M bridge site. Figure 6 shows the CO adsorption energy as a function of the metal-metal distance. It is seen that the adsorption strength is generally increased with decreasing distance.



Figure 6: The CO adsorption energy vs. the MM distance at the $\rm X_{0.25}$ X edge

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A.2 Paper II

A Grand Canonical DFT investigation of the CO2RR and HER reaction mechanisms on ${\rm MoTe}_2$ edges

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A Grand Canonical DFT investigation of the CO2RR and HER reaction mechanisms on MoTe₂ edges

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Abstract

 MoTe_2 has experimentally and theoretically been identified as a promising cathode candidate for electrocatalytic CO_2 reduction (CO2RR). A full understanding of its reactivity requires special consideration of the reaction kinetics, but this is challenging due to the varying electrode potential in the canonical DFT, which calls for grand canonical, constant potential methods. Here, the full reaction pathways for CO2RR to CO and the competing Hydrogen Evolution Reaction (HER) are investigated on a MoTe₂ edge in an alkaline medium using a Grand Canonical Ensemble DFT approach with hybrid solvent model to understand the explicit effect of the applied potential. Our results show that the barrier of the first CO2RR step, the CO_2 adsorption, is lower than the first HER step, the Volmer step, which implies that CO2RR is favored. We also find that at more negative potentials the first CO2RR steps become more favorable, whereas CO desorption becomes less favorable, indicating that further CO reduction is expected instead of CO desorption. However, the potential dependence of the Volmer step depends more strongly on potential than CO_2 adsorption, making HER more favorable at more negative potentials. Overall, our study identifies edge-rich MoTe₂ nanoribbons as possible catalysts for alkaline CO2RR.

Introduction

The electrocatalytic reduction of CO_2 (CO2RR) is a promising pathway towards closing the anthropogenic carbon cycle.^{1,2} In this process, CO_2 gas captured from point sources or directly from ambient air (DAC) is converted into various carbon products, which can be used as both fuels or chemicals. Among the most common products are CO and formate/ formic acid, while only a few proposed catalysts have been observed forming further reduced products, such as alkanes or alcohols.^{3–5} While copper is the only "beyond CO" producing transition metal, it is associated with high overpotentials and poor selectivity.^{6–9} Recently, transition metal dichalcogenides (MX₂, X=S, Se, Te) have attracted significant interest for electrocatalysis.^{10–15} In particular, MoS_2 has been widely studied for various applications of electrocatalysis and energy materials.^{14–17}

The transition metal dichalcogenides (TMDC) have also attracted growing attention for CO2RR.^{18–22} In our recent study, we showed that transition metal tellurides exhibit promising thermodynamic properties for CO2RR, as they adsorb H weakly and CO strongly compared to sulfides and selenides.²³ This behaviour is expected to lead to the formation of beyond-CO products²⁴ in agreement with an experimental study identifying CH₄ as a major product of MoTe₂ nanoflakes in an ionic liquid.²⁵ Interestingly, in the same study, some CO2RR activity was measured even in an aqueous electrolyte, further indicating of the suppression of the competing HER. In particular, the edge sites have been proposed to be important for the TDMC catalysts and they can, for example, enhance electronic conductivity. In the case of MoTe₂, its most stable phase, the 2H-phase, is a semiconductor in bulk but metallic edge states arise upon formation of nanostructures.^{26,27} The pristine 2H-MoTe₂ edges are assumed to be the active sites for catalysis^{28–30} while defects are required to activate the basal plane of 2H-MoTe₂^{31,32} and the high acidic HER activity of MoTe₂ is associated to the basal plane anion vacancies.³³ Based on these findings, we expect that pristine 2H-MoTe₂ edges will exhibit high CO2RR activity and suppress HER in alkaline electrolytes.

To test the validity of this proposal, the reaction kinetics of CO2RR and the competing HER needs to be addressed. However, modeling reactions at the electrochemical solid-liquid interface is not straightforward.^{34–37} During an electrochemical reaction, electrons are transferred to or from the working electrode, kept at constant potential. While in an experimental setup, this is achieved via an external circuit, in common canonical simulations, the number of electrons is fixed and the Fermi level of the electrode, *i.e.* the electrode potential, fluctuates over the course of an electrochemical reaction.³⁸ Common post-processing approaches such as the Computational Hydrogen Electrode (CHE)³⁹ have proven successful in describing the potential dependence of reaction thermodynamics of proton coupled electron

transfer reactions. However, it cannot be used when charge is directly transferred during the simulation, e.g. in reaction barrier calculations.³⁹ Furthermore, charge transfer reactions not involving a simultaneous proton transfer cannot be described with CHE. The electrode potential effects can be explicitly described with Grand Canonical Ensemble (GCE) based methods, such as GCE-DFT, where the electrochemical potential of an electron, *i.e.*, the electrode potential, rather than the number of electrons is kept fixed.^{38,40} GCE-DFT -based approaches have previously provided detailed descriptions of various electrochemical reaction pathways, such as the NRR/ HER on $Ru-N_4$,⁴¹ Au-Catalyzed Glycerol Electro-oxidation,⁴² and the HER at MoS_2^{43} and $MoTe_2$ basal planes.³³ Also, the CO2RR has been the subject of GCE-DFT investigations. On the Cu(100) surface, a potential dependence of the C-C bond formation mechanism was demonstrated considering reaction barriers and thermodynamics,⁴⁴ while a later study identified the hydrogenation of CO_2 to be the rate limiting step of the CO2RR on Ag(110) using a multiscale modelling approach including reaction kinetics.⁴⁵ The CO2RR/ HER competition has also been investigated and significantly different potential dependencies for reaction energies of CO2RR and HER elementary steps were reported on various (111) transition metal surfaces⁴⁶ but kinetic considerations were excluded. Most recently, the pH and potential dependence of the rate limiting step in the formation of multi-carbon species on Cu was investigated.⁴⁷

In this paper, the alkaline CO2RR and HER reactions at a MoTe₂ edge is investigated considering reaction thermodynamics and kinetics as a function of the electrode potential. Specifically, the potential dependence of relevant reaction barriers of the CO2RR and competing HER reactions at MoTe₂ edges are evaluated through GCE-DFT calculations. We show that CO2RR is kinetically favored over HER, explaining the CO2RR activity observed in an aqueous electrolyte.²⁵ We also find that the barrier for a CO desorption step is increased at more reducing potentials, indicating that beyond-CO reduction could become increasingly favorable compared to CO desorption. Our findings identify edge-rich MoTe₂ as an active and selective catalyst towards CO2RR in alkaline electrolytes.

Computational methods

All DFT calculation were performed in a projector augmented wave (PAW) formalism as implemented GPAW 21.6.0^{48,49} integrated with the Atomic Simulation Environment (ASE).⁵⁰ Most calculations were performed in Finite Difference (FD) mode using a grid spacing of 0.16 Å but the minima hopping calculations (see below) were carried out in LCAO mode with a DZP basis set in order to limit the computational cost. The employed exchange-correlation functional is in all cases the the BEEF-vdW functional,⁵¹ which includes van der Waals effects for accurate thermodynamics of adsorption reactions. The electrons are smeared using a Fermi-Dirac smearing with a width of 0.05 eV. Atomic positions are relaxed until all residual forces are below 0.06 eV/ Å. Periodic boundary conditions are applied in the x and y directions with an employed (5x1x1) k point mesh), while an added empty space of 8 and 10 Å respectively is added to each side of the structure in the y and z directions respectively, to create the nanoribbon with edges. The configuration of the edge is motivated by our recent findings and will be addressed in detail below. A dielectric-dependent dipole correction⁵² is applied in the xy direction to allow for a potential difference across the system.

The electrochemical solid-liquid interface is modelled by an implicit/explicit hybrid solvent approach combining the Simple Continuum Model based on Volumetric Data (SCMVD) dielectric continuum model with 4 explicit water molecules.⁵³ The implicit solvent is defined within a box-shaped region above the MoTe₂ edge in the z-direction ranging from 1 Å above the outermost atom in the cell and 1 Å below the top of the cell. The vdW-radii are adapted from the GPAW database, except for Mo, for which a value of a value of 2.1 Å is employed.⁵⁴ The Minima Hopping method as implemented in ASE is used to optimize the location and orientation of the explicit water molecules.⁵⁵ For the CO2RR the water layer is optimized for CO₂ adsorbed at the edge, whereas for the HER the water layer is optimized for the pristine surface. In each case four water molecules are included in the water layer. Each initial and final state for the different reaction steps is then constructed using the obtained minimum energy water layer structure as the starting point. The proton donor for the proton coupled

electron transfer reactions is the explicit water molecule closest to the reaction site. In these reactions, the final state involves an OH^- ion, which subsequent reaction step is replaced by a H₂O molecule and the original water layer is regained. Initial and final states are obtained by relaxing the three outermost rows of edge atoms (Te, Mo, Te), the adsorbed species and all explicit water molecules, while keeping the additional surface atoms fixed.

Grand canonical free energies at fixed potentials are obtained using the Solvated Jellium Model (SJM) method as implemented in GPAW.⁵² In this approach, a homogeneous counter charge (a jellium slab) positioned within the implicit solvent region is added to keep the system charge neutral, while the number of electrons in the cell is iteratively adjusted until the target potential (Φ_e) is reached within a tolerance threshold of 0.025 V. The implicit solvent and neutralizing jellium counter charge screeen the surface charge and high electric field originating from the charge surface. In SJM the electrode potential is defined as the Fermi level (E_f) referenced to the electrostatic potential deep in the implicit solvent (Φ_w), where no electric field is present:

$$\Phi_e = \Phi_w - E_f \tag{1}$$

The experimentally determined relation between Φ_e and the potential against the Standard Hydrogen Electrode (U_{SHE}) is given by:⁵⁶

$$U_{SHE} = \Phi_e - 4.44V \tag{2}$$

For better comparison with experiments, the potentials are converted to the Reversible Hydrogen Electrode (RHE) scale using:

$$U_{RHE} = U_{SHE} + k_B T \cdot p H \cdot ln(10) \tag{3}$$

Where k_B is the Boltzmann constant and T is the absolute temperature. The energies used

in this study are the grand free energies, Ω , defined as:

$$\Omega = E_{tot} + \Phi_e N_e \tag{4}$$

Here, E_{tot} is the DFT calculated energy and N_e is the number of excess electrons. For molecular references, the gas phase Gibbs free energy including zero-point energy and entropy is employed. In the special case of H⁺+ e⁻, the energy is calculated by:

$$G_{H^++e^-} = 0.5G_{H_2} - eU_{RHE} \tag{5}$$

where G_{H_2} is the Gibbs free energy of a dihydrogen molecule. The potential is corrected for by the $-eU_{RHE}$ term, where e is the number of electrons, and U_{RHE} is the applied potential. Finally, reaction grand free energies are calculated by:

$$\Delta \Omega = \Omega_{products(*)} + G_{products(g)} - \Omega_{reactants(*)} - G_{reactants(g)} \tag{6}$$

where * denotes surfaces and adsorbed species and g denotes gas phase species.

Nudged Elastic Band (NEB) calculations as implemented in ASE^{57,58} are performed to obtain the grand free energy barriers. In some cases the bond length between the reacting species in the solvent and the Mo reaction site is additionally constrained to ensure a shorter NEB path, while preventing recombination of reactants. In this case, an intermediate image from a previously non-converged NEB run is chosen as the initial guess for relaxation. Linear interpolation between initial and final state is employed to construct the initial guess for the NEB path. Finally, the climbing image method is employed to get a better description of the saddle point.⁵⁹ The atomic charges are computed using the Bader charge analysis scheme.^{60–63} The charge difference between an atom in the final and initial state is then

calculated as

$$\Delta q = q_f - q_i \tag{7}$$

where q is the Bader charge of the atom in question, and i and f indicate the initial and final states, respectively.

Results and discussion

A single layer of the 2H phase of MoTe₂ consists of a hexagonal layer of Mo atoms sandwiched between two layers of Te atoms stacked in an eclipsed configuration, so that each Mo atoms upholds a trigonal prismatic lattice coordinating to six Te atoms. Cutting the 3D sheet stoichiometrically in the so-called "zig-zag" direction creates a nanoribbon with two edges terminated by Te atoms (X edge) and Mo atoms (M edge), respectively. However, under experimental conditions, reorganization of the edge configuration is likely to occur.⁶⁴ In our previous study of the edge termination of TMDC nanoribbons using the CHE model, we found that OH terminated configurations of the X edge were favored under experimental conditions relevant for CO2RR, while also the adsorption energies for CO and H were more favorable at the M edge.²³ Hence, in this study, the Mo edge is selected as the reaction site.

Based on the previous results,²³ 5 different edge terminations were selected for investigations, here denoted as Te₂ (OH₂) with each Mo-Mo bridge site occupied by a Te (OH), Te₁ (OH₁) with every second gap occupied, and Te₁OH₁ with the terminating group alternating between Te and OH as shown in the insets of Figure 1. Furthermore, one termination in which CO₂ is adsorbed to the Mo site at the Te₁ terminated edge is considered, as it is expected to be the active site for CO2RR. All the terminations are initially considered without explicit solvent molecules.

The explicit potential and pH dependencies of the relative stabilities of different Mo edge terminations were investigated using the GCE-DFT. Figure 1 shows the grand free energies



Figure 1: Variation of the Grand free energy, Ω , as a function of potential, U vs RHE, for six different terminations of the MoTe₂ M edge (shown as insets. Turquise=Mo, brown= Te, gray=C, red=O, white=H). The solid lines are second order fits to the data points, each corresponding to a GCE-DFT calculation at different potential. Here, a negative $\Delta\Omega$ value means that the reaction is thermodynamically favorable

of six different terminations (shown as insets in Figure 1), each calculated at seven different potentials. The data has been fitted to second order polynomials in accordance with the expected potential dependence.^{42,65,66} The data generally follow the expected trend, only for the OH terminated edges some deviation is observed. The grand free energy curvatures and maxima correspond to the capacitance and potential of zero charge (PZC), respectively. These are provided for each termination in SI (Table S1), and show that the PZC depends on the edge termination while the capacitance is fairly structure insensitive.

The obtained grand free energy fits are used to map the potential and pH-dependent edge stabilities according to Equation 3 and the corresponding plots are given in Figure 2. The OH_2 termination is excluded from the analysis, as it is highly unstable in the entire region considered. Our results show that the relative stability of the terminations depends sensitively on potential with the lower Te coverage becoming more favorable with a decreasing electrode potential (top left) in agreement with our previous results.²³ The stabilities of the two OH terminated structures, OH_1 (bottom left) and Te_1OH_1 (top right), also increase at more negative potentials. For the Te terminated edges, the pH dependence is minimal, whereas the two OH terminations show a significant pH dependence; the Te₁OH₁ becomes relevant at low pH even for intermediate potentials. We attribute observed stabilization to the stronger dipole-field interactions resulting from inclusion of the polar OH-group and the large difference in the PZC for these to different surface terminations (see Table S1). The presence of a CO_2 adsorbate at the Te_1 termination does not notably alter the relative stability, indicating that adsorption of CO_2 is thermodynamically feasible and it does not significantly change the surface stability. In the earlier experimental study, the CO2RR activity was measured for potentials below -0.6 V at neutral conditions (ionic liquid/ 0.1 M KHCO₃).²⁵ At these conditions, we expect the Te_1 termination to dominate, hence it is chosen as the model system for the mechanistic analysis.

Potential-dependent reaction thermodynamics and kinetic barriers of CO2RR and HER

In order to calculate reaction barriers for the CO2RR and the competing HER, a layer of explicit water molecules was included above the most stable, Te₁ edge, see the Supplementary Figures S1-S3. The reactions and elementary steps considered are listed in Table 1 along with possible additional constraints employed in the optimization of the initial and final states for the NEB path. The optimized structures are shown in the SI Figures S2 and S3.

The NEB paths calculated at three different potentials are given in Figure 3. For all four elementary steps, the charge of the system varies monotonously going from initial to final



Figure 2: Heatmaps showing the relative stabilities of different edge termination relative to the Te₂ termination. $\Delta\Omega$ has been normalized to the number of electrons transferred.

state over the transition state (SI Table S2), which is observed also for metallic systems.^{52,67} Generally electrons are gained over the course of the reaction, except for CO desorption, where the number of electrons is decreased. CO₂ adsorption is found to be exergonic and sensitively depend on the electrode potential; this can only be captured with explicitly considering the electrode potential. The kinetic barrier is below 0.3 eV at all three potentials. The potential-dependency can be rationalized by the charge analysis given in Figure 4, which shows that the adsorbed CO₂ carries a substantial, $\sim -0.8e$ charge. Table S2 displays that the total system gains 0.5 additional electrons during the adsorption to maintain fixed electrode potential. Projected density of states plots (PDOS) for CO₂ SI Figures S4 and 5 clearly show the σ donation from the adsorbate to the Mo d-states and the π backdonation from the d-states to the adsorbate π^* orbitals upon bonding. Together the charge and PDOS analyses demonstrate notable charge transfer from the surface to the orbitals of CO₂: the

Table 1: The reactions steps considered. r_{Mo-C} is constrained in the initial state of the CO₂ adsorption step to minimize the length of the reaction path; necessary to converge the NEB calculation. For the Volmer steps, r_{Mo-O} is constrained in the final state to prevent recombination of H and OH.

Reaction	Step		Additional constraints
CO2RR	CO_2 adsorption	$CO_2 + * \rightarrow *CO_2$	r _{Mo-C} fixed in IS
	H transfer 1	$H_2O + *CO_2 \rightarrow *COOH + OH^-$	
	H transfer 2	$H_2O + *COOH \rightarrow *CO + OH^-$	
	CO desorption	$*CO \rightarrow CO + *$	
HER	Volmer 1	$^{*} + H_{2}O \rightarrow^{*}H$	r_{Mo-O} fixed in FS
	Heyrovsky	$^{*}\mathrm{H} + \mathrm{H}_{2}\mathrm{O} \rightarrow ^{*}\mathrm{H}_{2}$	
	Volmer 2	$^{*}\mathrm{H} + \mathrm{H}_{2}\mathrm{O} \rightarrow 2^{*}\mathrm{H}$	r_{Mo-O} fixed in FS
	Tafel	$2^*\mathrm{H} \rightarrow^*\mathrm{H}_2 + ^*$	
	H_2 desorption	$^*\mathrm{H}_2 \to \mathrm{H}_2 + ^*$	

first CO2RR step corresponds to an electron transfer event.

While, the first H transfer leading to *COOH is thermodynamically uphill, the second H transfer leading to adsorbed *CO is exergonic. Note that the final states of the H transfer reactions involve an OH^- ion, which is subsequently replaced by a water molecule before the next elementary step achieving significant energy gain. As expected, both barriers decrease at more negative potentials but the second H-transfer barrier is generally slightly lower than the first one (0.52 eV vs 0.68 eV at -1.23 V vs RHE).

The final CO2RR step, considered in this study, is the CO desorption, which is found to be thermodynamically unfavorable by more than 1.4 eV and associated with a correspondingly large forward reaction barrier. Interestingly, the barrier for CO desorption increases at more negative potentials indicating that CO formation becomes less favorable. This also implies that "beyond-CO" product formation may be enhanced for more negative potentials.²⁴ CO adsorption strength at the metal site is enhanced for TMDCs with decreasing polarity of the M-X bond and thereby increasing electron density on the metal.²³ A linear increase of the electron density would be likewise expected for decreasingly negative potentials, which possibly explains the increased barrier for CO desorption. This implies that π -backbonding is involved in the CO-bonding and the PDOS analysis, in SI Figure S5, clearly shows the



Figure 3: Free energy profiles for the CO2RR elementary steps calculated at different potentials. The value of the forward energy barriers, Ω_{\ddagger} is given for each potential in the legends.

 σ donation from the CO adsorbate to the Mo d-states and the π backdonation from the d-states to the adsorbate π^* orbitals. The charge analysis for CO desorption in Figure 4 shows that charge transfer takes place from the surface to the adsorbate orbitals. While charge transfer is enhanced at more reducing potentials, it is more pronounced for CO than CO₂, which explains the stronger potential dependence of the CO desorption barrier (Figure 6). The precise number of water molecules and the structure of the explicit water layer can potentially influence the computed barrier values and thermodynamics. SI Figure S6 presents the NEB paths for the first H-transfer and the CO desorption steps using different water layers and demonstrates the impact of the water layer structure is minor.

The HER can proceed either via the Volmer-Heyrovsky or the Volmer-Tafel mechanism. In both cases, the reaction starts with the Volmer step, where H adsorbs from the solvent,


Figure 4: Δq calculated by the Bader charge analysis scheme for C and O atoms in CO₂ and CO, the Mo atom in the adsorption site, and the neighboring Te atom. CO₂ adsorption (left) and CO desorption (right). The positive charge difference correspond to charge transferred to the atom over the course of the reaction

followed either by the Heyrovsky step (Table 1) or an additional Volmer step and a subsequent Tafel step (Table 1) and finally H_2 desorption. The NEB paths calculated at three potentials are shown in Figure 5). For all the elementary steps the charge monotonously increases (Volmer 1, Volmer 2 and Heyrovsky) or decreases (H_2 desorption) over the course of the reaction (shown in SI Table S2). The only exception being the Tafel reaction, for which a slight non-linearity is observed; the charge is decreased from the initial to the transition state and increased from the transition to the final state. This indicates higher sensitivity of the reaction barrier than the reaction energy to the potential.⁴¹ The change in charge through the reaction is minor for the Tafel step. The reaction barriers for the two Volmer and one Heyrovsky steps are rather high (1.07 eV, 1.20 eV and 0.84 eV at -1.23 V vs RHE) and all three reactions are also thermodynamically unfavorable. It should, however, be noted that the reformation of the charge-neutral water layer upon OH⁻ ion replacement is associated with large energy gain, so that the reactions actually become thermodynamically downhill.

Comparing the barriers for the Heyrovsky step and the second Volmer step (the second step in the Volmer-Heyrovsky and Volmer-Tafel mechanism respectively) shown in Figure 5, the Volmer-Heyrovsky mechanism is expected to be the relevant HER mechanism at the



Figure 5: Free energy profiles for the HER elementary steps calculated at different potentials. The value of the forward energy barriers, Ω_{\ddagger} is given for each potential in the legends.

electrode potentials considered here. The reaction barriers of the Volmer1, Volmer2, and Heyrovsky steps decrease as more reducing potentials are applied. The final elementary step of the HER pathway is the desorption of H₂. In the preferred adsorption geometry, the H₂ molecule adsorbs flat on the Mo-site with both H atoms bonding to the Mo atom and the H-H bond being elongated. Two different configurations, shown in SI Figure S3, are found with bond lengths of 1.86 Å (*H₂^a) and 0.82 Å (*H₂^b) with *H₂^a being 0.26 eV lower in energy than *H₂^b. The desorption barrier is 0.30 eV larger for *H₂^a than for *H₂^b. *H₂^a is found to be the prefered final state of the Tafel step. The Heyrovsky mechanism is conversely found to proceed via *H₂^b as the barrier to *H₂^a is found to be larger. The desorption of H₂^a is found to involve two reaction steps; *H₂^a \rightarrow *H₂^b and *H₂^b \rightarrow H₂(g) +*. At highly reducing potentials, the first step is found to be negligible, whereas it becomes increasingly important at less negative potentials (visible as the shoulder in the NEB path in Figure 5 bottom center,



Figure 6: Forward grand free energy barrier, Ω_{\ddagger} as a function of potential. Linear fits for each CO2RR (left) and HER (right) step are given in the plots.

which arises for low potentials). The barrier for the direct desorption of the energetically less favorable H_2b is lowered by approximately 0.2 eV compared to that of H_2^a .

Figure 6 summarizes the grand free energy barriers of the CO2RR and HER elementary steps for different potentials. Interestingly, the potential-dependency for the first Volmer step is more pronounced than for the CO₂ adsorption, and thus HER becomes relatively kinetically more favorable at more negative potentials. However, the barrier for the first Volmer step is more than 1 eV larger than for the CO₂ adsorption at -0.8 V vs RHE and therefore CO₂ adsorption is kinetically preferred at the experimentally relevant potentials. The potential dependency is slightly smaller for the Heyrovsky step than for the second Volmer step, implying that at higher negative potentials a shift towards the Volmer-Tafel mechanism compared to the Volmer-Herovsky mechanism is expected.

Figure 7 displays the energy diagrams for the CO2RR and the HER at -0.8 V vs RHE, *i.e.* under the experimentally relevant CO2RR conditions. Comparison of the three reaction



Figure 7: The Full grand free energy diagram for CO2RR and HER reaction pathways at -0.8 V vs RHE. (H^++e^-) is abbreviated "H". Grey text denotes energy levels that are the same for the Volmer-Heyrovsky and Volmer-Tafel mechanisms. TS denotes a transition state.

pathways shows that while the HER is thermodynamically favored over the CO2RR, the CO2RR is kinetically more facile: all CO2RR barriers to *CO are smaller than the first Volmer barrier. The more facile CO2RR kinetics at the MoTe₂ edge are the likely reason for the experimentally observed CO2RR activity in aqueous electrolytes.²⁵ These results emphasize the importance of computing reaction kinetics as a function of the electrode potential as the standard CHE approach including only thermodynamics would be unable to predict the preference for CO2RR over HER.

Conclusions

The reaction mechanisms of the CO_2 reduction reaction (CO2RR) and the competing Hydrogen Evolution Reaction (HER) at 2H-MoTe₂ edges were investigated employing a grand canonical ensemble DFT approach to explicitly include the electrode potential into calculations. We find that while HER is thermodynamically favored, the CO2RR is kinetically preferred over HER at the experimentally relevant potentials. This finding is in agreement with previous experimental results showing a relatively high CO2RR activity on MoTe₂ in an aqueous electrolyte.²⁵ The potential dependency of energy barriers vary from one elementary step to the other. Interestingly, while the CO_2 adsorption barrier decreases for increasingly negative potentials, the reaction barrier for desorption of CO is increases, indicating that reduction beyond-CO could be enhanced at highly negative potentials. Furthermore, the first Volmer step depends more sensitively on the potential than CO2RR, so that the competing HER reaction will become relatively more important at high negative potentials. Overall, we find that the MoTe₂ edge is predicted to be an active and selective catalyst for alkaline CO2RR.

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Supporting Information Available

Atomic structures for the different water layers, Final and initial states for the NEB calculations, projected density of states plots, calculated capacitances and potentials of zero charge, number of excess electrons for the initial, transition and final states and a discussion about the imppact of the water layer size and configuration are available free of charge on the ACS Publications website.

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Supporting Information: A Grand Canonical DFT investigation of the CO2RR and HER reaction mechanisms on MoTe₂ edges

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Water layer structures

Four different water layer structures are considered. The structures are obtained using the minima hopping approach and are subsequently re-relaxed using the computational methods described in the methods section in the main text. The structures are shown in Figure S1. The calculated energy difference between 4wa and 4wb is 0.115 eV. The local water coordination to CO₂ are similar to all structures (the distance between the carbon atom and the transfering H atom, $r_{C-H}= 2.680$ Å, 2.558 Å and 2.825 Å for 4wa, 4wb and 5wa respectively).



Figure S1: Atomic structures for water layers 4wa, 4wb and 5wa. Top view (left) and side view(right). Turquise=Mo, brown= Te, gray=C, red=O, white=H.

NEB states

The initial and final states used for the NEB calculations are shown for -0.43 V vs RHE in Figures S2 and S3, using the 4wa water layer structure for the CO2RR reactions and the 4w(HER) water layer structure for the HER reactions. The structures at -0.8 and -1.2 V vs RHE do not exhibit any significant differences from the ones shown. All structures are made available as ASE database files from data.dtu.dk (DOI: 10.11583/DTU.23587149)



Figure S2: Initial (left in each panel) and final (right in each panel) states for the NEB calculations for CO2RR at -0.43 V vs RHE. Turquise=Mo, brown= Te, gray=C, red=O, white=H.



Figure S3: Initial (left in each panel) and final (right in each panel) states for the NEB calculations for HER at -0.43 V vs RHE. Note, that the structures for the Volmer2 reaction are shown from the opposite direction for a clearer view. Turquise=Mo, brown= Te, gray=C, red=O, white=H

PDOS

Projected density of states (pdos) plots for MO (d) and C+O (p) for the initial and final states of CO₂ adsorption and CO desorption are shown in Figures S4 and S5 respectively. For the desorbed states, the bonding and antibonding π -orbitals of CO₂ and CO are observed as sharp lines in the spectrum. Upon adsorption, additional C+O p-peaks arise within the Mo d-band and are indicative of π -backbonding. Furthermore, a small peak located at the position of the CO(p) HOMO orbital also arises in the Mo d-spectrum demonstrating the formation of a σ -bond.



Figure S4: Projected density of states for the C and O orbitals of CO_2 and the adsorption site Mo d-orbital before (left) and after (right) adsorption. The energy, E is plotted relative to the Fermi level, Ef.



Figure S5: Projected density of states for the C and O orbitals of CO and the adsorption site Mo d-orbital before (right) and after (left) desorption. The energy, E is plotted relative to the Fermi level, Ef.

Capacitance and potential of zero charge

The capacitance and potential of zero charge (PZC) are tabulated in Table S1 for each termination considered in Figure 1 (main text). The capacitance is calculated as the slope of the number of excess electrons (ne) vs potential (V), while PZC is calculated as the intercept at 0 V vs SHE.

Table S1: Capacitance and potential of zero charge (PZC) for the nanoribbon terminations considered in Figure 1 in the main text.

Termination	Capacitance $[ne/V]$	PZC [V vs SHE]
Te ₂	1.64	0.30
Te_1	1.96	0.07
OH_1	1.951	-0.02
OH_2	1.941	-0.20
$\mathrm{Te_1OH_1}$	1.78	-0.19
Te_1CO_2	1.79	0.02

Table S2: Evolution of excess electrons of the DFT region for different CO2RR/ HER elementary steps at -1.23 V vs RHE

Elementary step	Initial state	Transition state	Final state
CO_2 adsorption	2.61	2.82	3.10
H transfer 1	2.87	3.22	3.31
H transfer 2	2.54	2.89	3.71
CO desorption	2.89	2.65	2.57
Volmer 1	2.68	3.14	3.37
Volmer 2	2.81	3.18	3.42
Heyrovsky	2.80	3.18	3.40
Tafel	2.84	2.75	2.83
H_2 desorption a	2.83	2.63	2.59
H_2 desorption b	2.80	2.62	2.59

Charge evolution

The system charge for the initial, final and transition states of the elementary steps considered are examplified for a potential of -1.23 V vs RHE in Table S2. It is found that the reactions generally show a monotonous change in charge over the course of the reaction.



Figure S6: Reaction pathways for the CO2RR reaction steps calculated at -0.8 V vs RHE for different water layer configurations and sizes. The forward grand free energy, Ω_{\ddagger} , barriers are given in the legends.

This indicates a similar sensitivity of the reaction energy and barrier. The Tafel step is the only elementary reaction to show a non-linear variation but the charge variation is generally weak.

Influence of water layer configuration

The size and the configuration of the explicit water layer is likely to influence the computed thermodynamics and barriers. We therefore compare the results for selected reactions (H transfer 1 and CO desorption) for the water layer considered so far $(4w_a)$ with a different local minimum configuration obtained from the minima hopping with 4 water molecules $(4w_b)$, as well as one minima obtained from a minima hopping with five water molecules $(5w_a)$, as shown in Figure S6. It is observed that the reaction barriers are within 0.04eV (6%) (H transfer 1) and 0.19 eV (12%) for CO desorption. This indicates that while the water layer size and geometry will influence the magnitude of the reaction barriers and energies, the effect is expected to be minor.

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