

The factors contributing to oxygen reduction reaction (ORR) activity improvement in Pd-based alloy catalysts

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INTRODUCTION

Alloying precious metal with the transition metal (TM: Co, Fe) has been reported in literature for the improvement of ORR activity in low temperature fuel cells, especially, with Pt and Pd. Pt alloys show ~30 mV positive shift in half-wave potential of ORR relative to Pt. On the other hand, Pd-alloys show ~85 mV shift in half-wave potential of ORR relative to that of Pd. The ORR activity improvement is either explained on the basis of lattice contraction and consequent changes in the electronic properties upon alloying or based on the thermodynamic guidelines reported in the literature [1, 2, 3]. We discuss the contribution of each factor such as lattice parameter, electrochemical surface area (ESA) and surface segregation in ORR activity improvement with Pd-alloys and comment on the huge improvement observed with Pd alloys.

EXPERIMENTAL

Alloys of Pd-based with transition metal (TM) of various compositions were synthesized by a single step borohydride reduction method at low temperature (80°C). For a typical synthesis of Pd-TM alloy catalyst, the required amount of Pd(NO₃)₂·2H₂O was mixed in 400 mL of water and heated upto 80°C; the pH of the solution was adjusted to 10 by adding 1% NaOH solution. After adjusting the pH, required amount of 0.01 M Co(NO₃)₂·2H₂O was added to the above solution and stirred for 10 min. to mix it properly. Then, the required amount of carbon-slurry was added (to obtained 20 wt% precious metal loading) to it and subsequently reduced with drop-wise addition of 1% NaBH₄ solution. The catalyst prepared was filtered, washed with distilled water, and dried in an oven for 12 h. After drying, the catalyst was collected, ground well and used for further analysis. For the comparison, Pt and Pd catalysts were also synthesized using a similar method without using cobalt. The catalyst was subjected to heat-treatment in inert and reducing atmospheres. The catalysts synthesized were characterized using various physical techniques and electrochemically characterized in an RRDE configuration.

RESULT AND DISCUSSION

Fig. 1 shows the cyclic voltammograms (CVs) and ORR voltammograms of Pt, Pd, and Pt₃Co, Pd₃Co. The ESAs of the catalysts were estimated from the H_{upd} region of the voltammograms. Pt and its alloys show comparable H_{upd} area. At the same time, we observe a doubling of the ESA with the Pd-alloy (for e.g., Pd ~45 m² g⁻¹ and Pd₃Co ~85 m² g⁻¹). This perhaps happens because of the stabilization of Pd with Co at potentials beyond the H_{upd} region. Further evidence for the stabilization of Pd is obtained from the electrochemical results. The ~30 mV ORR activity improvement with Pt-alloy (Fig.1c) is usually explained by the lattice contraction and shift in the center of d-band position, *i.e.* electronic effect, in the literature

[1, 2]. The inset to the Fig. 1c shows the CV-corrected ORR voltammograms of the Pd and Pd₃Co normalized with ESA of the respective catalysts. On normalizing the background-corrected ORR voltammogram by the ESA, we still observe an activity improvement of ~55 mV. Thus, with Pd-alloy, the ESA account for ~30 mV improvement in ORR activity. Pt₃Co, with almost same ESA as that of Pt, shows comparable improvement in ORR activity. A comparison of the ORR voltammograms of the as-prepared and heat-treated catalysts provides an estimate of the activity improvement due to surface segregation of Pd and it is found to be about 15 mV. An activity improvement with expanded, and contracted lattices, and even with oxide phase of the catalyst suggest the need for an alternative explanation for the activity improvement in alloy catalysts. The rest of the improvement (~35 mV) may be attributed to the contribution due to the electronic effect (though no clear shift was observed in the XPS peak position of Pd₃Co and Pd, and only peak broadening was observed).

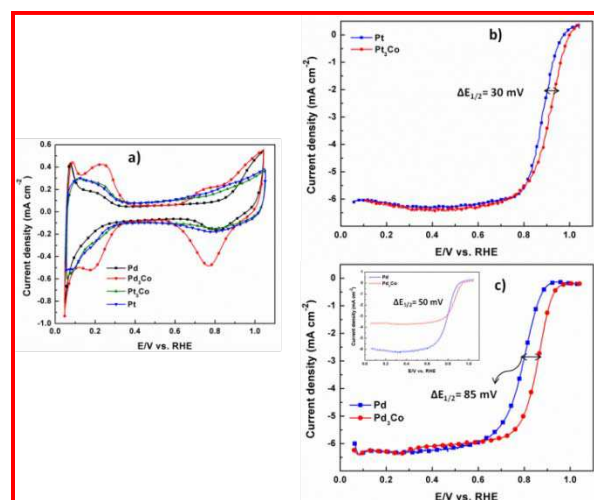


Fig.1 a) CVs of the carbon-supported Pd, Pt, Pt₃Co, and Pd₃Co; the ORR voltammograms of b) Pt, and Pt₃Co and c) Pd and Pd₃Co, respectively. Inset to Fig. 1c shows CV-corrected ORR voltammograms of Pd and Pd₃Co normalized with respective ESA.

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