



The Impact of Ru Contamination of a Pt/C Electrocatalyst on Its Oxygen-Reducing Activity

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Rotating disk electrode experiments were used to demonstrate the influence of dissolved Ru species on the oxygen reduction activity of a Pt/C electrocatalyst. Dissolved Ru in micromolar levels was found to deposit instantly onto Pt, thereby blocking the electrode surface for ORR at low overpotentials. Ru contamination can decrease oxygen reduction kinetics by eightfold or increase the overpotential by ca. 160 mV. This facet of fuel cell durability needs special attention from the perspective of appropriate materials choice, i.e., preventing the leaching of Ru from PtRu anodes and its crossover to the cathode across the membrane electrolyte.

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The aim of commercializing proton exchange membrane fuel cells (PEMFCs), especially direct methanol fuel cells (DMFCs), have resulted in a wealth of prior work for improvements in overall performance capabilities. However, studies on performance losses such as those pertaining to factors related to the anode and the cathode interfaces are relatively recent.¹⁻⁷ The electrocatalysts in moderate-temperature PEMFCs, and DMFCs in particular, exhibit a significant susceptibility toward surface poisoning. This is evident in the case of reformate-based PEMFCs, where the noble metal alloy or mixed-phase anode electrocatalysts are not only prone to CO poisoning directly from the fuel but also from the CO₂ gas by the reverse-shift reaction.⁸ Surface poisoning of the anode electrocatalysts during methanol oxidation is more complicated.⁹ Nevertheless, the change in electrochemical surface area exerted by such undesired adsorbates is recoverable; the surface blocking species can be removed by offsetting the regular operating parameters such as by current (potential) pulsing.¹⁰ Meanwhile, the systematic investigation of irreversible performance losses, both short- and long-term, mostly due to electrocatalyst corrosion^{9,11-13} and irreversible poisoning,⁴ are scant.

In the context of low- and medium-temperature acid fuel cells, the investigation of durability issues has been on the backlog, in part because of the test-duration requirements and the complexity of analysis due to the ongoing parallel-failure modes.⁵ In fuel cell cathode operation conditions, the dissolution of noble metals, in particular of Pt, was unequivocally demonstrated to impair electrocatalysis as well as cell performance.^{12,14} For anode applications, PtRu compounds remain as the most effective electrocatalysts for PEMFC and DMFC.^{9,15-18} Knights et al.¹ investigated several of the key mechanisms attributed to fuel cell power loss over extended periods of time and provided an overview of those operating conditions that influence durability. The authors claimed that by enhancing the water retention at the anode side combined with advanced electrocatalyst designs, the degradation of PtRu via the dissolution of noble metals could be avoided. However, most PtRu materials were found to be prone to preferential leaching of Ru, especially in the presence of methanol,¹⁹⁻²¹ thereby entailing undesired changes in the composition and, consequently, in the activity of the electrocatalyst.²¹ Focusing on the mechanism behind Pt and Ru corrosion, Chen et al.²⁰ demonstrated through potential cycling of the anode in a DMFC that dissolution of the anode electrocatalyst contributes to a lower catalytic activity for methanol electro-oxidation. A study by Piela et al.¹⁸ showed that the impact of Ru dissolution on fuel cell performance is complicated by Ru crossover from the anode to the cathode side.

Because the mobility and transport of metal ions in PEMs are well documented,²²⁻²⁴ it is reasonable to evaluate the indirect effects

of Ru corrosion and mobility in terms of overall PEMFC performance, especially because the concentration of the leached Ru is expected to exceed trace levels.^{18,21} Ruthenium crossover in DMFCs was recently discovered by the Los Alamos Group.¹⁸ In their pioneering work, X-ray fluorescence and CO-stripping data evidenced the transport of Ru across the PEM and its deposition on the Pt cathode, respectively, under various DMFC operating conditions. Such series of events with Ru was also confirmed in single-cell experiments,²¹ in which the DMFC was operated in the mass-transport-limited region under massive methanol crossover. Interestingly, no accumulation of Ru in the Nafion membrane could be detected by energy dispersive X-ray spectroscopy (EDS). Rather, dissolved Ru species are assumed to travel across the PEM and fill the drained voids in the cathode electrocatalyst layer. In those pores, Ruⁿ⁺ concentration is predicted to reach the several moles per liter level.⁴ Polarization curves recorded for fuel cells with clean and Ru-contaminated Pt cathodes suggest that Ru contamination may play a crucial role in the unrecoverable performance degradation of PEMFCs.

In this work, we intend to explicitly present the effect of Ru contamination on the oxygen reduction reaction (ORR) kinetics on Pt/C in order to provide a link to PEMFC performance degradation. In our simplistic experimental approach, Ru was dissolved from a commercial unsupported PtRu electrocatalyst-based fuel cell electrode (referred to as sacrificial electrode) directly into the liquid electrolyte, in which oxygen reduction was performed on a thin-film Pt/C working electrode. Ruⁿ⁺ concentration was monitored using inductively coupled plasma-mass spectrometry (ICP-MS), while changes in ORR kinetics were addressed by rotating disk electrode experiments. A detailed study showing Ru contamination under various fuel cell cathode operating conditions such as cathode overpotential, temperature, and choice of electrocatalyst (Pt alloy vs Pt) will be presented in the full version of this manuscript.

Experimental

All electrochemical experiments were performed in a conventional three-electrode cell containing 50 cm³ solution of 0.5 mol dm⁻³ redistilled sulfuric acid (GFS Chemicals, Inc., USA) or 1 mol dm⁻³ triple-distilled trifluoromethane sulfonic acid (triflic acid or TFMSA; Strem Chemicals, Inc., USA). A glass compartment accommodated the interface between the same electrolyte and hydrogen gas at a Pt mesh, which served as a sealed reference hydrogen electrode (RHE). The RHE was connected to the main cell compartment through a fine-pore-sized frit that impeded the transport of Ruⁿ⁺ species. A Pt wire of ca. 1.7 cm² electroactive surface area [measured from the hydrogen underpotential deposition (H_{UPD}) charge] was used as counter electrode. The instrumentation was based on an ASAFR Rotator (Pine Instruments Company, USA) and an Autolab PGSTAT-30 potentiostat equipped with a SCAN-GEN module (Eco Chemie B.V., The Netherlands).

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As working electrode (oxygen reduction) material, the E-TEK HP 30 wt % Pt/C electrocatalyst (E-TEK, A BASF Company, USA) was chosen to prepare a thin layer ($15 \mu\text{g}_{\text{Pt}}/\text{cm}^2$)²⁵ on a glassy carbon substrate ($d = 0.6 \text{ cm}$). To make the electrode robust, a thin (ca. 0.05 mm thick) Nafion film was cast onto the top of the electrocatalyst layer.²⁶ Pt surface area of the electrodes was $1.1 \pm 0.1 \text{ cm}^2$ from measuring independently the H_{UPD} areas using cyclic voltammetry. After temporarily removing the working electrode from the solution and storing it under Millipore water, Ru was dissolved into the electrolyte from a Toray paper-based PtRu gas diffusion electrode (GDE) which was sandwiched between two Nafion layers to prevent mechanical degradation. Commercially available unsupported PtRu electrocatalysts with 1:1 nominal Pt/Ru atomic ratio (Johnson & Matthey HiSpec6000 and Tanaka Kikin-zoku International K.K TEC90110) were used at $4 \text{ mg}/\text{cm}^2$ loadings in the sacrificial electrodes (geometric area, $A = 2.25 \text{ cm}^2$). For three days before Ru dissolution, the Tanaka-based GDE had been washed in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ in order to mitigate the instant Ru leaching from thermodynamically instable compounds. Ru dissolution from the sacrificial electrode was confirmed by performing EDS [Hitachi 5800 field-emission scanning electron microscope (SEM) attached to a Genesis 136-10 energy dispersive analysis by X-ray (EDAX) EDS unit]. Prior to repositioning the Pt/C working electrode into the cell, the concentration of dissolved Ru species was measured by using a VG-Elemental PlasmaQuad 2 ICP-MS (Windsford, U.K.). The HiSpec6000 PtRu (1:1) electrocatalyst was used also for an RDE experiment in clean electrolyte to compare the ORR performance of Pt/C surface in Ru-contaminated electrolyte solutions.

Results and Discussion

Reduction of surface oxides and molecular oxygen on Pt in Ru-containing electrolyte.—Evidences for Ru leaching from a DMFC anode and its transport across the PEM have been revealed previously.^{4,18,21} It was also proposed that Ru might appear in the voids of the cathode electrocatalyst layer in extremely high concentrations.^{4,18,21} Without discussing here the nature of dissolved and mobile Ru species, it is expected that Ru in the form of aqueous oxides and hydrated ions can be reduced to the metallic state in acidic media in the potential range at which typical ORR occurs.²⁷ Given that the oxidation state of Ru in the dissolved species might vary, we simply refer to those as Ru^{n+} in the text. At the cathode side, typically carbon-supported Pt or Pt-based alloys are used to provide an acceptable, yet in comparison to the typical hydrogen oxidation anode reaction sluggish, rate for the electroreduction of molecular oxygen. Our preliminary goal was to assess the activity of Pt/C toward ORR in the presence of Ru^{n+} .

Cyclic voltammetry (CV) was applied as a first approach to observe how the fundamental electrode reactions on a Pt/C are affected in Ru-contaminated aqueous electrolyte. Although the specific adsorption of sulfate ions can yield a considerable anion coverage level between 0.6 and 1.1 V [on Pt(111) up to 19%²⁸], H_2SO_4 (0.5 mol dm^{-3}) was chosen as supporting electrolyte in favor of the nonadsorbing electrolytes ($\text{CF}_3\text{SO}_3\text{H}$ and HClO_4) because sulfuric acid is highly stable at the platinum surface over a broad electrode potential window over long durations. Ru was dissolved directly into the supporting electrolyte from a high-surface-area PtRu fuel cell electrode (HiSpec6000) by cycling the electrode potential to as high as 1.4 V, where electrochemical dissolution of Ru metal occurs.^{18,29,30} Before Ru dissolution, the Pt/C working electrode was removed from the electrolyte and was stored under Millipore water. We note that no change in the surface area as well as in the ORR activity of the Pt/C electrocatalyst could be evidenced in a separate series of experiments, when the working electrode was removed and repositioned into the same Ru-free solution several times. The repeated CV and RDE polarization curves completely overlapped with the previous ones, i.e., the act of removal of the working electrode did not cause any changes to the original surface

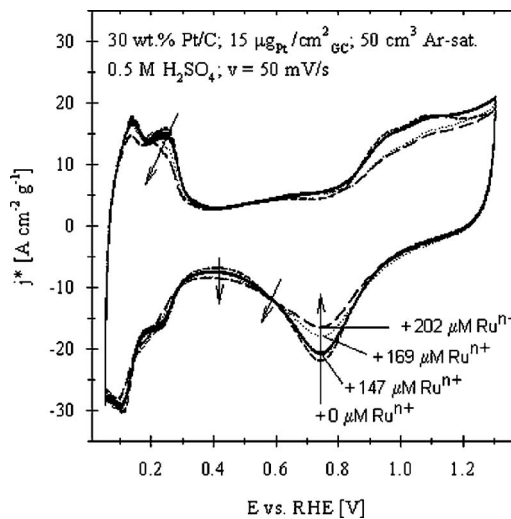


Figure 1. CV curves for a thin-film 30 wt % Pt/C electrode in Ar-saturated $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ solution containing dissolved Ru species in various concentrations.

properties of the Pt/C thin-film electrode. In between Ru dissolution and the readmission of the working electrode, samples were taken from the electrolyte to measure Ru^{n+} concentration by ICP-MS.

Figure 1 shows CV curves for the Pt/C thin-film electrode in deaerated sulfuric acid electrolyte containing various amounts of dissolved ruthenium. After the Ru^{n+} concentrations were adjusted, overlapping voltammograms could be recorded after the first few cycles. This observation indicates the rapid onset of a steady-state Ru coverage on the Pt surface. Progressive changes in the voltammetric profile (indicated by arrows in Fig. 1) were found as a function of increasing Ru^{n+} concentration. A smaller H_{UPD} charge and an increase in the double-layer charging are measured according to the morphological preferences of Ru deposition on Pt¹⁵ and the higher capacitance of Ru oxides,^{31,32} respectively. With increasing Ru^{n+} concentration, a broad Faraday current emerges and grows immediately following the Pt-oxide reduction peak at around 0.6 V in the cathodic sweep of potential cycling. The small broadband corresponds to the reduction of surface oxides from Ru sites. The magnitude of the Pt oxide reduction peak (at ca. 0.73 V) decreases as a function of Ru^{n+} concentration without any concomitant peak shift. While there is a significant decrease in the number of Pt sites available for oxide formation (and thereby corresponding reduction), the reaction potential of the Pt surface might retain its original characteristics after Ru deposition.

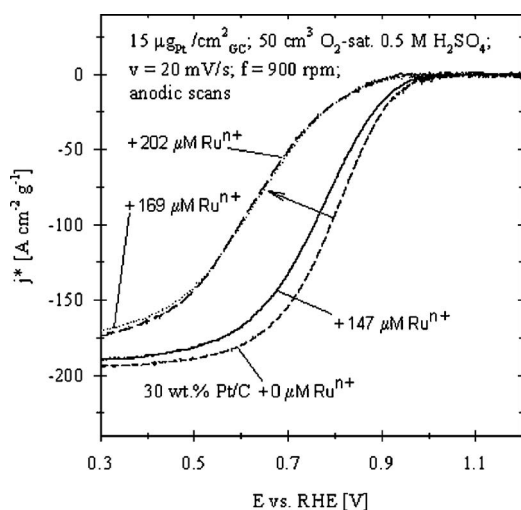
Ru deposition on various Pt surfaces is a well-investigated process for the preparation of highly active low-temperature fuel cell anode materials.¹⁵ Ru is considered as a promoter for the electro-oxidation of small organic molecules because it can provide the adsorbed oxide species (OH^-) to the removal of chemisorbed carbon monoxide from Pt at low electrode potentials ($\geq 0.24 \text{ V}$).³³ Aqueous Ru^{n+} species are found to deposit onto Pt under electrode potential control but can also do so spontaneously.³⁴ Because of the lack of analytical tools to observe Ru adatoms and adislands on macroscopically rough nanoparticle surfaces [such as scanning tunnel microscopy (STM)³⁵ or Auger electron spectroscopy (AES)³⁶ for single-crystal surfaces], the surface Ru coverage (Θ_{Ru}) can only be estimated based on the decrease of the H_{UPD} charge.³⁷ Assuming that a Ru^{3+} ion masks three Pt atoms,³⁷ and protons can adsorb on Ru similarly to Pt, we could convert the decrease in H_{UPD} charge to an estimated Ru coverage. Table I summarizes those values ($\Theta_{\text{Ru}}^{\text{est}}$) as well as shows how many equivalent Pt monolayers correspond to a given Ru^{n+} concentration if all the dissolved Ru atoms were to deposit onto the working electrode ($\Theta_{\text{Ru}}^{\text{max}}$). Our electrochemical cell

Table I. Maximum possible ($\Phi_{\text{Ru}}^{\text{max}}$) and estimated actual ($\Phi_{\text{Ru}}^{\text{est}}$) Ru coverage levels on Pt/C and the corresponding Pt mass-specific kinetic current density (j_k^*) values for ORR.

	0.5 M H ₂ SO ₄				1 M TFMSA	
c_{Ru}^{n+} ($\mu\text{mol dm}^{-3}$)	0	147	169	202	0	23
$\Theta_{\text{Ru}}^{\text{max}}$ (ML Pt)	0	2790	3210	3840	0	500
$\Theta_{\text{Ru}}^{\text{est}}$ (ML Pt)	0	0.12	0.18	0.31	0	0.14
j_k^* 0.90 V ($\text{A cm}^{-2} \text{ g}^{-1}$) 0.85 V	28.59	20.27	3.55	3.42	39.32	23.11
0.80 V	179.10	112.98	21.44	21.01	291.30	197.89

also accommodates a platinum wire auxiliary electrode with a surface area ca. one and a half times larger than that of the thin-film Pt/C working electrode (vide supra). The Pt counter electrode is also expected to pick up and release Ruⁿ⁺ from or into the solution in an unknown quantity. The above explains why solution Ruⁿ⁺ concentration data are discussed in terms of surface Ru coverage (Θ_{Ru}) values. In our experimental configuration, micromolar levels of Ruⁿ⁺ concentration in the electrolyte mean a roughly thousand-fold excess of Ru atoms in comparison to the number of Pt atoms exposed on the surface. Figure 1 manifests that such excess in Ruⁿ⁺ species is able to decrease substantially the capacity of Pt to adsorb surface oxides.

Ru contamination can impair oxygen reduction activity more severely, as is evidenced from the corresponding rotating disk electrode study. Figure 2 presents RDE polarization curves for the Pt/C thin-film electrode as recorded in oxygen-saturated 0–202 $\mu\text{mol dm}^{-3}$ Ruⁿ⁺ electrolytes at the same scan direction and rate. Taking the measured current at 0.3 V as limiting current and plotting it as a function of the square root of the rotation rate (i.e., by taking the Levich plot), a linear relationship could be obtained for all Ru concentrations. By looking at the half-wave potential values which shift toward more negative electrode potentials in Ruⁿ⁺-contaminated electrolytes (as indicated by an arrow in Fig. 2), the changes become readily apparent on the reduction waves. The negative shift is maintained throughout the entire mixed-kinetics and mass-transport regime. The detrimental effect of Ruⁿ⁺ contamination of the electrolyte on the ORR activity is evident even at the onset potential of ORR for clean Pt/C. A systematic study to understand the stability region of Ru adatoms is currently underway and will be reported later. However, unlike the observed progressive decrease in surface oxide coverage on Pt with increasing Ruⁿ⁺ contamination

**Figure 2.** Rotating disk electrode polarization curves for a thin-film 30 wt % Pt/C electrode, 0.28 cm², 15 $\mu\text{g}_{\text{Pt}} \text{cm}_{\text{GC}}^{-2}$ in O₂-saturated 0.5 mol dm⁻³ H₂SO₄ solution containing dissolved Ru species in various concentrations.

(Fig. 1), oxygen reduction seems to occur on a minimum activity level beyond a certain Ru coverage on Pt. This is demonstrated in the overlapping oxide reduction RDE curves for Ruⁿ⁺ concentrations higher than 169 $\mu\text{mol dm}^{-3}$ Ruⁿ⁺ in Fig. 2. Such a lower limit of ORR activity beyond a threshold Ruⁿ⁺ concentration is attributed to the ability of Ru adatoms to reduce molecular oxygen at sufficiently high overpotential.^{38,39}

The kinetics of oxygen reduction on Pt/C can be explicitly followed up from the measured RDE current values after correcting for the mass-transport-related contributions. The mass transport of oxygen at a pure Pt surface can be treated in a straightforward fashion because the surface is uniformly accessible to molecular oxygen at a given electrode potential. When the Pt surface is partially covered by Ru, the ORR activity becomes dependent on surface elemental composition due to the different reaction kinetics on the pure metals. Assuming that all Ru adatoms on Pt are oxidized and thereby inactive toward the adsorption of molecular oxygen at low ORR overpotentials (say at or above 0.8 V), such Pt–Ru bimetallic surfaces should perform like a pure Pt, albeit blocked by Ru to various extents,⁴⁰ unless the reaction mechanism changes (*vide infra*). Finding the electrochemical surface area for oxygen reduction at Pt–Ru electrodes however, is a rather complicated task which requires the exact knowledge of elemental composition and surface structure⁴⁰ as well as the adsorption energy of surface oxides at a given electrode potential.⁴¹ Nevertheless, the blocking mechanism exerted by Ru is exactly what is analyzed here. This is attained by the comparison of the kinetic current values, which were calculated using Eq. 1⁴²

$$i_k = \frac{i_L \times i_m}{i_L - i_m} \quad [1]$$

i_k was extracted from data corresponding to the mixed kinetics mass-transport region of the RDE polarization curve. We also mention that the current measured at 0.3 V (i_L) is a pseudo-limiting current because the exposed Ru is partially covered by surface hydroxides at that electrode potential.

In Table I, kinetic current density (j_k^*) values are summarized which were obtained for clean and Ru-contaminated Pt/C electrode in 0.5 M H₂SO₄. j_k^* was calculated from i_k using Eq. 1 after normalizing it to the mass of Pt. Oxygen reduction is found to be at least eight times more sluggish when the total number of dissolved Ru atoms is more than 3000 times higher than the number of surface Pt atoms, although the estimated Ru coverage of the Pt surface is less than 20%. This is conceived based on a comparison of the amount of Ru present in a known concentration within the volume of the electrolyte and the number of Pt atoms exposed, as determined independently from ICP-MS data and from the H_{UPD} area (from the cyclic voltammogram), respectively.

The Tafel plots in Fig. 3 do not evidence any significant changes in the mechanism of oxygen reduction in the low overpotential region (between 0.8 and 0.9 V) upon Ru contamination as observed in H₂SO₄. For Pt/C in clean electrolyte, the Tafel slope was found to be -122 mV dec^{-1} , which is quite close to those obtained for PtRu (-115 mV dec^{-1}) and upon various Ru contamination (-113 mV dec^{-1}). This hints that at low ORR overpotential, oxygen reduction seems to proceed on the platinum sites exclusively, with-

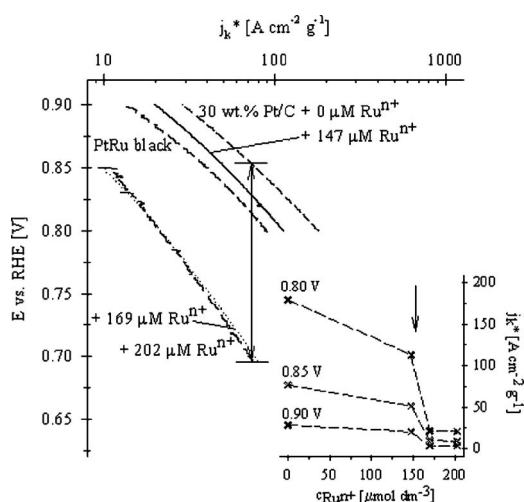


Figure 3. Mass-transport-corrected Tafel plots for oxygen reduction on a thin-film 30 wt % Pt/C, 0.28 cm², 15 µg_{Pt} cm⁻²_{GC} and PtRu black electrode in O₂-saturated 0.5 mol dm⁻³ H₂SO₄ solution containing dissolved Ru species in various concentrations. (Inset) Corresponding changes to the mass-specific kinetic current densities of oxygen reduction on Pt as a function of Ru concentration of the electrolyte at three electrode potentials.

out the influence of other electrode reaction. The dramatic drop in ORR kinetics at Pt/C as a result of Ru contamination is readily evident from the Tafel plots. In terms of overpotential, this can translate to a ca. 160 mV increase as the arrow demonstrates in Fig. 3. It is interesting to match the kinetic current values obtained for the Pt/C electrode in Ru-contaminated solutions to those measured for a PtRu electrocatalyst (Johnson & Matthey HiSpec6000) in clean electrolyte. For the PtRu electrocatalyst, we have estimated the initial Pt/Ru surface atomic composition to be 0.67 by copper underpotential deposition and subsequent removal,²¹ and also we consider here that Ru is in intimate contact with Pt in the PtRu electrocatalyst sample. Furthermore, one can presume that above 0.85 V the Ru surface atoms are completely oxidized and thus do not reduce oxygen. Correcting for a surface blocking factor of 0.43 due to an inactive higher Ru oxidation state, indeed similar kinetic current values could be calculated in the clean electrolyte for both Pt/C and PtRu at low ORR overpotentials. However, several-fold lower kinetic current values were measured for the Pt/C electrode when the Ruⁿ⁺ concentration exceeded 150 µmol dm⁻³ as compared to those obtained for the Pt/Ru electrocatalyst in clean electrolyte. The CV data showing H_{upd} -based electrochemically active surface area ascribed to Pt sites is contrary to the above observations on the basis of Ru atoms present on the surface (Table I). This is exemplified on the basis of the Cu underpotential-deposited (UPD) measurements of Ru presence on PtRu electrocatalyst, where surface coverage of 43 atom % is reported. The blocking effect of Pt/C in Ruⁿ⁺ solutions was significantly lower (Table I) when compared in electrolyte containing different Ruⁿ⁺ concentrations. This apparent discrepancy is explained by taking into account the nature of Ru accumulation on Pt in the atomic level. Namely, Ru is expected to reach higher coverage levels on Pt according to the Volmer–Weber growth mechanism, viz. by the formation of three-dimensional clusters with heights of several atomic layers.¹⁵ For such electrode structures, the transport and reduction of oxygen can be limited to the topmost Ru atoms while the underlying Pt sites might be less utilized. In other words, the electrode blocking factor is higher than what can be calculated from the ratio of Ru-covered Pt/C and the clean Pt/C H_{UPD} . (Note that the H_{upd} area does not reflect the transport of dissolved oxygen.) This simplistic model can explain why the ORR activity diminishes progressively on Pt as a function of Ruⁿ⁺ concentration and why the contaminated electrode behaves just as a pure Ru electrode beyond a threshold concentration³⁹ (see inset in

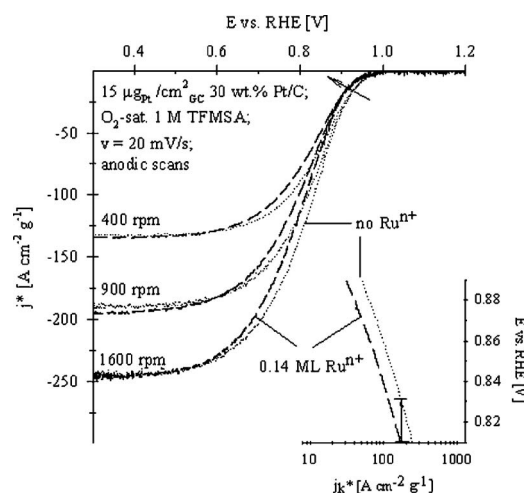


Figure 4. Oxygen reduction polarization curves in O₂-saturated 1 mol dm⁻³ TFMSA solution in the presence and absence of dissolved Ru species in concentration equivalent to a ca. 0.5 Ru monolayer on the thin-film 30 wt % Pt/C rotating disk electrode. Ru was dissolved from a PtRu electrode in conditions relevant to fuel cell anode operation (see text for further details). (Inset) Corresponding mass-transport-corrected Tafel plots.

Fig. 3). A detailed investigation of the dynamics of Ru adlayer formation as a function of electrode potential with and without the presence of dissolved oxygen is currently in progress.

The impact of Ru leaching from a PtRu PEMFC anode on the kinetics of cathodic oxygen reduction with Pt/C.— Another objective of this work is to demonstrate the effect of Ru dissolution from a PtRu electrode and its subsequent deposition onto a Pt/C cathode on the ORR activity under normal operation of PEMFCs. To mimic the perfluorinated membrane (Nafion) of PEMFCs, nonadsorbing triflic acid liquid electrolyte (1 mol dm⁻³) was used for the RDE experiments. As anode electrocatalyst, a PtRu black (Tanaka, TEC90110, 1:1 atomic ratio) was used because it exhibits a somewhat lower tendency for Ru dissolution in comparison to other samples.²¹ In order to avoid the instant leaching of Ru from PtRu, the electrode was washed in 0.5 mol dm⁻³ H₂SO₄ solution for 3 days prior to the experiments. This sacrificial electrode was then exposed to potential excursions between 0.2 and 0.4 V for 6 h with simultaneous bubbling of hydrogen gas into the triflic acid electrolyte. Earlier reports have proposed that the onset potential of Ru oxidation can be somewhere between 0.2 and 0.4 V vs RHE.^{15,33,43} Therefore, the electrode potential region to generate dissolved Ru was chosen so as to enable the formation of Ru hydroxides on the surface during hydrogen electro-oxidation (HOR).

The change in metallic composition for the PtRu sacrificial electrode was confirmed after the chronoamperometry experiment using SEM/EDAX. Interestingly, the Ru/Pt atomic ratio was decreased from the nominal 50 atom % Ru and 50 atom % Pt to 30.3 atom % Ru and 69.7 atom % Pt after washing in acid solution and was further decreased to 28.3 atom % Ru and 71.7 atom % Pt during HOR in the potential cycling experiment. This observation indicates that a large amount of Ru leaves by the dissolution of the thermodynamically unstable (oxide) phases which can largely be removed by washing. At the same time, the PtRu alloy matrix seems less prone to leach Ru. Nevertheless, all the studied commercial PtRu electrocatalysts were found to preferentially lose Ru in fuel cell conditions.²¹ Using ICP-MS, the Ruⁿ⁺ concentration of the electrolyte was measured to be 23 µmol dm⁻³, which corresponds to a 500 equivalent monolayer coverage of Ru on the 30 wt % Pt/C working electrode. From the CV H_{UPD} charges however, only ca. 14% of the initially exposed Pt atoms were estimated to be covered by Ru.

Figure 4 presents the RDE polarization curves for oxygen reduc-

tion with an E-TEK 30 wt % Pt/C-based thin-film electrode, before and after contaminating the electrolyte with Ru from the PtRu sacrificial electrode in PEMFC-mimicking conditions. The cathodic polarization wave shifts to more negative electrode potential values in the presence of Ruⁿ⁺, as indicated by the arrow in Fig. 4. The kinetic current was calculated to decrease by as much as 40% at 0.9 V (Table I). It reflects a more drastic impact than what was determined at a ca. six times larger Ruⁿ⁺ contamination in sulfuric acid solution (ca. 30%). Such a difference is speculated to originate from either the lack of anion adsorption in the triflic acid electrolyte or from the ICP-MS data evidencing no traces of dissolved Pt at this time. Note that in the case of the previous series of experiments, the electrode potential was cycled in a wide voltage window where a moderate Pt dissolution could also occur. In sulfuric acid electrolyte, the concentration of dissolved Pt was 5 μmol dm⁻³, hence its redeposition on the surface cannot also be excluded. The Tafel plots corresponding to ORR with Pt/C in clean and Ru-contaminated TFMSA electrolyte solutions reveal a ca. 20 mV penalization at moderate and low ORR overpotentials (inset in Fig. 4).

Conclusions

Ru leaching from PtRu fuel cell anode electrocatalysts can have a dramatic impact on the activity of a Pt/C oxygen-reducing cathode. Even from highly diluted Ru-containing electrolytes (micromolar concentration range), Ru deposits instantly onto Pt and remains stable on its surface in the electrode potential window of ORR. Rotating disk electrode data show that the rate of oxygen reduction can decrease by a factor of eight, which can translate to a ca. 160 mV overpotential penalization in galvanostatic conditions. Because a typically ten-times larger Pt loading in fuel cell cathodes is not expected to compensate for the suspected several orders of magnitude higher Ruⁿ⁺ concentration in the voids of the cathode electrode layer,¹⁸ the presented data stress that Ru contamination can indeed have a major role in the performance degradation of PEMFCs and especially of DMFCs. Unless highly stable PtRu anode electrocatalysts are developed, the problem of Ru crossover and contamination at the cathode should be addressed by either novel fuel cell designs such as the laminar-flow fuel cells^{44,45} where crossover is omitted, by less Ru-permeable membranes, or by more Ru-tolerant ORR electrocatalysts in PEMFCs.

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