

Shape-controlled core (Pd)–shell (Pt) catalysts for electrocatalysis of ORR in fuel cells

Naresh Nalajala^{1,2,3}, Bradley P Ladewig² and Manoj Neergat³

¹IITB-Monash Research Academy, IIT Bombay, Powai, Mumbai, India

²Department of Chemical Engineering, Monash University, Clayton, Victoria 3800, Australia

³Department of Energy Science and Engineering, IIT Bombay, Powai, Mumbai, India

INTRODUCTION

Platinum is the only promising candidate material for oxygen reduction reaction (ORR) with required activity and stability in the corrosive atmosphere of the fuel cells; but, the ever-increasing cost of Pt hinders the commercialization of fuel cells. Research efforts in using Pt-alloys and core-shell materials for ORR have shown convincing evidence for the incremental improvement of the ORR activity. Another strategy that can be adopted to improve the activity is to take advantage of the hkl dependence of ORR activity. In the literature, the ORR activity of Pt reported is in the order of Pt(100)<Pt(110)<Pt(111) in acidic solutions, whereas, the order is (111)<(110)<(100) in the alkaline solutions [1,2]. Since the activity is crystallographic orientation dependent, synthesis of materials with dominant exposure of active crystallographic orientation can improve the ORR activity. Here, we report the combined approach of shape-control, alloying, and core-shell structure so that we can take the advantage of both geometric and electronic effects simultaneously from the same catalyst. The core is the shape-controlled Pd (sphere, cubic, truncated octahedra) and the shell is Pt.

EXPERIMENTAL

Synthesis of carbon-supported Pd NC core-Pt shell catalyst: In a 50 ml RBF, 8 mL of aqueous solution of polyvinylpyrrolidone (PVP, 105 mg), L-Ascorbic acid (60 mg), and potassium bromide (KBr, 300 mg) were pre-heated in air at 80 °C for 15 min. Then, 3 ml of DI water containing K₂PdCl₄ (57 mg) was added to the above solution and waited for 3 h. The product was collected by centrifugation and it was washed with acetone once and then 3–4 times with ethanol and n-hexane (1:3). At the end, the prepared Pd NCs were dispersed in 5 ml of ethanol solution and mixed under ultra-sonication for one hour with required amount of carbon in such a way that the metal loading on the catalyst is 20 wt%. The core-shell procedure followed reported in the literature [3] with modification and is as follows: Initially, 100 mg of carbon-supported palladium nanoparticles (20 wt. %) were dispersed in 50 ml of ethanol and water mixture and it was sonicated for 30 min. The suspension was taken in a 100 ml bubbler and it was kept for hydrogen gas purging. After two hours of hydrogen purging, 20 ml of 5 mM CuCl₂·2H₂O was added to the solution and the purging was continued for 6 hrs. The catalyst was collected from the solution by centrifugation and it was redispersed in the 20 ml of ethanol and water mixture. 7 ml of 5 mM K₂PtCl₄ was added to the above solution and it was kept for argon-purging for 6 hrs at 60 °C under argon atmosphere. Finally, the Pt coated catalyst was separated from the solution by centrifugation at 5000 rpm for 10 min. The catalyst was dried at 80 °C overnight and was ground well before using it for further characterization.

RESULTS AND DISCUSSION

The catalysts, Pd NCs/C and Pd/C, were coated with platinum as mentioned earlier with a Pd to Pt ratio of 4:1. The Pt monolayer is expected to deposit on different Pd nanoparticles because the purged hydrogen gas would be able to deposit Cu and that is further displaced with Pt. From the **Fig. (1a)** the TEM images of Pd NC coated with Pt seems to suggest that there is no change in the shape and size after coating but with minor agglomeration.

The cyclic voltammograms were recorded in argon-saturated 0.1 M HClO₄ solution from 0.0 to 1 V. The CVs of Pd NCs/C coated with platinum (blue), Pd/C coated with platinum (black), and for comparison the respective catalysts without coating are shown in **Fig. (1b)**. The H_{upd} region of Pt-coated Pd shows entirely different features when compared to that of uncoated Pd. The H_{upd} area is more than twice that of the as-prepared catalyst. This is expected with Pd-based core catalysts; it is happening on both core-shell structures. Similarly, in the oxide formation region, the charge due to formation of OH species on polycrystalline palladium coated with platinum is picking up very early (~0.5 V), when we compare with the other catalysts. The formation of oxygenated species that are active towards the ORR are generated before the complete oxide formation. These oxygenated species are more oxophilic in nature, as can be seen from the huge reduction peak at more positive potential (~0.8 V). We conclude that the addition of platinum over the palladium changes the electronic properties in such a way as to obtain better activity towards ORR. After obtaining reproducible CVs in argon-saturated solution we have replaced with oxygen-saturated electrolyte for testing ORR. The half-wave potentials of ORR of the prepared catalysts are as follows: 871, 855, 833 and 793 mV for Pd(PC) core-Pt shell/C, Pt/C, Pd(NC) core-Pt shell/C and Pd/C catalysts, respectively.

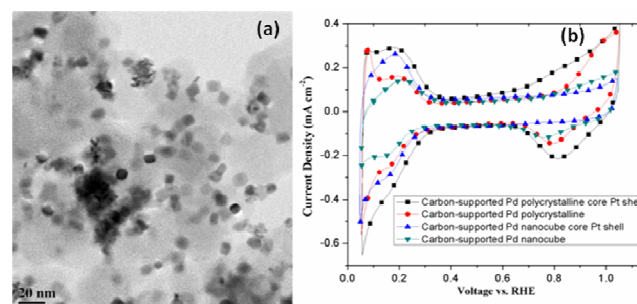


Figure 1 (a) TEM image of Pt-coated Pd nanocubes (b) cyclic voltammograms of Pd nanocube core Pt shell and Pd polycrystalline core Pt shell; CVs of Pd nanocube and Pd polycrystalline are included for comparison.

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