ORR Kinetics of Pt based alloys using a RDE and a correlation with their Fuel Cell performance

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ABSTRACT

The effect of water on the electrocatalytic activity of Pt based transition metal alloy for oxygen reduction reaction was investigated using a rotating disk electrode (RDE). 1M and 6M Trifluromethane sulfonic acid (TFMSA) was used as the electrolyte to control the amount of water. The diffusion coefficient and solubility of oxygen in this electrolyte was measured using a micro disk electrode. The ORR activity of a polycrystalline Pt was compared with that of a 20wt.%Pt/C and a 20wt.%PtCo/C and the results indicate that although in 1M TFMSA PtCo/C shows enhanced ORR activity than the Pt plug and Pt/C in 6M TFMSA it shows lower or no change in the ORR activity. The polycrystalline Pt plug shows two tafel slopes of 59 and 112 mV/dec. in the low overpotential region (l.o.r) and the high overpotential region (h.o.r) respectively whereas Pt/C and PtCo/C shows only a single tafel slope of 120 and 140mV/dec respectively. This shows that the surface Pt is clean for a larger potential range which indicates that the surface poisoning due to Pt-OH formation is diminished and hence the enhanced ORR activity.

INTRODUCTION

Over potential loses at the cathode of a fuel cell for oxygen reduction reaction is one of the main sources of loses of power. ORR, because of its complex kinetics and the need for better electrocatalysts, continues to be in the focus. The rate determining step for ORR on an electrode surface is something that has been debated for years. There have been a few mechanisms that have been proposed so far. Yeager et al. [1,2] have suggested three possible models including a dual site model for a four electron direct oxygen reduction and a single site pathway through a peroxide intermediate. The effect of different electrolytes for ORR has been extensively investigated by [3-6]. The focus during that period was to investigate a better medium compared to phosphoric acid which has detrimental effects due to strong adsorption of the phosphate anion on Pt and reduces its ORR activity. TFMSA was used as an additive in phosphoric acid fuel cells to increase oxygen solubility and thereby increasing ORR kinetics. Extensive work done by Arvia et al. [7, 8] using TFMSA on Pt single crystals found that the ORR kinetics depended on the crystal structure of Pt.
Many Pt-based transition metal alloys have been suggested for use as a cathode catalyst \[^{9-14}\]. These Pt-based alloys perform much better than Pt in a completely hydrated PEM fuel cell. Changes in short range atomic order, particle size, Pt d-band vacancy, Pt skin effects and Pt-OH inhibition are some of the reasons attributed for the enhanced performance by these alloys \[^{15-18}\]. Inhibition of the formation of Pt-OH at potentials above 800mV thereby leaving more number of Pt sites available for oxygen reduction reaction in these alloys is widely accepted by electrochemists. The Pt-OH formation has been proposed to be derived from the interaction of water with Pt and not from the reaction of O\(_2\). A number of indirect evidence has been shown to this effect \[^{19}\]. Watanabe et al. \[^{20}\] have shown that O\(_2\) adsorption increases with Pt 5d-band vacancy. Mukerjee et al. \[^{9-13}\] used in-situ EXAFS to study various Pt transition metal alloys and have shown that the ORR activity decreases with increased Pt d-band vacancy. Increase in d-band vacancy in Pt makes it difficult to loose an electron for oxygen reduction. Hence PtCr which has the lowest d-band vacancy and minimal formation of Pt-OH does not impede the charge transfer process for oxygen reduction significantly and shows enhanced performance compared to other alloys. Another reason attributed to the formation of Pt-OH is the property of the alloying metal that may lie below the surface of the Pt skin but yet have surface accessibility which may have a higher affinity for water than Pt \[^{22}\].

Whether these alloys perform the same way under higher temperature and low humidity conditions is unknown. The activity of water in TFMSA decreases with increase in concentration as a result of protonation of most of the water molecules by TFMSA \[^{9}\]. As a result, the formation of Pt-OH is minimized. If the inhibition of Pt-OH is the reason why these alloys perform better then the ORR activity of pure Pt should improve with decreasing water content since its affinity for water is lower than the transition metals used as alloying metals. The investigation of different alloys in varying contents of water attempted in this work is aimed towards a better understanding of the role of the alloying metal.

### EXPERIMENTAL

For the measurements described in this study we used a commercially available 20 wt.% Pt/C (E-TEK Inc.) and a 20 wt.% PtCo/C (Johnson-Mathey). Measurements were also made on a polycrystalline Pt disk obtained from Pine Instruments as a control experiment. All electrochemical measurements were made using an interchangeable ring-disk electrode setup from (Pine Instruments) connected to either an Autolab (Ecochemie Inc.) or Voltalab (Radiometer Analytical) potentiostat and at room temperature. The potentials were measured with respect to a reversible hydrogen electrode (RHE) made from the same solution as the electrolyte in the experiment.

Trifluoromethane sulfonic acid (TFMSA) was obtained from 3M Co. and doubly distilled under vacuum below 60° C and converted into its monohydrate. A detailed description of the distillation process is given in \[^{23}\]. The monohydrate of TFMSA was then diluted further to form the required concentrations. The diffusion coefficient of oxygen and its solubility in these solutions were determined by a transient method using a Pt microelectrode.

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Electrodes were prepared as follows. Suspensions of 1mg catalyst per ml in iso-propanol were obtained by ultrasonication for 30 min. 20 µl of 5wt.% Nafion® was added prior to mixing to act as a binder. Glassy carbon disk electrodes (0.283 cm²) were used as the substrate for the supported catalysts and were polished to a mirror finish using 0.05µm alumina (Buehler). A 20 µl aliquot of the suspension was then loaded onto the glassy carbon to give a Pt loading of 14µg/cm² (geometric) and was allowed to dry before introducing it into the electrolyte.

After preparation, the electrodes were immersed in oxygen-free electrolyte solutions and cycled several times between 0 and 1.2 V at 100mV/sec and then cycled further at 5mV/sec. For oxygen reduction studies the electrode was immersed in oxygen saturated electrolyte and conditioned initially between 0.2 and 1.2 V at 1000 rotations per minute. For ORR experiments the electrode was scanned between 0.2 and 1.2 V at 25mV/sec for 10 cycles at each rotation and the last 3 scans at each rotation rate were used for data analysis. The rotation rates were limited between 400 rpm and 1600 rpm because of viscosity issues in high concentrations of TFMSA.

RESULTS AND DISCUSSION

The validity of the clean assembly of the rotating disk electrode was verified by the cyclic voltammetry recorded on the 20%Pt/C and 20%PtCo/C in nitrogen saturated 1M TFMSA (fig. 1). Comparison of the voltammetry also shows the difference in the formation of Pt-OH at 0.8 V vs. RHE. The PtCo/C shows the formation of the hydroxide to a lesser extent thus consistent to the previous results. Fig. 2 shows the potential vs. current curves at different rotations (625, 900, 1225 rpm) for the Pt plug in 1M TFMSA and 6M TFMSA at room temperature. The diffusion limited currents in 6M TFMSA is lower than that in 1M TFMSA because of differences in diffusion coefficient and concentration of oxygen in these solutions. It can be seen from the plot that the rate at which the current drops in 6M TFMSA is slower than that in 1M TFMSA even though the limiting current density is higher. Comparison of the same for PtCo in 1M TFMSA and 6M TFMSA (fig. 3) shows the same trend but to a lesser extent, thus raising the doubt if Pt-transition metal alloy catalysts would perform much better than Pt under low water content. The diffusion coefficient of oxygen and its concentration in these solutions are given in table 1 along with the values found in literature for 1M TFMSA.

A koutecky-levich plot of I/I versus ω⁻¹/² (fig. 4 and 5) for Pt/C and PtCo/C in 6M TFMSA at various potentials yields straight lines with intercepts corresponding to the kinetic currents I_k showing that the reaction order for oxygen reduction does not change over these potential regions in high concentrated acid solutions. Since the amount of Nafion® in the catalyst alcohol suspension is only 20µl (which corresponds to a weight ratio of 1:20 Nafion® to Pt loading on the glassy carbon electrodes), it was decided to neglect its effect on the limiting currents. Fig. 6 shows a plot of current vs. potential of Pt/C and PtCo/C in 1M TFMSA at 1225 rpm. It is observed that PtCo shows a better performance than Pt plug and Pt/C. The calculated I_k at 0.9V is much higher for PtCo/C than Pt/C and the Pt plug (table 2). At 0.8V, PtCo continues to show better I_k than the Pt plug but is almost close to Pt/C. The anomalous behavior of high surface area Pt/C evident from the single Tafel slope of 120mV/dec in 1M TFMSA is not very well...
understood and provides a scope for further investigation. The comparison of Pt/C and PtCo/C in 6M TFMSA at 1225 rpm (fig. 7) shows that Pt/C is a better catalyst than PtCo/C. The kinetic current density of Pt/C at 0.8 V (0.67 mA/cm²) is much higher than that of PtCo/C (0.458 mA/cm²). However, the exchange current density of Pt/C and PtCo/C are very close (table 1). Mass corrected Tafel slope (fig. 8) of Pt plug in 1M TFMSA shows 59 mV/dec and 112 mV/dec. at the low overpotential region (l.o.r) and high overpotential region (h.o.r) respectively. In 6M TFMSA, it shows a single Tafel slope of 110 mV/dec consistent with a clean platinum surface. This shows that in 6M TFMSA, where the water content is low and hence its activity, Pt has a cleaner surface even in the low over potential region. This would mean that the surface poisoning due to the formation of a hydroxide species and adsorption of anions and other species on to the Pt surface is minimized. Since the anion adsorption effect due to TFMSA is insignificant the single Tafel slope would mean that the surface poisoning due to Pt-OH is minimized. Figures 9 and 10 show a single Tafel slope of ~140 mV/dec for PtCo in both 1M and 6M TFMSA. Unlike Pt plug and Pt/C, the kinetic currents at 0.9 V and 0.8 V for PtCo/C do not show an enhancement in 6M TFMSA over that in 1M TFMSA. Table 2 summarizes the kinetic currents for the three electrocatalysts in 1M and 6M TFMSA at 0.9 V and 0.8 V and the respective Tafel slopes and exchange current density. Comparing the kinetics of Pt/C and PtCo/C in 6M TFMSA where the activity of water is low, Pt/C indicates a higher kinetic current than PtCo/C. This further confirms the explanation for Pt-OH formation based on water binding energy. Even though PtCo shows enhanced performance in the presence of excess of water, it fails to show any improvement under low water content.

CONCLUSIONS

1. Kinetic currents (i_k) values of Pt plug compared at1M and 6M TFMSA shows considerable improvement which reflects on the effect of water content on the kinetics for oxygen reduction reaction.
2. The same trend is seen in Pt/C although to a lesser extent. However the shift is much smaller in the case of PtCo/C which is consistent with the shift in the formation of Pt-OH.
3. Tafel slopes of Pt plug show a classic 60/120 mV/decade at the l.o.r and h.o.r in 1M TFMSA and a single slope of 120 mV/decade in 6M TFMSA which is consistent with the shift in water activation. Whereas PtCo/C shows 140 mV/decade in both 1M and 6M TFMSA.
4. The kinetic currents measured in a 1M TFMSA shows that PtCo/C is significantly better than Pt plug and to a lesser extent with Pt/C. 6M TFMSA data indicates that Pt/C is better than PtCo/C in terms of kinetic currents under low water activity conditions.

The data presented above illustrate the possibility of another step involved in the rate determining step for ORR involving Pt-transitional metal alloys. The interaction between water and the alloying metal has to be investigated in detail. If the reaction mechanism did not involve an interaction between water and Co then by alloying Pt, we are not increasing the activity for ORR. On the other hand, if there is an interaction between water and Co in the rate determining step, then it now becomes important to understand
the behavior of different alloys at low water content as a function of the alloying metal property and to tie in the fundamental properties of the alloy metal surface to the true kinetics of ORR. The possibility of peroxides as an intermediate cannot be ruled out in these acid electrolytes and needs further investigation.

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| Electrolyte | $C \times 10^6$ (mol/cm³) | $D \times 10^6$ (cm²/s) | $C_{[Ref.]} \times 10^6$ | $D_{[Ref.]} \times 10^6$ |
|-------------|--------------------------|-------------------------|--------------------------|--------------------------|
| 1M TFMSA    | 0.63                     | 9.67                    | [24]1.6                  | [24]9.5                  |
| 6M TFMSA    | 6.88                     | 0.29                    | *                        | *                        |

* Not available

Table 1. The concentration and diffusion coefficient of oxygen in 1M and 6M TFMSA at room temperature.

| Electrolyte | $i_k$ 0.9V mA/cm² | $i_k$ 0.8V mA/cm² | $i_0$ mA/cm² | Tafel slope mV/dec |
|-------------|-------------------|-------------------|--------------|-------------------|
| Pt plug     |                   |                   |              |                   |
| 1M          | 6.3 $\times$ 10⁻³ | 0.076             | 0.056 $\times$ 10⁻⁶ | 59/112            |
| 6M          | 0.014             | 0.114             | 2.6 $\times$ 10⁻⁶ | 110               |
| Pt/C        |                   |                   |              |                   |
| 1M          | 0.057             | 0.426             | 2.56         | 120"              |
| 6M          | 0.122             | 0.67              | 3.65         | 123               |
| PtCo/C      |                   |                   |              |                   |
| 1M          | 0.106             | 0.413             | 3.39         | 140               |
| 6M          | 0.101             | 0.458             | 3.35         | 142               |

Table 2. Kinetic data for Pt, 20wt.%Pt/C and 20wt.%PtCo/C in 1M and 6M TFMSA.
Fig. 1. Cyclic voltammetry of Pt and PtCo rotating disk electrodes in 1M TFMSA. Pt loading of 14μg/cm²; Pt (-----); PtCo (— — ).
Fig 2. Disk currents obtained on Pt during ORR cathodic sweep using rotating disk electrodes in 1M and 6M TFMSA. Pt loading of 14μg/cm².

Fig 3. Disk currents obtained on PtCo during ORR cathodic sweep using rotating disk electrodes in 1M and 6M TFMSA. Pt loading of 14μg/cm².
Fig. 4. Koutecky-Levich plots for the ORR on Pt/C at various potentials in 6MTFMSA. Current density normalized to the geometric area of the disk electrode.

Fig. 5. Koutecky-Levich plots for the ORR on PtCo/C at various potentials in 6MTFMSA. Current density normalized to the geometric area of the disk electrode.
Fig. 6. Disk currents obtained on Pt/C and PtCo/C during ORR cathodic sweep using rotating disk electrodes in 1M TFMSA at 1225 rpm.

Fig. 7. Disk currents obtained on Pt/C and PtCo/C during ORR cathodic sweep using rotating disk electrodes in 6M TFMSA at 1225 rpm.
Fig. 8. Tafel plots for the ORR at room temperature, 1225 rpm on a smooth Pt in 1M and 6M TFMSA.

Fig. 9. Tafel plot for the ORR at room temperature, 1225 rpm on PtCo/C in 1M TFMSA.
Fig. 10. Tafel plot for the ORR at room temperature, 1225 rpm on PtCo/C in 6M TFMSA.