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Improved Performance of Proton Exchange Membrane Fuel Cells with *p*-Toluenesulfonic Acid-Doped Co-PPy/C as Cathode Electrocatalyst

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Great efforts have been made to reduce costs and improve activity of non-noble-metal catalysts for oxygen reduction reaction (ORR) at the cathode of a proton exchange membrane fuel cell (PEMFC).[1,2] Cobalt- and iron-based nitrogen-containing catalysts (i.e., Co−N/C and Fe−N/C) are among the most promising substitutes for the currently used Pt/C catalyst owing to their comparable catalytic activities toward ORR and much lower cost.[3,4] It has been shown that N content and surface morphology in these catalysts are of great importance for catalytic activity toward ORR.[5,6]

One type of N-containing compound, polypyrrole (PPy)—a conducting polymer with altering surface, plenty of pyrrole-type N atoms, high conductivity, and easy preparation and doping—has been extensively used to prepare Co−N/C catalysts in recent years, and Co-PPy/C for ORR has demonstrated excellent catalytic activity and high stability in acid media.[7−9] Many reports indicated that the catalytic activity and stability of Co-PPy/C could be improved by optimizing the heat-treatment temperature, ligand structure, synthesis method, and metal precursor, as well as the carbon support.[10−12] However, the mechanism of catalytic activity for ORR in such catalysts remains unclear,[7,8,13] as little is known about the formation of the catalytically active sites and the origin of ORR activity enhancement of these catalysts.

In this work, we report a new catalyst, Co-PPy-TsOH/C, which is synthesized with *p*-toluenesulfonic acid (TsOH)-doped PPy/C as a N-rich and morphological support together with cobalt salt. The catalyst shows much better ORR activity than Co-PPy/C. The function and mechanism of doping have been analyzed using Raman and elemental analysis, from which the origin in the enhancement of ORR activity of the doped catalyst is discussed and the catalytically active site is postulated.

Figure 1 shows the Raman spectra of BP2000 (a), PPy/C (b), and PPy-TsOH/C (c) along with those of PPy (d) and PPy-TsOH (e) for comparison. Assignment of the Raman spectral bands is presented in the Supporting Information. The prominent bands that emerged in the spectra of PPy and PPy-TsOH, within experimental errors, can also be observed in the spectra of PPy/C and PPy-TsOH/C, respectively, while the characteristic peaks of BP2000 overlap with those of PPy/C and PPy-TsOH/C, indicating that PPy and PPy-TsOH have been successfully synthesized on the surface of BP2000 and there is also interaction of the polymer backbones with BP2000.

The presence of peaks at 936, 1084, and 1261 cm^{-1} has been associated with the dication (bipolaron) structure and those at 984 and 1051 cm^{-1} with the radical cation (polaron) structure, and the C=C stretching peak at 1595 cm^{-1} is considered to be an overlap of the two oxidized structures.[14−16] Therefore, comparison between traces b and c in Figure 1 implies that PPy-TsOH/C has an increased portion of bipolarons relative to polarons compared with PPy/C in all vibrational groups, especially in the antisymmetric CH in-plane bending mode.

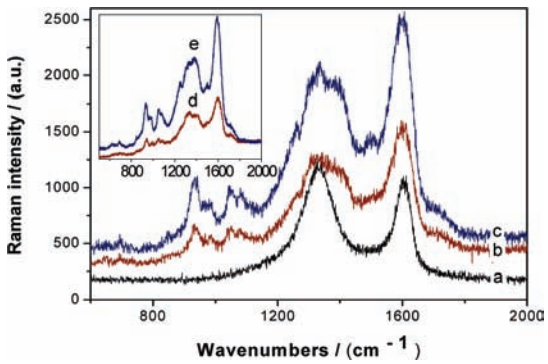

Figure 1. Raman spectra of BP2000 (a), PPy/C (b), PPy-TsOH/C (c), PPy (d), and PPy-TsOH (e).

To understand the increase in the number of bipolarons in PPy-TsOH/C, consider the effect of additional charge carriers on the polymer structure. It is believed that electronic conjugated polymers possess a spatially delocalized band-like electronic structure (delocalization of the π electrons),[17,18] and the doping-induced charge carriers are self-localized based on a strong phonon interaction with the polymer chains. In the case of bipolarons, the deformation by two neighboring charge carriers (polarons) is strong enough to form a common potential well and to overcome the coulomb repulsion due to the low ionization potential and electron affinity of bipolarons. It is the charge carrier mobility attributed to the property of bipolarons in this localization effect that leads to the high conductivity of these polymers, per Gupta et al.[19] Therefore, doping TsOH into PPy/C tends to increase the total number of dications and maximize conformational defects such as twists and links of the polymer structure.

The elemental contents of C, N, S, and Co in Co-PPy/C and Co-PPy-TsOH/C are shown in Figure 2, where the N and S contents are increased and almost doubled while the C and Co contents are slightly decreased by doping TsOH to Co-PPy/C. The probable reason for N content increase is that, with help of the anion dopant, polarons are inclined to form a common potential well and lead to conformational defects such as twists and links of the polymer structure, as discussed earlier. Therefore, it is favorable for Co to be absorbed at N-rich spots in the polymer structure, allowing more N atoms to bond with Co atoms. During heat-treatment, the Co−N coordination number will not change, and the Co−Co and Co−N distances may be shortened according to Yuasa et al.,[8] although PPy decomposes below 600 °C and does not exist in the catalyst after pyrolysis at 800 °C in Ar for 1 h (Figure S1). Hence, more N remains in Co-PPy-TsOH/C than in Co-PPy/C after pyrolysis. The reason for S content increase is that the S in Co-PPy/C comes from oxidant ammonium peroxydisulfate

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(APS), while that in Co-PPy-TsOH/C comes from both oxidant APS and dopant TsOH. The slight decrease in C and Co contents results from the N and S content increase. The average size of micropores in the catalyst is slightly enlarged from 12.8 to 14.5 nm after doping.

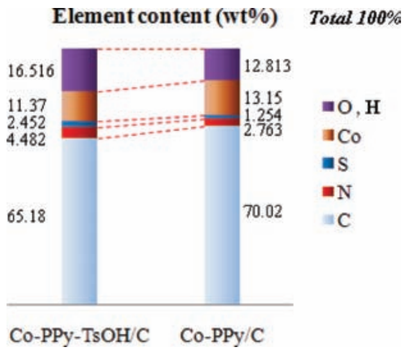

Figure 2. Elemental analysis of Co-PPy-TsOH/C and Co-PPy/C.

According to the above analysis, schematic representations of the structure for PPy-TsOH/C (Figure S2a) and the presumed configuration of catalyst Co-PPy-TsOH/C (Figure S2b) are proposed. In Figure S2a, the polypyrrole chains form a twisted structure due to the bipolaron induced by dopant TsOH, and the sulfo group doped to the polypyrrole may be helpful for entrapping Co ions in an environment rich in pyrrole-type nitrogen. Figure S2b highlights the linkage between N atoms and Co atoms in the pyrolyzed catalyst.

To characterize the catalytic performance and gain further insight into the ORR mechanism of these catalysts, rotating ring disk electrode analysis was performed, and Figure S3a shows the polarization curves recorded at potential $E_{\mathrm{ring}} = 1.0$ V vs SCE. The disk current of catalyst Co-PPy-TsOH/C is much larger than that of catalyst Co-PPy/C, while the ring current of Co-PPy-TsOH/C is apparently smaller, clearly indicating a better catalytic activity of Co-PPy-TsOH/C toward ORR. To further understand the difference in ORR between Co-PPy-TsOH/C and Co-PPy/C, the number of exchanged electrons (n) and the yield of produced hydrogen peroxide ($Y(H_2O_2)$) during ORR were calculated; the results are presented in Figure S3b. As shown, the number of electrons exchanged by catalyst Co-PPy-TsOH/C for ORR is apparently larger than that of Co-PPy/C, while the percentage of H_2O_2 produced by Co-PPy-TsOH/C is much smaller. Therefore, it can be concluded that it is more likely for doped catalyst Co-PPy-TsOH/C than Co-PPy/C to follow a four-electron-transfer reaction to reduce oxygen directly into H_2O, and Co-PPy-TsOH/C has better electrocatalytic performance for ORR than Co-PPy/C.

The ORR electrocatalytic activity of the catalysts was also evaluated in a 5 cm^2 single H_2-O_2 PEMFC, and the polarization curves are shown in Figure 3. The performance of PEMFCs with Co-PPy-TsOH/C as the cathode catalyst is much better than that with Co-PPy/C, with both cells exhibiting an open circuit voltage of ~0.81 V. The PEMFC with Co-PPy-TsOH/C generates a current density of 0.21 A cm^{-2} at 0.40 V, nearly double the current density of the cell with Co-PPy/C (0.12 A cm^{-2}) under the same voltage. Moreover, the PEMFC with Co-PPy-TsOH/C produces a maximum power density of 203 mW cm^{-2}, significantly higher than that with Co-PPy/C (161 mW cm^{-2}). The performance of the PEMFC with Co-PPy-TsOH/C is greatly improved compared to those reported in refs 7, 20, and 21 with Co-PPy/C-based cathode catalyst, even in the absence of any backpressure for the cell.

In summary, we show that the increase of N content, a key factor for catalytic activity of Co- and Fe-based N-containing catalysts toward ORR, is a main reason for the much enhanced electrocatalytic activity of Co-PPy-TsOH/C toward ORR compared to that of Co-PPy/C, while the slightly changed C content and micropores have little influence, and the correlation between S content and catalytic activity is still unclear. Moreover, a H_2-O_2 PEMFC with Co-PPy-TsOH/C as the cathode catalyst has demonstrated much higher current density and power density than the best performance reported in the literature for PEMFCs with Co-PPy/C-based cathode catalyst, with the maximum output power density reaching 203 mW cm^{-2}. Clearly, doping TsOH to Co-PPy/C is a valuable way to improve the catalytic activity of Co-PPy/C toward ORR, and Co-PPy-TsOH/C is a promising cathode catalyst for PEMFCs.

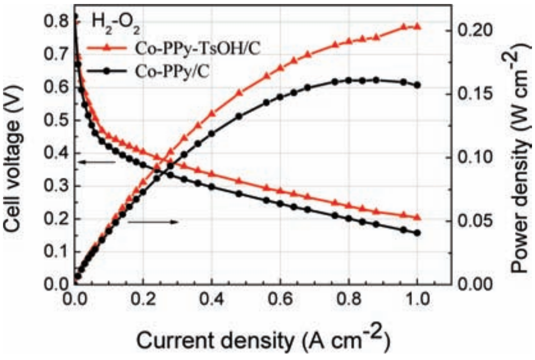

Figure 3. Polarization and power density curves for H_2-O_2 PEMFCs with commercial Pt (10 wt %)/C as anode catalyst and Co-PPy/C or Co-PPy-TsOH/C as cathode catalyst. Conditions: Co loading, 0.35 mg cm^{-2}; Pt loading, 0.15 mg cm^{-2}; cell temperature, 80 °C; flow rate of hydrogen and oxygen, 300 and 540 mL min^{-1}, respectively; anode and cathode reaction gases humidified at 90 and 80 °C, respectively; no backpressure for both sides of the cell.

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Supporting Information Available: Experimental procedures, additional figures, and references. This material is available free of charge via the Internet at http://pubs.acs.org.

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