

# Communications

## Anion-Dependent Electrocatalytic Activity of Supported Palladium Catalysts onto Imidazolium Salt-Functionalized Carbon Nanotubes in Oxygen Reduction Reaction

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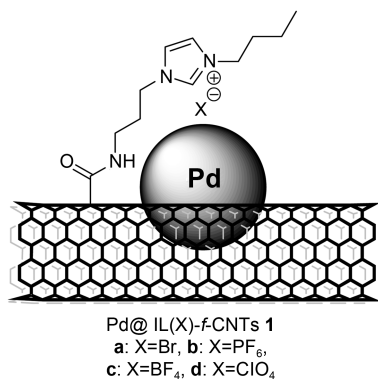
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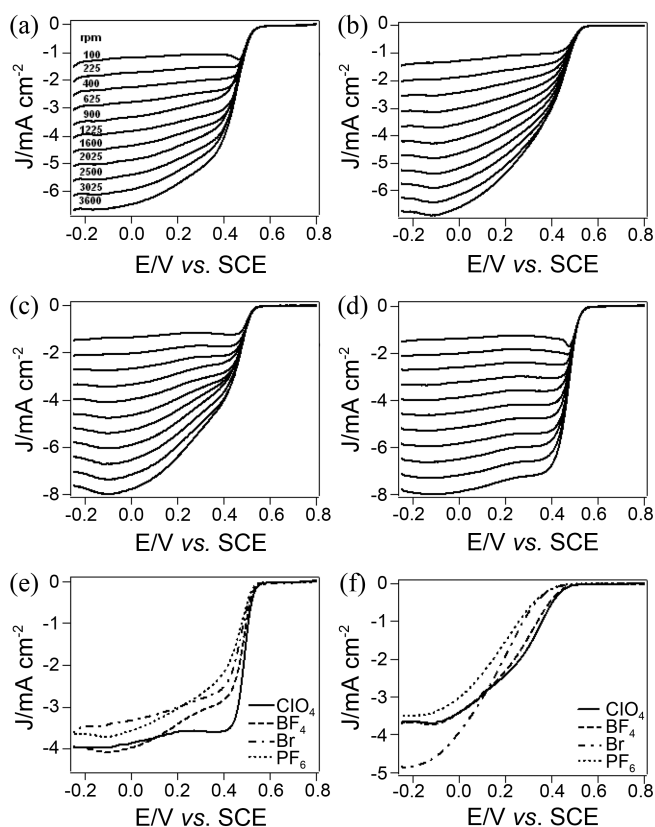
Ionic liquids (ILs) have attracted an increasing amount of interest, owing to their high thermal and chemical stability with considerable electric conductivity and wide electrochemical windows.<sup>1</sup> Initial investigation concerning ILs mostly focused on employing them as green solvents in chemical synthesis and catalysis.<sup>2</sup> Recently, ILs have emerged as “molecular tuner” for functional nanomaterials because the structures and properties of ILs can be easily tuned by selecting the appropriate combination of cation and anions.<sup>3</sup> Therefore, it is possible to utilize one ionic component to deliver a unique function and the other to deliver a different and independent function. We and others have recently found that covalently functionalized CNTs with imidazolium salts (an IL moiety), IL(X)-f-CNTs, exhibited preferential solubility in ionic liquids as compared to water and organic solvents.<sup>4</sup> Moreover, it has been also found that the functionalization of CNTs with imidazolium salt could not only facilitate the deposition of palladium nanoparticles (Pd NPs), but also increase the stability of the supported palladium nanoparticles onto IL(X)-f-CNTs, Pd@IL(X)-f-CNTs **1** (a: X = Br, b: X = PF<sub>6</sub>, c: X = BF<sub>4</sub>, d: X = ClO<sub>4</sub>), (Figure 1).<sup>5</sup> Importantly, a number of recent reports suggested that IL moiety enhanced the electron transfer pathway between CNTs and metal NPs such as Au, Pt, and PtRu

NPs increasing the electrocatalytic activity of the metal NPs for methanol oxidation or oxygen reduction reaction (ORR), which is one of the crucial reactions in the performance of a fuel cell.<sup>6</sup> Considering that Pd's electrocatalytic activity toward ORR is recently of great interest as a potential replacement and/or reduce the amounts of Pt in fuel cell cathode,<sup>7</sup> we investigated the electrocatalytic oxygen reduction reaction using the supported Pd NPs, Pd@IL(X)-f-CNTs **1**, and found that the electrocatalytic activity is affected by the nature of anion of imidazolium salt.

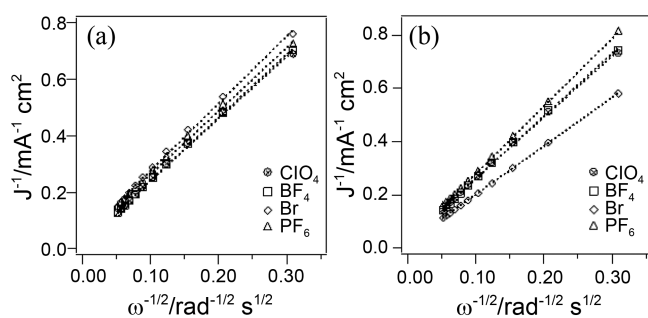
The electrocatalytic activities of the Pd@IL(X)-f-CNTs **1a-1d** (molar ratio of IL/Pd = 1:6) toward ORR in 0.1 M HClO<sub>4</sub> solution have been investigated by rotating disk electrode (RDE) voltammetry using **1a-1d** modified glassy carbon electrode as working electrode, a large-area Pt coil as a counter electrode and saturated calomel electrode (SCE) as a reference electrode (Detail experiment, see SI). Figure 2(a)-2(d) shows the polarization curves obtained with RDE for ORR on a Pd@IL(X)-f-CNTs **1a-1d** at various rpm. For the comparisons, the selected polarization curves of **1a-1d** at 900 rpm were depicted in Figure 2(e). Though not significant, the anion-dependence of the electrocatalytic activities has been observed in Pd@IL(X)-f-CNTs **1a-1d**, and the observed order of the ORR kinetic activity of Pd@IL(X)-f-CNTs **1** is X = ClO<sub>4</sub> > BF<sub>4</sub> > Br ≥ PF<sub>6</sub>. Because the catalysts **1c-1d** have been prepared from the same Pd@IL(Br)-f-CNT **1a** by simple anion exchange, the observed activity differences reflect the anion effect. In order to see more clearly the anion effects on the electrocatalytic activities, the molar ratio of imidazolium salt moiety in Pd@IL(X)-f-CNTs **1** increased to IL/Pd = 1:3. As shown in Figure 2(f) (Polarization curves at various rpm, see Figure S1), the ORR onset potentials with catalysts **1a** having Br anion and **1b** having PF<sub>6</sub> anion were slightly shifted to negative potential suggesting that anions effected on the electron transfer kinetics. Here again, the Pd@IL(ClO<sub>4</sub>)-f-CNTs **1d** having ClO<sub>4</sub> anion is considerably superior to those of the other supported catalysts **1a-1c** having Br, PF<sub>6</sub>, and BF<sub>4</sub> anions. In addition, the observed



**Figure 1.** Supported Pd NPs onto imidazolium salt-functionalized CNTs.



**Figure 2.** RDE polarization curves for the ORR obtained using a glassy carbon electrode loaded with Pd@IL(X)-f-CNTs **1** (IL/Pd = 1:6 molar ratio) (a) **1a**, (b) **1b**, (c) **1c** (d) **1d** in 0.1 M HClO<sub>4</sub> solution at different rpm and (e) at 900 rpm. (f) RDE polarization curves obtained with Pd@IL(X)-f-CNTs **1a-1d** (IL/Pd = 1:3 molar ratio) in 0.1 M HClO<sub>4</sub> solution at 900 rpm.



**Figure 3.** K-L plots obtained from the RDE data at  $-0.2$  V with Pd@IL(X)-CNTs **1** having (a) 1:6 molar ratio of IL/Pd, (b) 1:3 molar ratio of IL/Pd.

anion-dependent catalytic activity suggested that the anion exchange rate of the Pd/PolyIL(X)-CNTs with ClO<sub>4</sub> anion in standard acidic condition, 0.1 M HClO<sub>4</sub>, is very slow, which

is the underlying assumption of all related experiments with IL-CNT hybrids in acidic conditions. The Koutecky-Levich (K-L) plots (Figure 3), obtained from the current densities at a constant potential,  $-0.2$  V (vs. SCE), indicated that the ORR occurs *via* four electron transfer for all the Pd@IL(X)-f-CNTs (See, Table S1).

In conclusion, we have found that electrocatalytic activity of the supported palladium catalysts onto the imidazolium salt-functionalized carbon nanotubes in oxygen reduction reaction is influenced by the nature of counter anion of imidazolium salt. The results presented here suggested that molecular-level control of interfacial interactions between the ionic liquid moiety, CNT, and nanoparticle catalysts is important for the development of more reactive supported nanocatalyst using imidazolium-functionalized CNTs for fuel cells. The origin of anion effects on the electrocatalytic activity is remained to be elucidated, and studies on this direction are underway.

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