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The application of scanning electrochemical microscopy to the discovery of Pd–W electrocatalysts for the oxygen reduction reaction that demonstrate high activity, stability, and methanol tolerance

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Abstract An array of Pd–W alloys was fabricated, and the electrocatalytic activity of the alloys for the oxygen reduction reaction (ORR) in acidic media was screened by scanning electrochemical microscopy. The $Pd_{0.7}W_{0.3}$ showed the highest activity for the ORR, close to that for $Pd_{0.8}Co_{0.2}$ and Pt. A Pd–W electrocatalyst loaded on carbon black was formed by the $NaBH_4$-reduction method, exhibiting high activity and stability, suggesting that it is a good candidate for the proton exchange membrane fuel cell cathode.

Keywords Oxygen reduction reaction (ORR) · Scanning electrochemical microscopy (SECM) · Pd–W alloy electrocatalyst · Fuel cells · Combinatorial screening method

Introduction

One of the key issues to lower the cost and improve the performance of proton exchange membrane fuel cells (PEMFCs) is the search for better and less-expensive electrocatalysts for the cathodic reaction, the oxygen reduction reaction (ORR), in acidic media (Eq. 1.)

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad (1)$$

For more than a century, the reference catalyst for this reaction in 0.5 M H_2SO_4 has been platinum. Although other alternatives such as metal sulfides [1, 2], metal oxides [3], selenides [4], enzymes [5], and transition metal complexes

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[6, 7] have been studied, most of the PEMFC cathodes are still Pt-based materials [8], a metal that is expensive and not abundant. Thus, further improvement will require the development of ORR catalysts that are more active and based on abundant materials. Another consideration is the tolerance of the cathode material to a reactant that crosses over from the anode, such as methanol in the direct methanol fuel cell, or to a contaminant in the air feed.

In the discovery of new multimetallic materials, rapid methods of synthesis and screening are useful as the development of guidelines for predicting active and stable ORR materials. Our group has used a method based on scanning electrochemical microscopy (SECM) to screen electrocatalysts [9, 10] and proposed guidelines for the design of improved bimetallic (and related) electrocatalysts for the ORR in acidic media [11, 12]. These thermodynamic guidelines focused on the metal oxide route to oxygen reduction (i.e., the direct four-electron route) and were later investigated by DFT calculations [13]. This approach involves closely pairing a good oxygen-bond cleaving metal (e.g., Co) for first splitting of the O–O bond to form adsorbed oxygen, with a good metal (e.g., Pd) for efficient reduction of adsorbed oxygen atoms to water at a high potential. Based on the guidelines and the screening technique, a series of palladium alloys for the electrocatalysts of ORR have been studied, such as Pd–Co [10, 11], Pd–Au–Co [11, 12], Pd–V [13], Pd–Ti [12, 14], and Pd–Co–Mo [15].

Here, we focus on Pd–W catalysts. Tungsten is abundant and widely used in industrial applications, and the cost of Pd–W catalysts is about one sixth of the Pt-based catalysts. W is also stable and environmentally friendly. After we had started this research, a paper by Goddard and his coworkers [16] appeared that made the prediction that Pd_3W would be a prospective electrocatalyst for ORR. Pd_3W was seen as a particularly

promising catalyst since it is known experimentally to form an ordered alloy and was found to have a desirable d-band center. They also examined the critical energy barriers for various steps of the ORR with Pd_3W and compared them to the analogous barriers for Pt, Pt_3Co, and Pd. These results suggest that Pd_3W will exhibit ORR properties dramatically improved over pure Pd and close to that of pure Pt. The work presented here demonstrates that Pd–W alloys indeed show good activity for the ORR.

Experimental section

General

Glassy carbon (GC) plates (1 mm thick, 50×50 mm^2) were purchased from Alfa Aesar (Ward Hill, MA). Prior to use, the GC plates were cut into small squares (1 mm thick, 15×15 mm^2). $(NH_4)_2PdCl_4$ (Aldrich, Milwaukee, WI), $Na_2WO_4(H_2O)_2$ (Acros Organics, Geel, Belgium), and glycerol (Alfa Aesar, Ward Hill, MA) were of analytical grade, and sulfuric acid (98 %, Fisher Scientific, Pittsburgh, PA) was trace metal grade. All chemicals were used as received. Reagent solutions were prepared using Milli-Q water (Millipore Co., Bedford, MA). Electrochemical experiments were carried out using an SECM (CHI 900B, CH Instruments, Austin, TX) with a gold wire as the counter electrode. A homemade reversible hydrogen electrode (RHE) was used as the reference electrode. Before each experiment, a Pt wire (0.5 mm diameter) was assembled in a glass tube with a frit at its terminal and filled with 0.5 M sulfuric acid solution. By applying a negative potential (−2.5 V vs. Ag/AgCl) to the Pt wire, hydrogen bubbles were generated and maintained contact with the Pt wire. This arrangement produced an electrode that was close to that of a standard hydrogen electrode. The potential of our RHE is stable for more than 30 h, and all potentials in the text are referenced to it, except the measurements for long-time stability of electrocatalytic activity (continuously measured for several days). During the measurement of stability of the catalyst activity over a long duration, the reference electrode was Ag/AgCl with a K_2SO_4 salt bridge to avoid transfer of Cl$^-$ into the 0.5 M sulfuric acid, and a gold wire was used as the counter electrode. All electrochemical experiments were carried out at room temperature (~25 °C).

Local compositional analysis of the Pd–W alloy on the array was carried out using energy dispersive spectroscopic (EDS) analysis with a LEO 1530 scanning electron microscope (SEM) equipped with an IXRF EDS system. X-ray diffraction (XRD) measurements of carbon-loaded catalysts were carried out using a Bruker-Norius D8 advanced diffractometer. All XRD measurements were carried out in the ($\theta/2\theta$) mode.

Study of Pd–W alloys

Preparation of Pd–W alloy arrays

Catalyst spots consisting of mixtures of Pd and W arranged in high-density arrays were prepared on GC by reduction of metal salt precursors by the method described in previous papers [11]. In brief, solutions containing 0.3 M metal ions were prepared by dissolving the metal salt in a water/glycerol (3:1) mixed solvent. Binary arrays of spots containing mixtures of these solutions were deposited on GC plates using a piezo-based microarray dispenser (CHI 1550, CH Instruments, Austin, TX). The distance between each spot was 500 μm. After agitating to thoroughly mix the components, the array was dried under Ar at 150 °C overnight and then reduced with H_2 at 350 °C for 1 h in a tube furnace. The different compositions are indicated as Pd_xW_y or x/y Pd/W, where x/y represents the atomic ratio of Pd to W from the amounts of precursor solutions used.

Screening the Pd–W arrays with SECM

The images of the array were acquired using the tip generation-substrate collection (TG-SC) mode of SECM. The electrolyte was an aqueous 0.5 M sulfuric acid and was Ar purged at least 15 min before imaging to remove the oxygen in the solutions. An Ar blanket was kept above the electrolyte throughout the imaging process. A gold ultramicroelectrode (UME) tip (diameter=25 μm) served as an oxygen generator. The use of gold as a tip material and a counter electrode also eliminates the possibility of contamination of the electrocatalysts by small amounts of dissolved Pt. A constant oxidative current (200 nA) was applied to the gold UME tip by an external 9-V battery connected to the gold counter electrode. The tip was scanned in the XY plane over the Pd–W array substrate at a constant tip–substrate distance of 40 μm.

Study on carbon-supported catalysts

Preparation of carbon-supported electrocatalysts

After SECM screening, carbon-supported Pd–W catalysts with the appropriate alloy composition and a metal loading of 20 wt% were prepared by the sodium borohydride method. The required amounts of metal compounds (($NH_4)_2PdCl_4$ and $Na_2WO_4(H_2O)_2$) were added to a constantly stirred carbon slurry prepared by suspending 160 mg of Vulcan XC-72R carbon black in 100 mL of deionized water. This suspension was agitated in an ultrasonic water bath at room temperature for 30 min. A few drops of 1 M NaOH solution were then added to this mixture to raise the pH to 10 before adding 15 mL of 5 wt% sodium

borohydride solution. The resulting reaction mixture was stirred for 15 min, allowed to stand overnight, and filtered. The carbon-supported catalysts were thoroughly washed with deionized water and dried in air. A final thermal treatment at 350 °C in Ar for 1 h was applied to the catalysts.

Carbon-supported $Pd_{0.8}Co_{0.2}$ alloy and carbon-supported Pd catalyst with the metal loading of 20 % were also prepared by the same method and served as the references of the carbon-supported Pd–W catalyst.

Rotating disk electrode preparation

An ink of carbon-supported Pd–W alloy electrocatalyst powder was made by dispersing 10 mg of the powder in a mixture of 0.5 mL water and 0.5 mL ethanol, and agitated ultrasonically for 15 min. Three microliters of this ink was dropped on a 3-mm-diameter GC rotating disk electrode (RDE) (Pine Instruments, Grove City, PA) which was pre-polished with a 0.05-μm-diameter alumina. The deposited ink was allowed to dry in air and was then covered by 1.5 μL of Nafion solution (5 %, Aldrich, Milwaukee, WI) and dried at room temperature. The metal loading was 3 μg cm^{-2}.

RDE experiments were performed using a standard three-electrode cell configuration employing a gold wire counter electrode and a RHE reference electrode. A CHI model 900b SECM (CH Instruments, Austin, TX) was employed for electrochemical measurements; the RDE was rotated at 2000 rpm using a Pine Instruments Analytical Rotator Model ASR2 (Pine Instruments, Grove City, PA). Rotating disk polarization curves were recorded in O_2-saturated 0.5 M H_2SO_4 with a constant flow of O_2 (1 am) through the electrolyte at a potential sweep rate of 10 mV s^{-1}.

GC electrode used for long-term (several days) stability test

A model 173 potentiostat/galvanostat (Priceton Applied Research, Oak Ridge, TN) was used to measure the stability in long-term work with a three-electrode system. This equipment provides analog signals of electrochemical measurement. The equipment is very stable and suitable for the long term. The current data were recorded at certain time intervals. An analog-to-digital converter controlled by a Lab-View program (National Instruments, Austin, TX) was used to acquire the current data as a function of time. Carbon-supported Pd–W electrocatalyst was loaded to a GC electrode by the method similar to that used to prepare the RDE and was used as the working electrode. The ink (34 μL) formerly used in RDE preparation was agitated ultrasonically for 15 min and deposited dropwise 2 μL×17 times onto a GC electrode (3 mm diameter). The deposited ink was allowed to dry under air before every next ink deposition. After the required amount of ink was deposited and dried on the GC electrode, it was then covered by 2 μL of a 5 % Nafion solution. The metal loading was 34 μg/cm^2. Though the metal loading in long-term stability is 10 times more than that in RDE preparation, we cannot cover 10 times of Nafion solution on it. If too much Nafion solution is put on the dried ink on the GC electrode, the Nafion solution will cover not only the catalysts but also the Teflon of the GC electrode. Two microliters of 5 % Nafion solution is enough for the immobilization of the catalysts in our experiments. The electrolyte was a 0.5 M sulfuric acid solution under continuous bubbling of O_2 (1 atm). The potential applied to the GC electrode is 0.35 V vs. Ag/AgCl, a salt bridge with K_2SO_4 as electrolyte and a gold wire was used as the counter electrode. Potential and O_2 were applied continuously during the long-term stability test. With our equipment, we can observe the performance of electrocatalysts under ORR condition for days, months, even 1 year (if needed). In some papers, stability tests were performed by cycling the potential for limited cycles in a short time, such as 100 cycles or 1,000 cycles. However, the cyclic voltammetry method is rarely reportedly used in the test for days or even months because the number of cycles cannot be set to infinity.

Results and discussion

Screening Pd–W alloys on a GC plate

SECM images of ORR activity of a Pd–W array at 0.4 and 0.7 V vs. RHE were obtained using the TG-SC mode of SECM (Fig. 1). A Pd–W array was placed in a deaerated 0.5 M sulfuric acid solution, while an oxygen generator tip was scanned above the array. The tip-generated oxygen was reduced at the Pd–W array, and the ORR activity of each electrocatalyst spot was recorded in terms of their current responses. The ORR SECM activity maps of Pd–W spots presented in Fig. 1 detect alloys of Pd–W with 10–40 at.% W that could efficiently catalyze the electroreduction of oxygen at overpotentials (η) where no activity is observed for pure Pd, and $Pd_{0.7}W_{0.3}$ (70 at.% Pd in the precursor solution) showed the highest ORR activities. Positions of the spots were confirmed with the feedback mode of SECM to avoid false identification of a given spot. To make sure of the position of each spot, the array was also imaged by a feedback mode with the same probe travel parameters. The feedback mode is a useful method to image surface morphology of the substrate. This measurement involved the shielding mode, where both the tip and the substrate spot reduced dissolved O_2 in solution. When the spot is directly below the tip, the reduction of O_2 at the tip decreases the diffusion of oxygen to the substrate, i.e., the tip competes
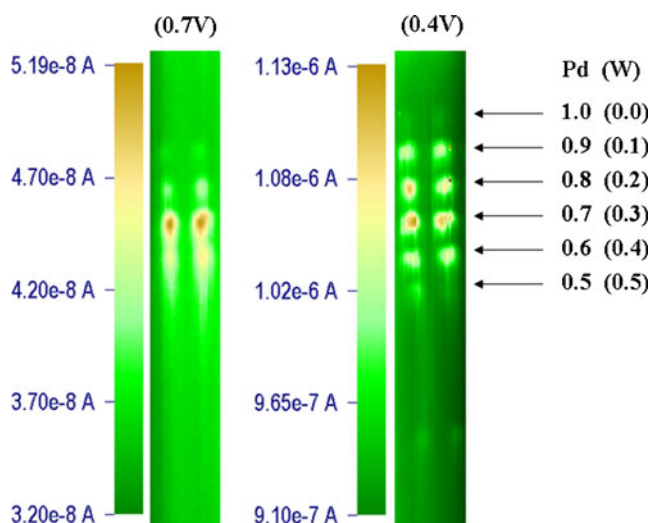
Fig. 1 SECM TG-SG images of ORR activity measured on Pd–W binary arrays in 0.5 M H_2SO_4. Only the forward images scanning from the top to the bottom (long travel direction) and from the left to the right are shown. Tip–substrate distance=40 μm, tip current=−200 nA. SECM probe travel parameters normally used: Incr. Dist=25 μm, Incr. time=0.1 s. Better resolutions and less translation error of images can be achieved at slower raster speed of the tip. The raster speed of the tip was a compromise for the scan area and the time desired for acquiring an image frame. Substrate potential E_S=0.7 and 0.4 V vs. RHE, respectively. The atomic ratio of metals in the dispensed solutions is also listed in the figure

with or shields the substrate, so the current decreases when the tip passes over the spots. The feedback image was used to compare with the TG-SC SECM image to make sure of the position of each spot.

The $Pd_{0.7}W_{0.3}$ spot obtained by thermal reduction with H_2 at 350 °C was investigated by SEM with EDS analysis. Figure 2a shows the SEM micrographs. While a SEM is useful for observing the morphology of a sample, the EDS analyses commonly used with it can only provide some semiquantitative elemental composition data [17]. The composition obtained by EDS analysis of the synthesized alloy in the nominal alloy of $Pd_{0.7}W_{0.3}$ (70 at.% Pd in the precursor solution) contains ~80 at.% Pd. Similar differences were also found in our early paper for the Pd–Co system [10].

After SECM imaging, the SEM topography of the $Pd_{0.7}W_{0.3}$ sample appeared more porous (Fig. 2b) compared with that before SECM imaging. EDS analysis showed that the atomic composition of Pd in the nominal $Pd_{0.7}W_{0.3}$ increased to ~90 % Pd after SECM imaging, which indicated that some W dealloyed from the alloy. Since a highly active ORR Pt-alloy catalyst can be made by selective dissolution (dealloying) of a nonprecious metal from the Pt-alloy surface [18], this factor could also contribute to the activity enhancement in our Pd-based catalysts.

Carbon-loaded Pd–W catalysts

The XRD curve of 20 % loaded $Pd_{0.7}W_{0.3}$ catalyst on carbon before electrochemical experiments is shown in Fig. 3. The main peaks are all contributed from elemental Pd with no peaks of W, which indicates that the W atoms have dispersed into Pd and there are no W crystals in the alloy. The shift to higher angle means a smaller lattice spacing, which also indicates the formation of a Pd–W alloy.

After identification of candidate electrocatalysts using the screening method, RDE technique was used to determine the electrocatalytic activity in configurations that approach more closely those encountered in fuel cell devices. To do this, i-E curves for 70:30 Pd/W supported on Vulcan carbon were obtained (Fig. 4). This figure also shows the response obtained for pure Pd as well as $Pd_{0.8}Co_{0.2}$, as reference ORR electrocatalysts. We have previously reported that $Pd_{0.8}Co_{0.2}$ was a very good nonplatinum catalyst for ORR. Clearly, by combining Pd with W, the overpotential for the ORR at Pd decreases substantially. This is in good agreement
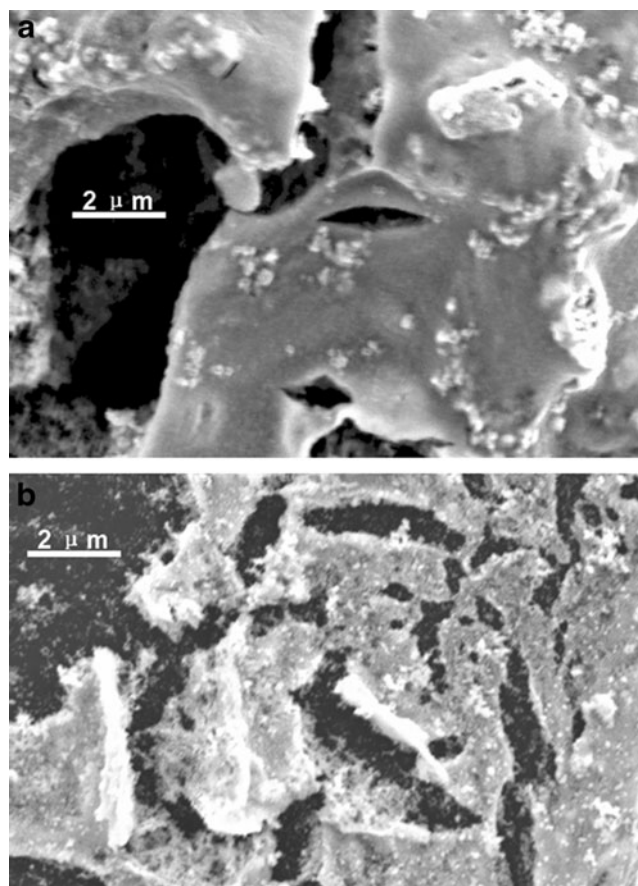

Fig. 2 SEM micrographs of $Pd_{0.7}W_{0.3}$ spot before SECM measurement (**a**) and after SECM measurement (**b**)
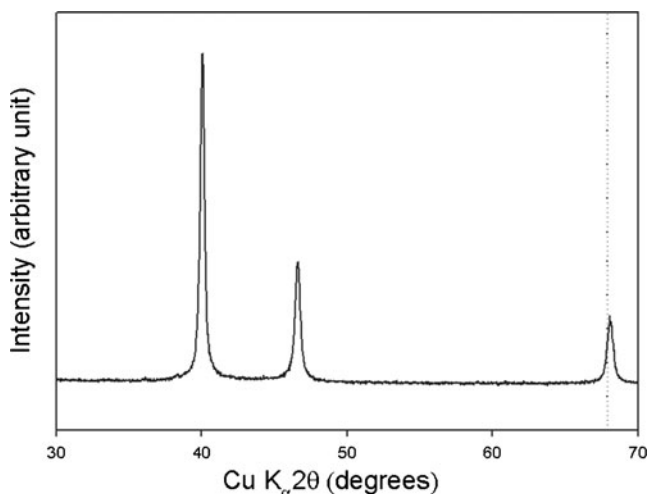
Fig. 3 X-ray diffraction pattern of the carbon-supported Pd–W (Pd/W=70:30 at.%) catalyst after heat treatment in Ar at 350 °C. Carbon-supported Pd–W catalyst was prepared by $NaBH_4$ reduction method before heating. The *dotted line* refers to the standard 2θ value corresponding to the (220) reflection of Pd metal

Fig. 5 ORR current density of carbon-supported $Pd_{0.7}W_{0.3}$ catalyst-loaded GC electrode (34 μg cm^{-2}) in 0.5 M H_2SO_4 saturated with continuous O_2 bubbling (1 atm). Potential and O_2 were applied continuously during the experiment. Potential, 0.35 V vs. Ag/AgCl. The instantaneous current was continuously monitored and recorded (e.g., 10 s per data point) to eliminate the fluctuation (caused by bubbles or other interferences); each point shown is the averaged value of about 1,000 data points

with the SECM screening observations. Thus, $Pd_{0.7}W_{0.3}$ is a good oxygen cathode material when the metals are supported on carbon, with a performance that can compete with $Pd_{0.8}Co_{0.2}$. Modifications of the preparation technique may yield better electrocatalytic materials, e.g., with decreased particle size, and its performance.

To test the stability of carbon-loaded Pd–W catalysts, a model 173 potentiostat/galvanostat (Priceton Applied Research, Oak Ridge, TN) interfaced with a LabView data acquisition system was used to apply a potential of 0.35 V vs. Ag/AgCl (~0.55 V vs. RHE) to a catalyst-loaded GC
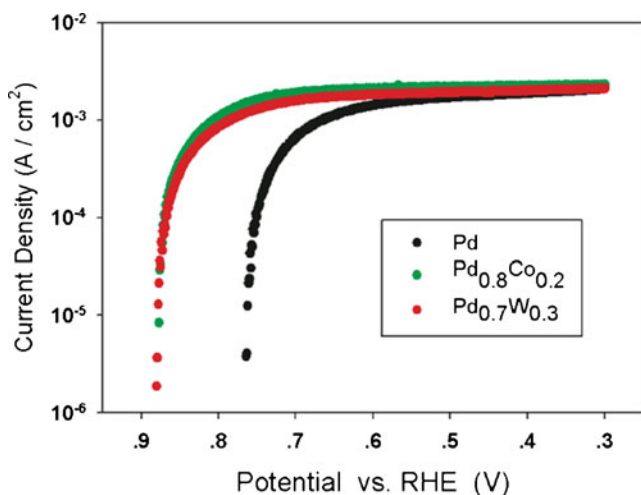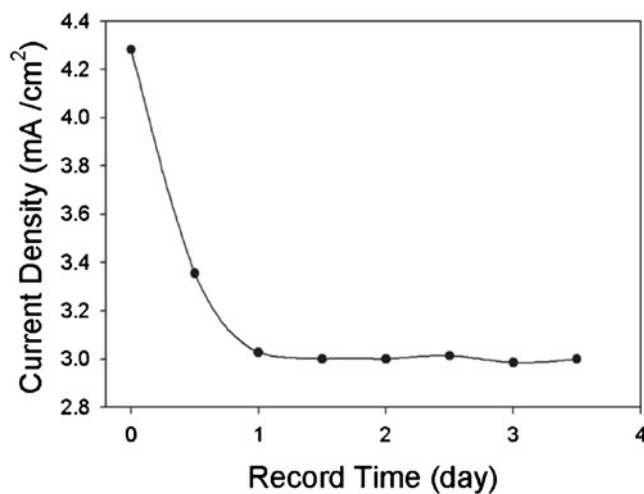
electrode in 0.5 M H_2SO_4 for more than 3 days (Fig. 5), accompanied with continuous O_2 bubbling. The Pd–W catalyst showed a drop of about 30 % over the first day and then remained stable for the remaining time of the experiment.

Generally, Pd-based catalysts have a better tolerance for methanol than Pt [15, 19], where the ORR reaction rate is greatly reduced by methanol at the cathode. CV curves of the ORR of $Pd_{0.7}W_{0.3}$ in 0.5 M H_2SO_4 with or without
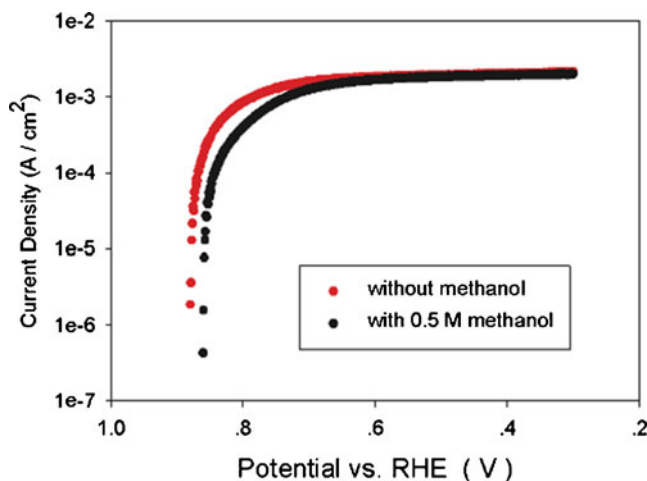

Fig. 4 Polarization curves of carbon black-supported Pd–W with 30 at.% W (*red line*), Pd (*black line*), and Pd–Co with 20 at.% Co (*green line*) rotating disk electrode in O_2-saturated (1 atm) 0.5 M H_2SO_4. Scan rate, 10 mV s^{-1}. Rotation rate, 2,000 rpm. Metal loading, 3 μg/cm^2

Fig. 6 Polarization curves of carbon black-supported Pd–W with 30 at.% W on a rotating disk electrode in O_2-saturated (1 atm) 0.5 M H_2SO_4 (*red line*) and in the mixture of 0.5 M H_2SO_4 and 0.5 M methanol (*black line*). Scan rate, 10 mV s^{-1}. Rotation rate, 2,000 rpm. Metal loading, 3 μg/cm^2. For data on the effect of MeOH on the ORR on Pt, see references [11, 12, 15, 19]

0.5 M methanol are similar, showing that the $Pd_{0.7}W_{0.3}$ catalyst has a good tolerance to methanol (Fig. 6).

Conclusion

Based on previously reported guidelines for the design of improved electrocatalysts for the ORR in acidic media, Pd–W bimetallic systems have been developed and their electrocatalytic activity probed. Pd–W bimetallic arrays were deposited on a GC substrate by the reduction of metal salt precursors, and electrocatalytic activities were determined using a rapid SECM screening technique. Pd–W bimetallic combinations exhibited enhanced electrocatalytic activity when compared with the pure, constituent metals. In particular, Pd–W (10 to 40 at.% W) exhibited remarkably higher activity for the ORR upon screening than Pd, and $Pd_{0.7}W_{0.3}$ showed the highest activity. RDE measurements were used to verify the high activity of $Pd_{0.7}W_{0.3}$ when the electrocatalyst was supported on Vulcan carbon, i.e., in a configuration closer to a fuel cell. Finally, the $Pd_{0.7}W_{0.3}$ electrocatalyst was compared with reported $Pd_{0.8}Co_{0.2}$ and Pd catalysts. We found that the Pd–W bimetallic electrocatalyst exhibited an activity remarkably similar to that of $Pd_{0.8}Co_{0.2}$ electrocatalyst and much higher than pure Pd.

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