Molecular catalysis of the oxygen reduction reaction by iron porphyrin catalysts tethered into Nafion layers: An electrochemical study in solution and a membraneelectrode-assembly study in fuel cells

## Abstract

This study was motivated by the need for improved understanding of the kinetics and transport phenomena in a homogeneous catalyst system for the oxygen reduction reaction (ORR). Direct interaction between the sulfonic groups of Nafion and an Fe(III) meso-tetra(N-methyl-4-pyridyl) porphine chloride (Fe(III)TMPyP) compound was observed using FTIR and in situ UV–Vis spectroelectrochemical characterizations. A positive shift of the half wave potential value (E1/2) for ORR on the iron porphyrin catalyst (Fe(III)TMPyP) was observed upon addition of a specific quantity of Nafion ionomer on a glassy carbon working electrode, indicating not only a faster charge transfer rate but also the role of protonation in the oxygen reduction reaction (ORR) process. A membrane electrode assembly (MEA) was made as a sandwich of a Pt-coated anode, a Nafion® 212 membrane, and a Fe(III)TMPyP + Nafion ionomer-coated cathode. This three-dimensional catalysis system has been demonstrated to be working in a H2/O2 proton exchange membrane (PEM) fuel cell test.