Determination of Hydrogen Peroxide Generation/Decomposition Kinetics Using RRDE on Ketjen Black, Vulcan, 20% and 50% Vulcan-Supported Pt Electrodes

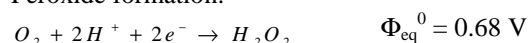Hadi Yehia[1], David A. Condit[2], Sergei F. Burlatsky[2], Thomas H. Madden[2]

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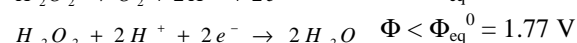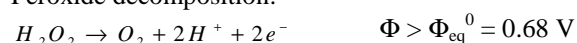
The investigation of the electrochemical reduction reaction of oxygen to hydrogen peroxide on different carbon and carbon-supported Pt electrodes at low potential is of interest with regard to the chemical stability of Nafion. This reaction was extensively studied using rotating ring-disk electrode (RRDE) where peroxide generation is formed by partial reduction of oxygen on a thin film electrode (Fig. 1) and detected on the Pt ring.[1-5] Kinetic data is needed to model peroxide generation/decomposition near a PEM (Polymer Electrolyte Membrane) fuel cell anode-membrane interface. In this study, we determined the rates of peroxide generation/decomposition at very low (close to hydrogen) potential and the impact of Pt/carbon ratio of typical anode catalysts.

Hydrogen peroxide is generated by 2e⁻ reduction reaction on the surface of carbon and Pt/Vulcan catalysts and decomposed on the ring according to the following reactions:

Peroxide formation:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad \Phi_{eq}^0 = 0.68 \text{ V}$$

Peroxide decomposition:

$$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^- \qquad \Phi > \Phi_{eq}^0 = 0.68 \text{ V}$$

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \qquad \Phi < \Phi_{eq}^0 = 1.77 \text{ V}$$

In this study, thin-film microelectrodes were prepared with two different Pt loadings (20% and 50%) on two different carbon supports, Vulcan XC 72 and Ketjen Black, and overlaid on a glassy carbon (GC) disk using published techniques.[1]

The electrochemical reaction rate, k (oxygen reduction to hydrogen peroxide) was determined by the RRDE experiments and presented as a function of disk-swept potential (0-1.2 V vs. SHE), and temperature (RT to 65°C).[6]

$$K_{O_2} = \frac{i_{O_2}^{(0)} \exp\left((\Phi_{eq}(O_2 \leftrightarrow H_2O) - \Phi)/b_{O_2}\right)}{4F \cdot C_{O_2}^{ref}}$$

Peroxide generation rate is governed by the product of the fraction of peroxide formation per unit of oxygen reaction rate, X_{HOOH}, and overall oxygen reduction rate K_{O2}:

$$K_{H_2O_2}^{(gen)} = X_{H_2O_2} K_{O_2}$$

Where $i_{O2}^{(0)}$ is the exchange current density of ORR, b_{O2} is the Tafel slope, Φ_{eq} =1.23 V is the equilibrium potential of ORR to water. The value for X_{HOOH} was obtained from the experimental data.

This data was used to refine our Nafion degradation model. The model calculates the steady state peroxide concentration in the membrane-electrode assembly (MEA) as a function of coordinate, potential, current density, electrode geometry and composition. It takes into account peroxide generation/decomposition at both, Pt and carbon, oxygen and hydrogen diffusion and reaction in the electrodes and oxygen, hydrogen and peroxide diffusion in the membrane. It indicates that carbon at the membrane-anode interface has a significant role in generating HOOH that leads to chemical degradation of Nafion in the vicinity of the anode/membrane interface during normal fuel cell (FC) operation. The rate of decomposition and location of the chemical attack depend on cell geometry, operational conditions and electrode composition.

References

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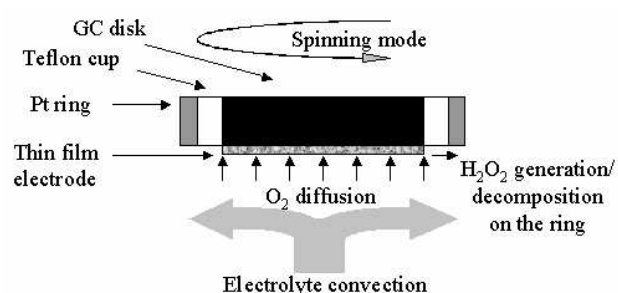
Figure 1. Peroxide formation on supported Pt/Vulcan rotating ring-disk electrode (RRDE). Peroxide decomposition is determined from the current measured when scanning the potential of a rotating disk in an argon-purged solution that contains a known peroxide concentration.