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# Improving $MnO_2$/ Porous Carbon Nanocomposites Electrocatalytic Oxygen Reduction Performance by Surface Modification Using Protic Ionic Liquid for Fuel Cell

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## Extended Abstract

**Background:** Fuel cells have garnered increased interest as a portable power source in recent times due to their superior efficiency and environmentally friendly nature compared to alternative energy conversion technologies [1-3]. There is anticipation for the commercialization of fuel cells across diverse applications such as transportation, space technology, and portable electronic devices. This advancement is poised to contribute to addressing the global energy supply challenge [4]. The basic idea behind fuel cells is the sustainable conversion of chemical energy into electrical current. Being the most effective ORR catalyst to date, Pt nanoparticles supported on carbon materials (Pt/C) provide large current densities and low ORR overpotential. Furthermore, they show selectivity for a straight four-electron pathway. However, significant barriers have thwarted the widespread adoption of fuel cells implementing Pt-based electrocatalysts on an extensive basis, including high cost, scarcity, restricted long-lasting stability, and the possibility for degradation of Pt occurs because of methanol contact. Many studies have been devoted to developing equivalent Pt-free ORR catalyst equivalents to overcome such issues.

**Methodology:** This study introduces a simple method for synthesizing $MnO_2$/porous carbon (PC) composites with tunable morphology to improve oxygen reduction reaction (ORR) kinetics in intermediate-temperature fuel cells. Using banana pseudo stem and $KMnO_4$ as precursors, the resulting carbon is highly nitrogen-doped with an interconnected porous structure. The catalyst surface is modified with 2-isopropyl imidazolium trifluoroacetate ([2-IPIm]$CF_3COO$), a hydrophobic protic ionic liquid (PIL), creating a solid catalyst with a protective PIL layer. Characterization using FTIR, XRD, SEM, BET, Raman, and XPS confirmed the successful synthesis, with XRD revealing tunnel rod-shaped $MnO_2$ and SEM showing PIL surface modification. BET analysis indicated a mesoporous structure with a specific surface area of 45.61 m²/g. Raman spectroscopy showed a high $I_D/I_G$ ratio for the carbon layer, while XPS identified nitrogen doping with pyridinic-N, pyrrolic-N, and N-oxide groups.

**Electrochemical Measurements:** ORR performance, evaluated using voltammetry in $O_2$-saturated 0.1 M KOH, showed an onset potential of 0.786 V and a half-wave potential of 0.713

V vs. RHE. Table 1 shows $E_{1/2}$ and Onset potential before and after surface modification of $MnO_2$/PC prepared at different temperatures with different PIL ratios.

**Table 1: $E_{1/2}$ and Onset potential before and after surface modification of $MnO_2$/PC prepared at different temperatures with different PIL ratios.**

| Sample | $E_{1/2}$ of catalyst (V vs RHE) | Onset potential (V vs RHE) |
|---|---|---|
| $MnO_2$/PC-400 | 0.616 | 0.666 |
| $MnO_2$/PC-400+PIL(1:1) | 0.686 | 0.696 |
| $MnO_2$/PC-400+PIL(1:2) | 0.713 | 0.786 |
| $MnO_2$/PC-400+PIL(2:1) | 0.626 | 0.706 |
| $MnO_2$/PC-500 | 0.606 | 0.676 |
| $MnO_2$/PC-500+PIL(1:1) | 0.616 | 0.696 |
| $MnO_2$/PC-500+PIL(1:2) | 0.706 | 0.766 |
| $MnO_2$/PC-500+PIL(2:1) | 0.556 | 0.666 |
| $MnO_2$/PC-600 | 0.606 | 0.747 |
| $MnO_2$/PC-600+PIL(1:1) | 0.696 | 0.779 |
| $MnO_2$/PC-600+PIL(1:2) | 0.708 | 0.78 |
| $MnO_2$/PC-600+PIL(2:1) | 0.686 | 0.77 |

The superior ORR activity, with 85% current retention after 18,000 seconds, is attributed to the synergistic effects of nitrogen-doped carbon and $MnO_2$, enhanced by the protective PIL layer, offering valuable insights for fuel cell electrocatalysts. Following PIL modification, the electrocatalysts exceeded commercial Pt/C in terms of catalytic efficiency and stability over the long term, while costing less than rare Pt. The PIL layer functioned as a reaction medium, discharging water and ORR byproducts, protecting the active sites from oxygenation or contamination, and considerably improving their long-term stability.

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