

An RRDE Evaluation of the C₂H₂ Effect on the ORR

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The commercialization of polymer electrolyte membrane fuel cells (PEMFCs) faces several challenges such as slow kinetics of the oxygen reduction reaction (ORR) and its impact on ionomer degradation by peroxide attack. Both problems originate from the Pt/C catalyst. Other species than O₂ also have an affinity for the Pt/C catalyst which leads to an even worse performance. For instance, the cathode is open to the ambient atmosphere which contains a multitude of undesirable species that leads to degradation. Thus, contamination mechanisms are important for both fundamental studies and practical applications.

The ORR kinetic loss and reaction mechanism changes resulting from fuel cell contamination were analyzed with a RRDE. Acetylene is a common welding fuel and chemical intermediate. Results obtained in our laboratory with a fuel cell demonstrated a very large performance loss due to C₂H₂ exposure. However, the effect of C₂H₂ on the ORR has not yet been explored.

The C₂H₂ was bubbled into the electrolyte (4040ppm C₂H₂ in N₂, or 0.14mM as calculated with Henry's law) for 1h to ensure electrolyte saturation and steady state electrode coverage. Cyclic voltammetry indicated a high C₂H₂ coverage on the Pt surface and an almost complete loss in electroactive surface area (Fig. 1). This observation is consistent with the loss in Pt oxidation/reduction peaks. The sharp increase in reduction current below 0.25V vs RHE was ascribed to acetylene hydrogenation to ethylene and ethane (1). Above 0.4V vs RHE, acetylene oxidation takes place at a rate that increases at higher potentials especially above 0.7V vs RHE. The oxidation peak is located at 1.18V vs RHE (not shown). The peak is associated with the oxidation of adsorbed hydrocarbon species.

The ORR polarization curves were measured with air (Fig. 2b). The half wave potential negatively shifted by 523mV, indicating that the ORR is severely retarded due to C₂H₂ adsorption. The performance loss is related to the shift toward the 2 electrons reduction path with H₂O₂ as the final product (ring current, Fig. 2a). The ring current significantly increased from 1μA with air to ~20 μA with C₂H₂/air at 0.2V vs RHE. Koutecky-Levich plots confirm the shift of ORR path from a 4 to a 2 electrons reduction process (Fig. 3). This is caused by the high C₂H₂ coverage on Pt, decreasing the availability of active and contiguous Pt sites, and hindering the bridge adsorption of O₂. As a result, the adsorption of O₂ mainly occurs with the end-on configuration and leads to H₂O₂ rather than H₂O. Therefore, acetylene not only reduces Pt/C performance for the ORR by decreasing the active area, but also shifts the reaction path toward H₂O₂ production, a detrimental species which leads to membrane decomposition and permanent cell degradation.

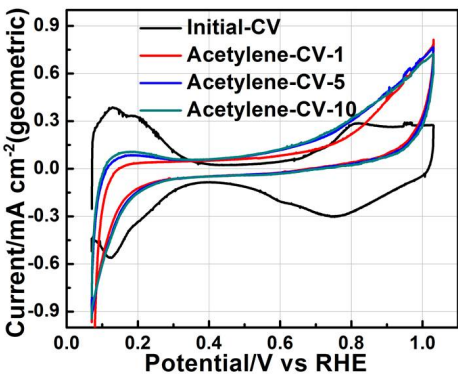


Fig.1. Cyclic voltammograms in the presence of 4040ppm C₂H₂ in N₂. 30°C, 20mV/s, 10 cycles.

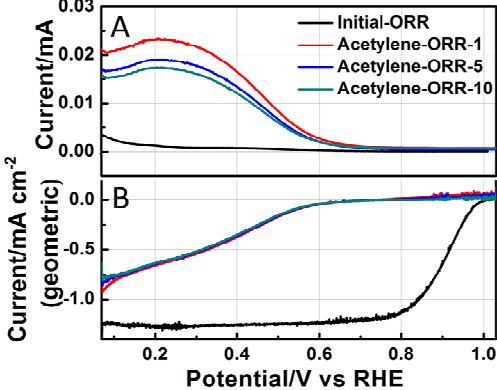


Fig. 2. RRDE ring (a) and disc (b) currents for the ORR in the absence and the presence of 4030ppm C₂H₂ in Air. 30°C, 20mV/s, 10 cycles, 1.2V vs RHE ring potential.

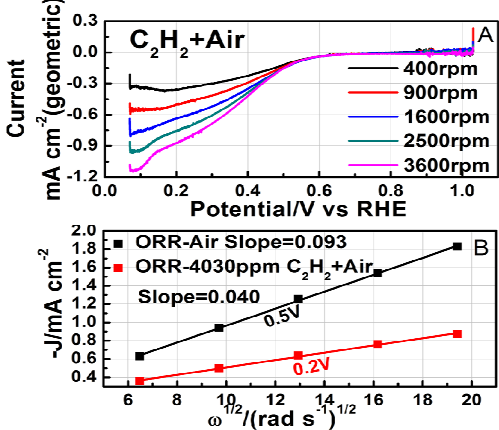


Fig. 3. ORR polarization curves in the presence of 4030ppm C₂H₂ at different rotation rates (a) and corresponding Koutecky-Levich plots (b). 30°C, 20mV/s, 10 cycles.

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