

Reducing Overpotential Losses for Oxygen Reduction Reaction with Pt based alloys: a RRDE Investigation

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Oxygen reduction reaction, because of its complex kinetics and the need for better electrocatalysts, continues to be the main focus for enhancing PEM fuel cell performance. The rate-determining step for ORR on an electrode surface is something that has been investigated 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 parallel pathway through a peroxide intermediate.

Many Pt based transition metal alloys have been suggested for use as a cathode catalyst^[3-7]. 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^[8-11]. The activation energy for oxygen reduction was also shown to be lower than that in Pt^[14].

Inhibition of the formation of Pt-OH at potentials above 800 mV vs. RHE on Pt alloys, resulting in greater number of available Pt sites for dissociative adsorption of molecular oxygen has been previously shown by our research group. The Pt-OH formation has been proposed to be derived from the interaction of water with Pt and not from the reaction of O₂. A number of indirect evidence has been shown to this effect.^[12] Further, Watanabe *et al.*,^[13] have shown that O₂ adsorption increases with Pt 5 d-band vacancy. However, increase in d-band vacancy in Pt makes it difficult to lose an electron for oxygen reduction. Hence PtCr which has the lowest d-band vacancy change (compared to others in the first row transition element series) 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. This has a potential for rendering higher affinity for water than Pt^[14].

Previously^[15] the effect of water on the electrocatalytic activity of 20wt.% PtCo/C for oxygen reduction reaction was investigated using a rotating disk electrode (RDE) in 1M and 6M Trifluoromethane sulfonic acid (TFMSA) and showed that although in 1M TFMSA PtCo/C shows enhanced ORR activity than the Pt plug and Pt/C (Fig. 1), in 6M TFMSA it shows lower or no change in the ORR activity (Fig. 2).

The present investigation focuses on the study of ORR kinetics of a variety of Pt alloys using a rotating-ring disk electrode. The ORR kinetics of Pt+Cr, Pt+Ni, Pt+Ga is compared with Pt/C in different concentrations of TFMSA. The reaction mechanism of these systems would also be discussed. The fuel cell performance of Pt and these alloys would be discussed in terms of their ORR kinetics.

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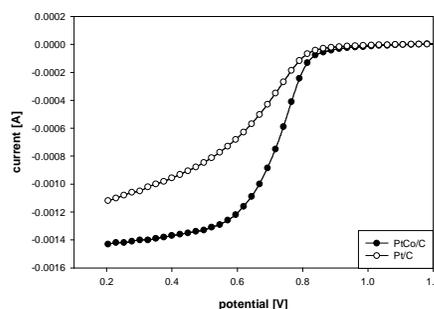


Fig. 1. Disk currents obtained on Pt/C and PtCo/C during ORR cathodic sweep using rotating disk electrodes in 1M TFMSA at 1225 rpm.

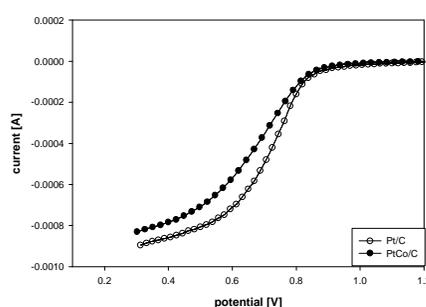


Fig. 2. Disk currents obtained on Pt/C and PtCo/C during ORR cathodic sweep using rotating disk electrodes in 6M TFMSA at 1225 rpm.

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