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Inhibition of Ostwald ripening through surface switching species during potentiodynamic dissolution of platinum nanoparticles as an efficient strategy for platinum group metal (PGM) recovery

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Abstract

Efficient recovery of platinum group metals (PGMs) from industrial spent catalysts through electrochemical means using mild conditions is of significant importance from both the industrial and the environmental points of view. Owing to their large surface-to-volume ratio, fast dissolution of PGM nanoparticles is possible through potential cycling between oxidizing and reducing potentials, leading to formation and dissolution of surface-oxide layer (transient dissolution). However, at reducing potentials, reduction of the dissolved metal species on the source nanoparticles leads to enhance the Ostwald ripening process and hence to decrease the overall dissolution efficiency significantly. We report a new concept to accelerate dissolution of Pt nanoparticles by use of surface switching species (SSS), e.g. Cu ions, functioning to selectively

block the Pt surface to inhibit redeposition induced particle growth at reducing condition and expose the Pt surface to facilitate dissolution at oxidation condition, respectively. The presence of SSS during potential cycling enhances Pt dissolution by a factor of 2 or more as compared to that without SSS. Such surface self-relegation property to depress unwanted process and assist desired reaction documents an alternative and efficient approach for precious metal electrochemical recovery in dilute acidic baths with/without complexing agents.

Keywords: Platinum dissolution, Recycling, Nanoparticle, Ostwald ripening, Inhibition

1. Introduction

Platinum group metals (PGMs), including Platinum, Palladium, Ruthenium, Iridium, Rhodium, Osmium, in nanoparticle form are of significant industrial importance in applications such as catalysts for exhaust gas purification in fossil fuel powered vehicles or systems, organic chemical reactions as well as renewable energy conversion including fuel cells and electrolyzer cells [1-6]. PGMs are known as one of the critical raw materials, and access to the natural reserves is dominated by South Africa and Russia [7]. However, the supply reliability of the PGMs turned out not to be related to the resource depletion, but to social, economic and environmental in nature [8], since PGM secondary production or recycling and its related behaviors play a substantial role in the PGM supply chain.

Recovery of PGM through conventional pyrometallurgical or hydrometallurgical routes is commonly used for PGM extraction and it has operated on commercial scale by world leading chemical plants for the past 40 years [8]. However, the extraction process based on smelting and refinery is of production risk due to the reliability of the infrastructure related to the classical

technology (requiring continuous operation and constant maintenance), large energy consumption (operating up to 1350 °C) [9] and environmental impact (releasing SO₂, NO_x, greenhouse gases, and using corrosive and toxic chemicals [10-12] such as aqua regia (HCl/HNO₃), piranha solution (H₂SO₄/H₂O₂) etc.). Alternative technologies are desperately needed to complement and finally replace the traditional PGM recovery technologies.

Owing to their high activity, recovery of the nanoparticulate PGMs through more industrially simple and environmentally friendly means is of significant interest [13]. With the advance of the scientific knowledge and analytical techniques, electrochemical dissolution of PGM nanoparticles utilizing their surface chemical and electronic properties to extract, dissolve and separate PGMs from other components was proven by several initiatives [13-15], which has demonstrated a pioneer advance in comparison to the classic method of separation based on physical properties of melting point and density [16-18]. Electrochemical dissolution under transient conditions through potential cycling between oxidizing and reducing potentials leading to formation and dissolution of metal-oxide layers may provide an alternative industrial process for fast recovery of PGM nanoparticles [19].

Formation of the PGM soluble species (e.g. [PtCl₄]²⁻ and [PtCl₆]²⁻ complexes in case of Pt) by dissolving the metal-oxide layer completely at a high rate industrial interest generally requires the potential to be lowered significantly below their standard reduction potentials (E°). This renders a redeposition of the PGM soluble species on energy favorable sites, such as metal nanoparticles (especially PGMs), and has also been reported for nitrogen doped carbon species [20].

This redeposition of the PGM soluble species leads to the growth of the nanoparticles, which is well known as Ostwald ripening and has been reported by several groups [21-25]. Such dissolution and redeposition processes significantly reduces PGM dissolution efficiency, as illustrated in Fig. 1a.

This PGM dissolution-redeposition phenomenon might appear less significant under a dynamic condition or a flow cell configuration (in combination with highly sensitive analyzing techniques), as practiced by several groups [26, 27]. Since the dissolved species in proximity of the working electrode are carried away for analysis and therefore they can less likely participate in further redeposition. However, in a realistic static situation, the thermodynamic-driven spontaneous process to reduce surface energy contributes significantly in redeposition of the soluble species and causes a reduced dissolution efficiency. To overcome the above-described process, there are three rational solutions:

- To stabilize dissolved metal species to reduce the possibility for redeposition by using strong complexing reagents [10-12], which has been reported by many groups and will not be the emphasis of this work. However, typical disadvantage of this approach is the use of corrosive and toxic chemicals, which place high demand for processing facility, safety regulation and environment policy.
- To continuously remove the dissolved metal species through combination of additional chemical / electrochemical process to promote dissolution kinetics, e.g. collecting the dissolved PGM in metallic form using electrodeposition [28].
- To block the redeposition sites to prevent or reduce redeposition process. However, such approach is often complicated to be adapted to potential transient conditions, since coverage of the active sites needs to be reversible and synchronized with the potential change; otherwise further dissolution will be limited due to surface passivation.

Here we report a novel approach to enhance the efficiency of transient electrochemical dissolution through inhibition of the redeposition through use of surface switching species (SSS), which is capable of blocking the surface only for the potentials suitable for redeposition and opening the surface when the potential is suitable for dissolution.

Underpotential deposition of copper (Cu-UPD) on a Pt surface, a well-known phenomenon [29-35], can be utilized to block the Pt surface to prevent the redeposition through reduction of Pt-soluble species as depicted in Fig. 1b. Deposition of Pt on the Copper, although possible at lower potentials ($V < 0$ vs. RHE) [36], is negligible at the potentials of interest ($V > 0.4V$). Again, galvanic displacement of Cu with Pt, another possible mechanism for deposition of Pt on Cu [37, 38] has negligible effect within the time scales of the experiment as it is a comparatively slow process.

Fig. 1: Process mechanisms for dissolution of Pt through electrochemical potential cycling in (a) absence and (b) presence of Cu^{2+} acting as a surface switching species (SSS). For simplicity, formation and dissolution of the Pt-Oxide layer has not been depicted. In (a), redeposition of the dissolved Pt-soluble species takes place at reducing potentials during negative-going scan (a3), leading to poor overall dissolution efficiency. In presence of SSS (e.g. Cu^{2+}), normal dissolution takes place during the first positive-going scan and initial part of the negative-going scan (b1-b2). Deposition of SSS on the Pt surface takes place ideally just after the removal of the Pt-Oxide (b3, completion of dissolution cycle), to form a blocking layer on the Pt-surface for redeposition of the dissolved Pt at lower potentials (b4) of the negative-going scan of the first cycle. Positive-going scan of the second potential cycle starts with the removal of the SSS adlayer at potentials sufficiently below the standard potentials for Pt-Oxide formation (b5-b6). Dissolution of Pt takes place during the later portion of the positive-going scan and the initial part of the negative-going scan (b7), while the deposition of SSS is repeated at appropriate potential range during negative-going scan (b8-b9).

2. Materials and Methods

Materials: Hydrochloric acid (1 M HCl; Reagent Ph. Eur.; BDH chemicals;), nitric acid (HNO_3 ; assay: 65%, Sigma-Aldrich®), sulfuric acid (H_2SO_4 ; EMSURE® grade, assay > 95 – 97%, Merck, Germany), Copper(II) chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$; purity: >99.99% ; Sigma-Aldrich®), Copper(II) sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$; purity: >99.99% ; Sigma-Aldrich®), Copper(II) nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$; purity: >99.99% ; Sigma-Aldrich®), Sodium chloride (NaCl; purity: >99.99% ; Sigma-Aldrich®) were used as-received to prepare different electrolyte solutions in Milli-Q water; resistivity $\geq 18.2 \text{ M}\Omega \cdot \text{cm}$ at 25 °C). Ammonium chloride (NH_4Cl ; purity: >99.99%; Sigma-Aldrich®) and

ammonium hexachloroplatinate ((NH₄)₂PtCl₆; min. Pt: 43.4%; Sigma-Aldrich®) were used as received for Pt species determination and reference material.

Electrochemical studies: The electrochemical dissolution study was performed using a three-electrode setup consisting of a working electrode (WE), a counter electrode (CE; Graphitic carbon rod; ~5 mm diameter) and a reference electrode (RE; Hg/Hg₂SO₄; REF 601 Radiometer®). The WE, containing the Pt-nanoparticles for the dissolution study, was a 10 mm diameter circular disc stamped from a polymer electrolyte membrane fuel cell (PEMFC) cathode (HiSPEC 9100 Pt/C catalyst spray-coated on gas diffusion layer (GDL; BD34 SIGRACET) with a Pt loading of ~0.6 mg/cm² and an ionomer (Nafion®) content of ~30 wt.%) prepared at EWII fuel cells A/S. The potentials measured w.r.t. the Hg/Hg₂SO₄ RE have been reported w.r.t. the reversible hydrogen electrode (RHE). Electrochemical potential cycling between specified potential range (0.4 - 1.6 V; starting and end potential values: 1.2 V, if otherwise not mentioned) was performed using a Zahner®IM6e electrochemical workstation in different electrolytes (12 mL; without gas bubbling/stirring; at room temperature and pressure).

Dissolution quantification: The Pt-loading values on WE before and after the electrochemical treatment were measured using an X-ray fluorescence spectrometer (XRF; Thermo Scientific Niton XL3t GOLDD+ XRF analyzer). The Pt-loading values were used to estimate the dissolution% of Pt (eq. 1). Calibration of Pt loading using XRF is described in our previous work [22].

The %dissolution, was calculated using the following equation-

$$\%dissolution = \frac{W_0 - W_f}{W_0} \times 100 \quad (1),$$

where W_0 and W_f are respectively the initial and final Pt-loadings on the electrode.

Again, atomic absorption spectroscopy (AAS; Graphite Furnace Agilent 200 Series AA analyzer) was used to determine the amount of dissolved Pt in the electrolyte after the dissolution study. As

shown in table S1, the dissolution% of Pt calculated using both the methods (XRF and AAS) were in good agreement even for large variations of %dissolution values. This evidence also indicates, in the conditions studied, platinum dissolution is the major degradation mechanism among other possible reactions of Pt/C degradation [39]. Despite an anodic corrosion of carbon is known to occur at $E > +0.8 \text{ V}_{\text{RHE}}$ [40], its contribution is negligible under the current study.

Evolution of the Pt concentration in electrolyte with the electrode potential during potential cycling was examined by examining The Pt concentration in the electrolyte at different potentials during an electrochemical potential cycle (start: 1.2 V; upper potential: 1.6 V; lower potential: 0.4 V; end potential: 1.6 V). For the Pt concentration determination through AAS, the electrolyte samples (100 μL) were collected after each 0.2 V, starting from 1.2 V. A comparatively slow scan rate (10 mV/s) was used to enable the sample collection at a certain potential. Again, fast distribution of the dissolved Pt species in the electrolyte was ensured through magnetic stirring (RPM; 1000). For measurements with no initial Pt concentration in the electrolyte, samples were collected during a potential cycle in a fresh electrolyte. In other cases, to study the effect of accumulated Pt species in electrolyte, the electrode was subjected to 5 dissolution potential cycles (0.4 - 1.6 V; 100 mV/s) before the measurement potential cycle (0.4 - 1.6 V; 10 mV/s, start point; 1.2 V).

Structural characterizations: The change in average crystallite size (L) of the Pt-nanoparticles was estimated through X-ray diffraction (XRD) using a Rigaku Miniflex 600 X-ray diffractometer (X-ray radiation: Cu $K\alpha$ ($\lambda = 1.5418 \text{ \AA}$)). X-ray diffraction peak corresponding to Pt (111) at diffraction angle (2θ) = 39.8° (JCPDS# 65-2868) [41] was used to determine L using Scherer's formula ($L = 0.9\lambda/\beta\cos\theta$; where β is the full width at half maximum (FWHM; $2\Delta\theta$) of the diffraction peak). The FWHM was determined by fitting the peak using Lorentz distribution.

Again, transmission electron microscope (TEM) imaging using a JEOL JEM-2100 TEM operated at 100 kV was employed to observe the change in average particle size of the nanoparticles. X-ray photoelectron spectroscopy (XPS) was performed to confirm the formation/removal of Cu-adlayer on the Pt-nanoparticles. The XPS analysis was performed using a SPECS[®] system. The spectrometer was equipped with a hemispherical analyzer and a monochromator. The XPS data were acquired using Mg Ka (1253.6 eV) radiation. The binding energies of the C 1s, O 1s, F 1s, and Pt 4f of the samples were calibrated with respect to C 1s: graphitized carbon peak at 284.5 eV. Survey spectra were collected at pass energy of 50 eV, resolution 2.5 eV over the binding energy range 0 -1250 eV. Selected area electron diffraction, High-resolution TEM (HRTEM) in combination with electron energy loss spectroscopy (EELS) and scanning transmission electron microscopy (STEM) in combination with energy dispersive spectroscopy (EDS) was performed by using a JEOL 3000F operated at 300 kV and equipped with a GIF2000 spectrometer and an Oxford instruments EDS detector. The HRTEM images were analyzed with fast Fourier transform (FFT) and inverse FFT (IFFT) methods using digital micrograph software (Gatan). The IFFT images of individual nanoparticles were produced after masking the FFT image excluding the strong diffraction spots, as shown in Fig. S4.

Further, UV-vis spectroscopy (Perkin Elmer; Lambda 900 UV/VIS/NIR spectrometer) was employed to determine the oxidation state of the Pt species dissolved during electrochemical treatment. The UV/Vis spectra were recorded using a reference electrolyte of identical concentrations of all the species other than the Pt species. In addition to oxidation state investigation through the UV-vis spectroscopy, the Pt²⁺/Pt⁴⁺ molar ratio of the electrochemically dissolved Pt was also determined by precipitating the Pt⁴⁺ species present in the post-dissolution electrolyte of a known Pt concentration (C^i) in form of (NH₄)₂PtCl₆ through addition of NH₄Cl powder to a concentration of 2 M followed by centrifugal separation after overnight aging. Comparable values

of C^i for the 0.1 M HCl and the 0.1M HCl+0.01 M CuCl₂ electrolytes are achieved by potential cyclic (650 cycles; 0.4-1.6V, 100 mV/s) dissolution of Pt from the PEMFC electrodes (6.3×12.5 cm² GDL separated from a spent PEMFC MEA from EWII fuel cell A/S) with average Pt loadings of ~0.4 and 0.2 mg/cm², respectively.

The resultant yellow precipitation was separated by centrifuging and the concentration of Pt in supernatant (C^f) was determined by AAS. Assuming Pt²⁺ and Pt⁴⁺ are the only oxidation states of Pt present in the solution, the concentration of Pt²⁺ (C^{Pt2+}) was calculated using the relation— $C^{Pt2+} = (C^f - C^d)$, with C^d being the solubility of (NH₄)₂PtCl₆ in the corresponding electrolyte (0.1 M HCl or 0.1 M HCl+0.01 M CuCl₂) containing 1 M NH₄Cl, as determined by preparing saturated (NH₄)₂PtCl₆-solution in the electrolyte and measuring the Pt concentration through AAS. Similarly, the concentration of Pt⁴⁺ (C^{Pt4+}) was estimated using the relation— $C^{Pt4+} = (C^i - C^{Pt2+})$. The precipitated (NH₄)₂PtCl₆ was characterized through XRD after purification through ethanol washing and drying.

3. Results and discussion

Evolution of physical state of electrodes during dissolution: Evolution of the average crystallite size of Pt-nanoparticles during potential cycling in Cl⁻ containing dilute acidic baths has been revealed by the XRD patterns of Fig. 2a. The decreased Pt (hkl) peak widths for the electrochemically treated electrodes (50 potential cycles between 0.4 and 1.6 V at a scan rate of 100 mV/s in 0.1 M HCl or 0.1 M HCl + 0.2 M NaCl) as compared to that for a pristine sample suggest significant growth of crystallite size during the electrochemical potential cycling. Consistent increase of crystallite size even for %dissolution extents as high as 75% suggests redeposition of dissolved Pt on the source nanoparticles. In addition, with increasing %dissolution, the ratio between the %growth (defined as the % change of crystalline size w.r.t. that of the pristine

electrode) and the %dissolution increases (Fig. 2b) due to increased concentration of dissolved Pt leading to higher rates of redeposition.

Cyclic voltammograms of a typical Pt/C WE used in the present study recorded in 0.1 M HCl and 0.1 M HCl+0.01 M CuCl₂ at a scan rate of 10 mV/s are shown in Fig. 2c. (The corresponding cyclic voltammograms recorded at a scan rate of 100 mV/s, the actual scan rate used for the electrochemical dissolution study, are provided in Fig. S1 (supplementary information S1)). The cyclic voltammograms document the suitability of Cu²⁺ as SSS for inhibition of redeposition during electrochemical potential cycling. Cu-UPD on the Pt surface during the negative-going scan takes place over a wide potential range below ~0.9 V with no sharp current peak; while a Cu-stripping peak during the positive-going scan appears between ~0.5 and ~0.8 V. Further, large current for potentials above ~1.4 V during positive-going scan may be attributed to Cl₂ evolution through $Cl_2 + 2e^- \rightarrow 2Cl^-$ (1.358 V), while that for potentials > 1.3 V during negative-going scan corresponds to the reduction of Cl₂ [42]. Formation and removal of the Cu-adlayer on the Pt/C electrode during the negative-going and positive-going scans can be confirmed further through X-ray photoelectron spectroscopy (XPS). XPS spectra of pristine and electrochemically treated electrodes have been shown in Fig. 2d. The electrochemical treatment involved potential cycling between 0.4 and 1.6 V at a scan rate of 100 mV/s for 2 cycles in 0.1 M HCl+0.01 M CuCl₂ with the end potentials for cycling being 0.4 V (negative-going scan) and 0.8 V (positive-going scan) for the Cu-0.4-F and Cu-0.8-R electrodes, respectively (Fig. S2; supplementary information S1). The presence of Cu 2p peaks in the XPS spectrum of the Cu-0.4-F electrode suggest the deposition of Cu during the negative-going scan to 0.4 V. Further, for the Cu-0.8-R electrode, the relatively lower intensities of the Cu 2p peaks may be attributed to the partial stripping of Cu during the positive-going scan between 0.4 and 0.8 V. With further increase of the potential during positive-going scan, completion of the Cu stripping leads to the Pt surface being exposed to the electrolyte

completely. Hence, with presence of Cu^{2+} , the Pt surface is exposed to the electrolyte for the oxidizing potentials and remains inaccessible, at least partially to the electrolytes for reducing potentials.

Fig. 2: (a) XRD patterns of the pristine and electrochemically treated Pt/C electrodes. Inset shows the intensity normalized Pt (111) diffraction peaks revealing the effect of electrochemical treatment of the peak width (FWHM). (b) Variations of the Pt-crystallite size calculated using Scherer formula for Pt (111) XRD peak with the %dissolution during electrochemical potential cycling for 25 and 50 cycles in different electrolytes. (c) Cyclic voltammograms of Pt/C electrodes in different electrolytes at a scan rate of 100 mV/s. (d) XPS spectra of pristine and electrochemically treated Pt/C electrodes (Inset: Magnified Cu-2p peaks).

Chemical state of dissolved Pt species: Pt dissolution in Cl⁻-free electrolytes takes place preferentially through Pt²⁺ formation [43, 44]. On the other hand, dissolution of Pt in presence of Cl⁻ takes place by the formation of [PtCl₄]²⁻ or [PtCl₆]²⁻ complexes through equations (2) and (3) [42, 45], and possibly followed by the oxidation of [PtCl₄]²⁻ to [PtCl₆]²⁻ at higher potentials during potential cycling through eq. (4).

However, there may be different redox reactions involving Cu²⁺ and leading to an unusual Pt²⁺/Pt⁴⁺ ratio. To investigate such possibility, chemical state of the dissolved Pt species was examined by spectroscopic and solution chemistry methods.

Fig. 3 shows the UV-Vis spectra of various electrolytes containing electrochemically dissolved Pt species. For the electrolytes containing dissolved Pt species (irrespective to the presence/absence of Cu²⁺) presence of the absorbance peak centered at 260 nm (Fig. 3a) suggests the presence of [PtCl₆]²⁻ complex, which corresponds to the Pt⁴⁺ oxidation state. A comparison of the UV-vis spectra of the [PtCl₆]²⁻ and [PtCl₄]²⁻ complexes in 0.1 M HCl has been shown in Fig. 3b. The absence of absorption peak corresponding to Pt²⁺ for both the cases (presence/absence of Cu²⁺) indicates that Cu has no effect on the oxidation state of the dissolved Pt species (Pt⁴⁺ for both the cases). However, although the UV-vis spectra are measured using the relevant electrolyte as the reference to eliminate the absorption signal from the electrolyte, high absorbance of Cu²⁺ at wavelengths below 300 nm (Fig. 3d), might affect the measurement sensitivity making it inadequate to observe the low concentrations of Pt²⁺.

Fig. 3: UV-Vis spectra of (a) the electrolytes containing Pt species from electrochemically dissolved Pt with Pt concentrations of 2.7 and 6.7 μM respectively for Pt(0.1 M HCl) and Pt(0.1 M HCl-0.01 M CuCl₂), (b) the commercial Pt precursors, namely H₂PtCl₆ and K₂PtCl₄ solutions in 0.1 M HCl having equal Pt concentrations of 12.8 μM and (c) the electrolytes, namely 0.1 M HCl and 0.1 M HCl + 0.01 M CuCl₂ used in the study. The spectra (a) and (b) are recorded using the respective electrolytes as reference, while milliQ-water is used as reference for (c). (d) XRD patterns of the precipitated (NH₄)₂PtCl₆ samples corresponding to Pt dissolution studies in 0.1 M HCl ((NH₄)₂PtCl₆-No Cu²⁺) and 0.1 M HCl + 0.01 M CuCl₂ ((NH₄)₂PtCl₆-0.01 M Cu²⁺) electrolytes. For reference, XRD pattern of the commercial (NH₄)₂PtCl₆ ((NH₄)₂PtCl₆-Ref.) is also shown.

Therefore, another method based on classical Pt chemistry has been employed to determine the $\text{Pt}^{2+}/\text{Pt}^{4+}$ molar ratio. Hydrometallurgical PGM extraction methods employ precipitation of the Pt dissolved in chloride-containing electrolytes in form of the $(\text{NH}_4)_2\text{PtCl}_6$ salt [17], utilizing its very low solubility in aqueous NH_4Cl solution (Table 1). Here, we demonstrate that irrespective of the presence/absence of Cu^{2+} during potential cycling, the electrochemically dissolved Pt can be precipitated in form of $(\text{NH}_4)_2\text{PtCl}_6$. As shown in table 1, $\text{Pt}^{2+}/\text{Pt}^{4+}$ ratios for electrochemical dissolution in either of the electrolytes (0.1 M HCl or 0.1 M HCl+0.01 M CuCl_2) remain quite low ($\text{Pt}^{2+}/\text{Pt}^{4+}$ ratio 0.00 for 0.1 M HCl and 0.02 for 0.1 M HCl+0.01 M CuCl_2 ; with the difference being within the statistical error) suggesting majority of the dissolved Pt in form of $[\text{PtCl}_6]^{2-}$ complex. XRD patterns of the precipitated $(\text{NH}_4)_2\text{PtCl}_6$ samples from both the electrolytes show the characteristic $(\text{NH}_4)_2\text{PtCl}_6$ diffraction pattern [46] (expect for an extra peak at $\sim 32.7^\circ$, corresponding to the most intense diffraction peak from NH_4Cl ; JCPDS 73-0365), confirming no effect of presence of Cu^{2+} on the nature of the precipitation (Fig. 3d). Hence, during electrochemical dissolution in presence of Cl^- , the $[\text{PtCl}_4]^{2-}$ species are either not formed or oxidized spontaneously to the more stable $[\text{PtCl}_6]^{2-}$ species. Further, presence of Cu^{2+} has insignificant effect on the nature of the redox reactions responsible for the Pt dissolution.

Table 1: $\text{Pt}^{2+}/\text{Pt}^{4+}$ ratio of the Pt dissolved electrochemically in 0.1 M HCl or 0.1 M HCl+0.01 M CuCl_2

Electrolyte	Initial Pt conc. (μM)	Extract Pt conc. (μM)	$(\text{NH}_4)_2\text{PtCl}_6$ solubility (μM)	Pt^{2+} conc. (μM)	Pt^{4+} conc. (μM)	$\text{Pt}^{2+}/\text{Pt}^{4+}$ ratio
0.1M HCl	884	82	82	0	884	0.00
0.1M HCl+0.01 M CuCl_2	722	58	42	16	706	0.02

Pt concentration evolution with potential/time during potentiodynamic treatment: Fig. 4

shows the effect of presence of SSS on the redeposition of dissolved Pt species (Pt^{4+} in both

presence/absence of Cu^{2+}). Evolution of the Pt concentrations in electrolyte with the electrode potential during potential cycling (0.1 M HCl, 10 mV/s) shows significant difference in presence/absence of Cu^{2+} as the SSS. In 0.1 M HCl electrolyte, for initial cycle (no soluble Pt species already present in the electrolyte, Fig. 4a black) the Pt concentration builds up during negative-going scan ($E < 1.0$ V), which may be explained by mechanism of place exchange of oxygen atoms from surface to sub-surface positions during reduction [47]. The Pt concentration decreases marginally during the positive-going scan for potentials < 1.0 V before a sharp increase for potentials > 1.0 V (thermodynamic potential for platinum oxidation). The marginal decrease of the concentration (Inset: Fig. 4a) during the subsequent positive-going scan may be attributed to the redeposition of the dissolved Pt species on the Pt nanoparticles through adsorption of the $[\text{PtCl}_6]^{2-}$ species on fresh (oxide-free) Pt surface [48]. The redeposition becomes even clearer when a higher concentration of dissolved Pt species is present in the electrolyte. The concentration of dissolved Pt species is increased by applying a potential cycling treatment of 5 stress cycles (0.4–1.6 V; 100 mV/s) to the electrode before the concentration measurement cycle (0.4–1.6 V; 10 mV/s). Potential/time plot for the overall electrochemical treatment of the electrode for the Pt concentration vs. potential measurements is shown in Fig. S3 (supplementary information S1). As shown, the Pt concentration vs. potential profile shows a significant reduction of Pt concentration in 0.1 M HCl electrolyte during positive-going scan for potentials < 1.0 V (Fig. 4a, red) while no such Pt concentration reduction is observed for the electrolyte containing Cu^{2+} as the SSS (Fig. 4b, red). The observations can also be made through the Pt concentration/time plots of Fig 3c and Fig. 4d corresponding respectively to the 0.1 M HCl and the 0.1 M HCl+0.01 M CuCl_2 electrolytes. As can be seen, plots labeled with 0 and 5 stress cycles correspond to different initial ($t = 0$ s) concentrations of Pt species in electrolytes. The Pt concentrations corresponding to both the conditions (0 and 5 stress cycles) increase consistently for 0.1 M HCl+0.01 M CuCl_2 , while for 0.1

M HCl, a drop in Pt concentration is observed around $t = 175$ s due to redeposition of the dissolved Pt. This confirms the proposed mechanism of increased Pt %dissolution in presence of SSS.

Fig. 4: Variations of the Pt concentrations in (a) 0.1 M HCl and (b) 0.1 M HCl+0.01 M CuCl₂ electrolytes with the potentials during potentiodynamic dissolution of Pt. The inset of (a) shows a magnified view of the encircled concentration evolution curve during positive-going scan. Variations of the Pt concentrations with the treatment time during potentiodynamic dissolution of Pt in (c) 0.1 M HCl and (d) 0.1 M HCl+0.01 M CuCl₂. Plots labeled with 0 and 5 stress cycles correspond to different initial concentrations of Pt species in electrolytes.

Further, as the Pt recovery through potential cycling may prove energy inefficient due to low Coulombic efficiency (moles of Pt dissolved/charge), the impact of presence of Cu on the energy

efficiency of the dissolution process has been calculated. Here, the effect of presence of Cu^{2+} on the efficiency is studied by measuring the corresponding voltammogram areas (current $\times$ time) and hence the total charge (C) values for the first potential cycles in 0.1 M HCl and 0.1 M HCl+0.01 M CuCl_2 electrolytes recorded at a scan rate of 10 mV/s. Table 2 shows the effect of presence of Cu^{2+} on the Coulombic efficiencies, where the corresponding Pt concentrations after the first cycle are taken from Fig. 4. As compared to that for 0.1 M HCl, the Coulombic efficiency of Pt dissolution for the 0.1 M HCl+0.01 M CuCl_2 electrolyte shows an increase of $\sim 71\%$., suggesting significant improvement due to presence of the Cu^{2+} as SSS.

Table 2: Effect of presence of Cu^{2+} on Coulombic efficiencies of the potentiodynamic Pt dissolution

Electrolyte	Dissolved Pt concentration (μM)	Voltammogram area (C)	Coulombic efficiency ($\mu\text{M/C}$)
0.1 M HCl	2.7	0.48	5.6
0.1 M HCl+0.01 M CuCl_2	6.7	0.70	9.6

Structural characteristics of the electrodes: A HRTEM image of Pt/C catalyst from the electrode subjected to a negative-going scan to 0.4 V is shown in Fig. 5a. Owing to their similar crystal structure (FCC) and lattice constants (Cu: 3.6 Å; Pt: 3.9 Å), identification of lattice fringes corresponding to Cu or Pt-Cu alloy is difficult. The inverse fast Fourier transform (IFFT, obtained as shown in Fig. S5; supplementary information) image (Fig. 5b) of a Pt-nanoparticle (indicated in Fig. 5a by a rectangle) reveals bending of lattice fringes near the particle edge, possibly due to relaxation of the surface atoms. Further, EELS analysis of the same sample (Fig. 5c) confirms the presence of a weak edge at ~ 931 eV corresponding to the Cu-L₃ edge [49]. Also, the Cu-L₃ edge has been observed only in vicinity of the Pt surface and not on a carbon surface, which indicated the

preferential deposition of Cu on Pt. Hence, the HRTEM analysis confirms the presence of Cu either in form of Cu or Pt-Cu alloy deposition on the Pt-nanoparticles.

Fig. 5: (a) HRTEM image of the Pt/C standard electrode electrochemically treated by potential cycling in 0.1 M HCl+0.01 M CuCl₂ for 2 cycles between 0.4 and 1.6 V (scan rate: 100 mV/s; end potential: 0.4 V), revealing the presence of carbon supported Pt nanoparticles. **(b)** Inverse FFT (IFFT) image of Pt-nanoparticle portion (enclosed in rectangle in (a)) showing lattice fringes corresponding to Pt (111) and Pt (200) crystallographic planes with respective lattice spacing values of 0.23 and 0.20 nm. **(c)** Electron energy loss spectrum of the Pt/C sample (electrochemical treatment same to (a)) consisting of a weak edge at ~931 eV corresponding to Cu, confirming the presence of Cu.

Effect of Cu²⁺ in different electrolytes: The effect of the presence of Cu²⁺ on the Pt dissolution under different conditions is demonstrated in Fig. 6 and Fig. 7. The Pt-dissolution shows significant enhancement in the presence of Cu ions, both in the presence of a complexing agent such as Cl⁻ ions

or in their absence. As shown in Fig. 6a, in presence of Cl^- as a Pt-complexing agent (H^+ : 0.1 M; Cl^- : 0.1 M) ~60% of the Pt on the electrode dissolves in 25 potential cycles (0.4-1.6 V; 100 mV/s), suggesting a high rate of dissolution due to formation of Pt-Cl complexes. Under similar conditions, with addition of Cu^{2+} (H^+ : 0.1 M; Cl^- : 0.1 M; Cu^{2+} : 0.01 M) the inhibition of the redeposition enhances the dissolution to ~75% along with a relatively smaller increase of average crystallite size/%dissolution (shown as third y-axis in Fig. 6a). The corresponding XRD patterns of post-dissolution electrodes with/without Cu^{2+} are shown in Fig. 6b, with the average crystallite sizes being 3.3 nm for pristine electrode, 5.0 nm for post-dissolution electrode without Cu^{2+} (%dissolution: ~61%) and 4.8 nm for post-dissolution electrode with Cu^{2+} (%dissolution: ~75%). However, the numbers, being uncertain due to factors such as low intensity of XRD peaks for post-dissolution samples, uncorrected instrumental broadening, etc., provide qualitative variation of the crystallite size. Similarly, the average particle sizes of pristine and post-dissolution electrodes through TEM analysis (Fig. 6d-f) suggest smaller increase of average particle size/%dissolution (average particle sizes: (i) pristine: 2.5 nm, (ii) post-dissolution without Cu^{2+} : 3.1 nm and (iii) post-dissolution with Cu^{2+} : 3.20 nm). Hence, presence of Cu^{2+} during potential cycling seems to inhibit the redeposition through cyclic formation and removal of a Cu-adlayer on the Pt surface such that the Pt surface remains open for Pt dissolution but becomes inaccessible for redeposition. Fig. 6c shows the effect of different lower potentials (0.2, 0.4 and 0.6 V; with a fixed upper potential limit of 1.6 V) on dissolution of platinum through potential cycling. In the absence of Cu^{2+} as SSS, the decrease of %dissolution with decreasing lower potential is attributed to the redeposition of dissolved Pt species. On the other hand, in the presence of Cu^{2+} as SSS, the inhibition of redeposition helps maintaining a comparatively constant %dissolution when decreasing the lower potential from 0.4 to 0.2 V. In addition, a lower %dissolution for both cases (with/without SSS) in the case of a lower potential value of 0.6 V may be attributed to the incomplete dissolution of the

Pt-oxide layer formed during higher (> 1.0 V) potentials. As the formation of Pt-Oxides during positive-going scan and their subsequent reduction during negative-going scan is the dominant dissolution mechanism during potentiodynamic treatment, an upper potential limit > 1.0 V is required for efficient dissolution [47]. This confirms the requirement of the lower potential limit to be below 0.6 V and the higher potential limit to be above 1.0 V.

Fig. 6: Effect of presence of Cu²⁺ as SSS on the Pt-dissolution efficiency in electrolytes containing ions capable of Pt-complex formation. (a) Variations of %dissolution, crystallite size and crystallite %growth/%dissolution (third y-axis) for Pt/C standard electrodes

subjected to potential cycling in Cu-free (0.1 M HCl) and Cu-containing (0.1 M HCl+0.01 M CuCl₂) electrolytes containing Cl⁻ as Pt-complexing ions (50 potential cycles between 0.4 and 1.6 V; scan rate: 100 mV/s). (b) XRD patterns of the electrochemically treated electrodes (Inset: intensity normalized Pt (111) diffraction peaks). Lower absolute intensity of the XRD pattern corresponding to the electrode treated in presence of Cu²⁺ may be attributed to the lower residual Pt-loading on the electrode due to high %dissolution. (c) Variations of %dissolution from Pt/C standard electrode with lower potential limit during electrochemical treatment (25 cycles; scan rate- 100 mV/s; upper potential- 1.6 V) in Cu-free (0.1 M HCl) and Cu-containing (0.1 M HCl+0.01 M CuCl₂) electrolytes. (d-f) TEM images of Pt/C electrodes (specification: same as of (a)) showing Pt nanoparticle distribution in (d) pristine Pt/C catalyst and in the electrodes electrochemically treated as described in (a) with (e) and (f) corresponding respectively to 0.1 M HCl and 0.1 M HCl+0.01 M CuCl₂ electrolytes. Insets of TEM images (d-f) show corresponding particle size distribution histograms.

The effect of inhibition of redeposition on the Pt-dissolution in non-complexing electrolytes has been demonstrated in Fig. 7. The increased %dissolution and the decreased crystallite size growth/dissolution (Fig. 7a) during potential cycling in presence of Cu²⁺ as compared to their corresponding values in absence of Cu²⁺ confirm the mechanism proposed in Fig. 1b, the inhibition of redeposition and the exposure of Pt surface when relevant in the presence of Cu²⁺ as SSS. Again, similar conclusions can be drawn from Fig. 7c-d, showing the surface switching effect during potential cycling for 3000 cycles in 1 M HNO₃ as the non-complexing, yet stronger oxidizing electrolyte, and 0.1 M Cu(NO₃)₂ as the Cu²⁺ source. In the presence of Cu²⁺, electrochemical potential cycling exhibits a ~2.5 fold enhancement of %dissolution along with ~25% less growth of crystallite size for both of the non-complexing electrolytes.

Fig. 7: Effect of presence of Cu²⁺ as SSS on the Pt-dissolution efficiency in non-complexing electrolytes. (a) and (c) show variations of the %dissolution, crystallite size and crystallite %growth/%dissolution (shown as third y-axis) for Pt/C standard electrodes subjected to electrochemical dissolution treatment in Cu-free and Cu-containing electrolytes. The electrochemical dissolution treatment involved a potential cycling between 0.4 and 1.6V at a potential scan rate of 100 mV/s for (a) 10000 cycles in 1 M H₂SO₄ and 1 M H₂SO₄+0.1 M CuSO₄ electrolytes; for (c) 3000 cycles in 1 M HNO₃ and 1 M HNO₃+0.1 M Cu(NO₃)₂ electrolytes. XRD patterns of the electrochemically treated electrodes corresponding to (a) and (c) are shown in (b) and (d), respectively. The corresponding intensity normalized Pt (111) diffraction peaks for the electrodes have been shown as insets of (b) and (d). Lower XRD

peak intensities for the electrodes treated in presence of Cu^{2+} is attributed to their comparatively lower amount of undissolved Pt.

The electrochemical treatment of Pt/C in complexing or non-complexing electrolytes leads to the growth of crystallite size irrespective of the presence or absence of Cu^{2+} . However, lower relative growth of crystallite size and higher %dissolution in presence of SSS, along with the fact that the crystallite size increases with %dissolution in absence of SSS, confirm the successful inhibition of Pt redeposition and accessibility of fresh Pt surface by SSS without hindering the dissolution process. Again, the slight growth of crystallites despite the presence of Cu^{2+} as the inhibitor for redeposition may be attributed to an incomplete inhibition of Pt redeposition. This may be attributed primarily to the fact that formation of Cu-adlayer by Cu-UPD takes place over a broad potential range during the negative-going scan, which makes a fraction of the Pt-surface accessible for Pt redeposition. Hence, an ideal SSS should be able to curb this parallel process. Other metal ions, for example, having suitable reduction potential may be employed as SSS (e.g., $\text{Cu}^+ + e^- \rightarrow \text{Cu}$; $E^\circ = 0.521 \text{ V}$ is suitable for Pt (supplementary information: S3 and S4). However, use of the most stable Cu cation is preferred as oxidation of the deposited Cu on Pt from Cu^+ during first positive-going scan will form the more stable oxidation state (e.g. Cu^{2+}). Moreover, the enhancement of dissolution has been observed for two different concentrations of the SSS (Cu^{2+}). For example, the Pt concentration/time study (Fig. 4) and the potential limit study (Fig. 6c) are performed with a Cu^{2+} concentration of 0.01 M instead of the Cu^{2+} concentration of 0.1 M used more frequently in the other experiments of the study. As the amount of available SSS (Cu^{2+}) should be sufficient to cover the Pt surface during the negative-going scan, the minimum SSS concentration depends on factors such as the electrochemically active surface area of the electrode, the scan rate, the diffusivity of the SSS in the electrolyte, etc.

In principle, the inhibition effect through SSS (e.g. Cu^{2+}) may be applied to other metals using appropriate SSS, having suitable redox potential and compatibility towards formation of surface adlayer. For example, effect of presence of Cu^{2+} on dissolution of Au through potential cycling in HCl has been studied using an Au wire (0.1 mm diameter) electrode as working electrode. Similar to Pt, Au shows enhanced dissolution in presence of Cu^{2+} due to inhibition of redeposition of dissolved Au species (Au^{3+} supplementary information S2, S5). Finally, for the electrochemical dissolution process to be feasible for practical applications, high %dissolution ($\sim 100\%$) is desired. However, due to growth of particles during dissolution process, the rate of dissolution decreases with increasing number of potential cycles. Use of SSS may provide such high dissolutions ($>95\%$) within significantly lesser ($<50\%$) number of potential cycles required otherwise (supplementary information S6). Hence, the inhibition of redeposition through SSS may improve the industrial feasibility of the electrochemical recycling of PGMs.

4. Conclusions

Here, we introduce a new concept for platinum electrochemical dissolution by using an intelligent surface switching species (SSS), as an environmentally friendly, efficient and economic process for recovery of platinum nanoparticulate. We have demonstrated the effect of Cu-ions as a SSS for enhancement of dissolution of nanoparticulate Pt through electrochemical potential cycling. For negative-going scan (increasingly reducing potentials applied), the Pt surface is blocked through Cu-UPD; while for positive-going scan (increasingly oxidizing potentials applied), Cu strips away at potentials much lower than the Pt-oxidation potentials. The SSS enhances Pt dissolution significantly by inhibiting the crystallite growth through redeposition of dissolved Pt species, which

becomes intense for reducing potentials during negative-going scan and increases with the concentration of dissolved Pt species in electrolyte. We have observed that the dissolution process is improved by a factor of 2 or more with relatively low Pt crystallite growth in various electrolytes with/without Pt-complexing species. This leads to an overall dissolution efficiency of more than 95%. The SSS concept can be expanded to other metallurgical processing (e.g. this work have also demonstrated Au). By selecting an appropriate SSS, the technology may be used at industrial scales for efficient recovery of various precious metals.

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Competing interests

S.M.A and R.S. are inventors on EU patent application EP 18170312.5, submitted by University of Southern Denmark, which covers the herein-described PGM recovery process. Other authors declare no competing interests.

Supplementary Materials

S1: Cyclic voltammograms and potential profiles used for electrochemical treatment; S2: Characterizations; S3: Inhibition effect using Cu^+ as surface switching species (SSS); S4: Effect of

other metal ions on Pt dissolution; S5: Effect of Cu inhibition on other precious metals (PMs); S6: Effectiveness for industrial applications

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