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Published in:
Meeting Abstracts - Electrochemical Society

Publication date:
2009

Document Version
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

Citation (APA):
Graves, C. R., & Mogensen, M. B. (2009). Aspects of Metal-YSZ Electrode Kinetics Studied using Model Electrodes. In *Meeting Abstracts - Electrochemical Society* (pp. Abstract 1329). The Electrochemical Society.

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Aspects of Metal-YSZ Electrode Kinetics Studied Using Model Electrodes

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The typical negative-electrode of solid oxide cells is the nickel and yttria-stabilized zirconia (Ni-YSZ) composite. The electrochemical performance of this material is excellent for both fuel cell (H₂ and CO oxidation) and electrolysis (H₂O or CO₂ reduction) operation. Despite all the work that has been done, the detailed kinetics of the electrode reactions are not well known. Little work has been done comparing the same reactions on different metals, even though this may be a good way to examine the kinetics of reactions occurring at the metal/YSZ interface. Therefore, this work makes a comparative characterization of the electrode kinetics of several metals (such as Ni, Cu, Pt, etc) as the negative electrode of a solid oxide cell, using model wire electrodes contacting a yttria-stabilized zirconia (YSZ) pellet electrolyte. In comparison to studies with model negative-electrodes using some of the same metals [1, 2], we use additional H₂O- or CO₂-rich gas atmospheres relevant to electrolysis of H₂O and CO₂, and we study the dynamics of the materials in these conditions at open circuit voltage (OCV) and under polarization.

Cells with a metal wire electrode contacting a YSZ pellet and a porous Pt-paste counter electrode were assembled in a custom test rig. Electrochemical impedance spectroscopy (EIS) at OCV at varying temperature (700-1000 °C) and gas composition (CO/CO₂/Ar and H₂/H₂O/Ar) was employed to “fingerprint” the electrochemical performance of the metal-YSZ interfaces. Time was allowed for the cells to stabilize at each condition, measuring impedance spectra at OCV during the stabilization times. Potential sweeps were then performed, as well as impedance under polarization.

The electrochemical performance of a material was found to be reproducible. Normalization of the impedance data (by contact area, by three-phase boundary length, etc) is discussed. By analyzing the impedance spectra at the various conditions (e.g. Figure 1), the number of processes contributing to the cell impedance are identified and the limiting reaction steps suggested. By comparing these processes, the performance of the materials in CO/CO₂ and H₂/H₂O atmospheres is compared. Arrhenius relations of the electrode impedance parameters are also compared.

Furthermore, potential sweep measurements were used for the investigation and comparison of the electrochemical performance of the materials (e.g. Figure 2). Some electrode materials exhibit different behavior under anodic and cathodic polarization, as well as oscillating current (e.g. Ni, Figure 3) associated with side reactions (besides fuel oxidation). The effect of time proved to be more important for the wire electrodes than

than for composite porous electrodes. Monitoring the polarization resistance by OCV impedance spectra measured over time, some materials experienced an activation after a polarization, followed by passivation during many hours, finally reaching back to near the initial performance.

Figure 1. OCV impedance spectra of Ni wire electrode at 1000 °C with varying $p\text{H}_2\text{O}$.

Figure 2. Potential sweep of Ni and Cu model electrodes.

Figure 3. Potential sweeps of a Ni model electrode in different atmospheres of H₂ and H₂O.

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