Electrocatalytic oxygen reduction reaction (ORR) has been the focus of many studies because of its slow kinetics and a high Pt content in ORR cathodes. Further improvements are necessary, despite some recent advances, viz., the design of a Pt monolayer electrocatalyst on Pd nanoparticles, to name one. In this work an attempt was made at designing a non-platinum electrocatalyst for the ORR based on Pd. The studies involved a Pd monolayer deposition on different single crystal surfaces (i.e. Au(111), Pt(111), Rh(111), Ir(111) and Ru(1000)) using a Cu monolayer displacement, and synthesis of PdCo alloys. The kinetics of ORR was determined using a rotating disk-ring method and the density functional calculations (DFT) were used to elucidate the substrate effects on the activity of a Pd monolayer.

Slab DFT calculations were performed using the CASTEP suite of programs, and the GGA-RPBE description of the exchange and correlation. Pd/M alloys were described by a single layer of Pd placed on top of M (M=Au,Rh,Pt,Pd,Ru,Ir) surface using substrate’s lattice constant. Each surface was constructed by a four-layer slab with a 2x2 unit cell and a vacuum 11Å thick separating the top and the bottom of the slabs.

Experimentally, Pd/Pt(111) displays the best ORR activity. The Pd d-band center, calculated using DFT, is used as a descriptor of the surface reactivity. It has been found that the closer the position of metal d-band towards Fermi level, the stronger their interactions with adsorbates. We obtained a linear correlation between the O binding energies and the d-band position of Pd atom on M surfaces. As shown in Fig. 1, a volcano variation of the observed ORR activity of Pd/M was found with the increasing d-band of Pd in the surface. In agreement with the Sabatier principle, a Pd/Pt(111) surface with a Pd d-band lying in the middle that facilitates formation of a moderate bond with the adsorbates, is the best catalyst for the ORR. The plot also indicates that the bonding of oxygen intermediates with a Pd/Au surface is too strong due to the high d-band center of Pd. This is a consequence of a large tensile strain in a Pd monolayer on an Au substrate. As we found for Pt monolayers on several substrates, a higher lying d-band center tends to enhance the ORR kinetics, apparently by facilitating the O-O bond breaking. A small tensile strain for a Pd monolayer on Pt(111) is acting in that way. This is also supported by the disk-ring data for a Pd/Pt(111) surface.

The volcano plot in Fig. 1 shows a large variation of a d-band center of a Pd monolayer on different substrates, and a sizeable variation of its activity for the ORR. This indicates a possibility for useful modifications using other metals. We modified the carbon-supported palladium nanoparticles with cobalt. Since cobalt is from the same group as rhodium it was expected to produce a similar enhancement of the electrocatalytic activity of Pd. Indeed, the half wave potential for the ORR was found to be around 0.84 V (vs. RHE) in acidic solution (0.1 M HClO₄), which is comparable to that of the carbon supported platinum nanoparticles. Their mass specific activity was also found comparable.

Palladium-cobalt (2:1) nanoparticles without carbon nanoparticles support was also studied, and similar half wave potential for oxygen reduction was observed (about 0.8 V vs. RHE in 0.1 M HClO₄). Further analysis of these data and durability tests will be presented.

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