

Oxygen reduction reaction at MWCNT-modified nanoscale iron(II) tetrasulfophthalocyanine: remarkable performance over platinum and tolerance toward methanol in alkaline medium†

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Abstract

A nanoscale iron(II) tetrasulfophthalocyanine (nanoFeTSPc) catalyst obtained by coordinating with hexadecyltrimethylammonium bromide and subsequently anchored onto multi-walled carbon nanotubes (MWCNTs) for oxygen reduction reaction (ORR) has been reported. Two types of MWCNTs, hydroxyl/carboxyl-functionalized (o-MWCNTs) and sulfonate-functionalized (s-MWCNTs) were used as the supporting platforms for the catalysts (nanoFeTSPc-o-MWCNT and nanoFeTSPc-s-MWCNT, only 9 wt% loading of the nanoFeTSPc). The nanoFeTSPc-o-MWCNT gave the best performance towards ORR in terms of high catalytic current density, more positive onset potential ($E(\text{subonset}) = -0.02$ V vs. Ag/AgCl), half-wave potential ($E(\text{sub}1/2) = -0.32$ V vs. Ag/AgCl), and high catalytic rate constant ($k = 1.6 \times 10^2$ cm² s⁻¹) compared to the nanoFeTSPc-s-MWCNT counterpart or the Pt/XC-72 (80% Pt loading). The ORR performance generally follows this trend: nanoFeTSPc-o-MWCNT > Pt/XC-72 > nanoFeTSPc-s-MWCNT. The MWCNT-modified nanoFeTSPc complexes are much better than observed for the individual components, nanoFeTSPc, o-MWCNT and s-MWCNT. In addition, the nanoFeTSPc-o-MWCNT essentially followed a 4-electron pathway, while the nanoFeTSPc-s-MWCNT followed a 2-electron pathway. The excellent performance of the nanoFeTSPc-o-MWCNT correlates very well with the more homogenous dispersion and higher degree of attachment of the nanoFeTSPc on the surface of the o-MWCNT than on the s-MWCNTs. Unlike Pt/XC-72, the nanoFeTSPc-o-MWCNT exhibited excellent tolerance toward methanol contamination. The excellent ORR activity of the nanoFeTSPc-o-MWCNT at a very low catalyst loading, coupled with its excellent methanol tolerance compared to the commercial platinum, promises to serve as a viable non-noble alternative to the expensive noble metal catalysts (such as Pt and Pd) for alkaline fuel cells.