Catalysis

Carbon Nanotube-Modified MnO\textsubscript{2}: An Efficient Electrocatalyst for Oxygen Reduction Reaction

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In this work, manganese dioxide/carbon nanotube (MnO\textsubscript{2}/CNT) have been synthesized by sonochemical-coprecipitation method and demonstrated that it could be an effective electrocatalyst for oxygen reduction reaction (ORR). Moreover, the effect of CNT inclusion with MnO\textsubscript{2} was also investigated for ORR. The physical and electrochemical properties of the MnO\textsubscript{2}/CNT were examined by powder X-ray diffraction (XRD), Fourier Transform Infrared (FT-IR) spectroscopy, Brunauer-Emmett-Teller (BET), Transmission Electron Microscopy (TEM), Field Emission Scanning Electron Microscopy/Energy Dispersive X-ray (FESEM/EDX), Cyclic Voltammetry (CV), Electrochemical Impedance Spectroscopy (EIS), Mott-Schottky and Rotating Disk Electrode (RDE) analysis. CV showed higher currents for the ORR in MnO\textsubscript{2}/CNT than CNT; however, ORR current dropped when the MnO\textsubscript{2} loading was increased from 20–40%. The EIS analysis showed that charge-transfer resistance for MnO\textsubscript{2}/CNT was significantly lower compared to the MnO\textsubscript{2}, indicating that MnO\textsubscript{2} has good contact with CNT and the composite possess high electrical conductivity. Mott-Schottky results demonstrated that incorporation of CNT into MnO\textsubscript{2} resulted in producing larger electron density in n-type MnO\textsubscript{2}/CNT compared to MnO\textsubscript{2} which is liable for efficient electron donation from the Mn\textsuperscript{3+} to adsorbed oxygen in the rate determining step. RDE results showed that MnO\textsubscript{2}/CNT follows 4e\textsuperscript- transfer pathway, indicating its ability to act as an effective ORR electrocatalyst.

Introduction

Oxygen reduction reaction (ORR) is one of the most extensively studied reactions especially for the application of fuel cell and metal-air batteries.\textsuperscript{[1]} However, ORR is a kinetically slow process which significantly limits the overall reaction kinetics, resulting in a substantial loss in the performance.\textsuperscript{[2]} Therefore, in order to accelerate the reaction, numerous materials have been developed as electrocatalysts.\textsuperscript{[3]} The metals such as platinum (Pt), palladium (Pd), gold (Au) and their alloys exhibit good catalytic activity towards ORR.\textsuperscript{[4]} Among them, Platinum (Pt) is the most commonly used electrocatalyst for the ORR due to its higher electrocatalytic activity and stability.\textsuperscript{[5]} But, though the Pt has good catalytic activity, the high cost along with the catalyst poisoning limits its practical applications.\textsuperscript{[6]} So, several cheap alternative materials have been used as electrocatalysts to increase the ORR.\textsuperscript{[14]} Among them, non-precious metals such as manganese oxides had been widely investigated as one of the most promising catalysts for ORR\textsuperscript{[7]} both in fuel cells and in metal-air batteries applications due to its distinctive properties such as lower cost, easier preparation, good ORR catalytic activity and least harmful to the environment.\textsuperscript{[8]} Stoerzinger, et al.\textsuperscript{[9]} reported that among the catalysts, manganese based oxides have the highest activities close to that of precious metals. The same group also reported that α-MnO\textsubscript{2} possesses higher activity per cost (approximated on a metal basis) than Pt/C.

Besides that, in ORR, the 4-electron reduction reaction is favourable since the 2-electron reduction reaction could involve in hydrogen peroxide production leading to high over potential.\textsuperscript{[10]} However, the poor electrical conductivity restricts the electrochemical activity of manganese oxides. Therefore, several kinds of materials such as Graphite, Monarch carbon black 1000 and Vulcan XC-72 have been used as conductive supports to increase the ORR performance.\textsuperscript{[11]} However, these materials have poor ORR activity.\textsuperscript{[12]} So, in order to enhance the ORR performance of MnO\textsubscript{2}, a better electron conducting material can be incorporated, such as multiwalled carbon nanotubes (MWCNTs), which possess excellent electronic conductivity, high thermal stability, chemical stability, high porosity, high surface area, nano-size morphology and good mechanical