

Ruthenium Crossover in the Direct Methanol Fuel Cell with a Pt-Ru Black Anode

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The last decade has brought significant progress in the fundamental direct methanol fuel cell (DMFC) research, including anode and cathode electrocatalysis, membrane-electrode structure, and cell design. Although an impressive level of initial performance has been achieved,¹⁻³ a satisfying DMFC durability is yet to be demonstrated, especially in the context of recent reports indicating a rather fragile nature of the high-activity electrocatalysts used in PEM fuel cells.⁴⁻⁶ In line with the durability requirement, a large part of effort at Los Alamos National Laboratory has been directed at studying the mechanism of DMFC performance loss and developing appropriate procedures to prevent it.

In this contribution, we present the problem of ruthenium crossing from the DMFC anode catalyst, typically a Pt-Ru alloy black, through the polymer electrolyte membrane to the cathode, typically a Pt black. We focus on the nature of the process, the impact it has on the cathode activity, and the ways of avoiding it.

Ru contamination of the DMFC cathode has been studied in this work with the electrochemical CO stripping technique.⁷ In this method, CO is first chemisorbed on the electrode from the gas phase and then stripped off the surface in a single positive-going voltammetric scan. The position, shape, and charge of the CO stripping peak are all indicative of the surface area and composition. Example CO stripping voltammograms for one of the cathodes in a six-cell DMFC stack running for 850 hours are shown in **Figure 1**. The stack was operated on 0.3 M methanol at 75°C, current density of 80 mA cm⁻² and cathode air “stoichiometry” of 3.4. A comparison of the data for that cathode with stripping voltammograms recorded for reference Pt and Pt-Ru black electrodes indicates gradual contamination of this, and other cathodes in the stack (not shown), by Ru. **Figure 2** demonstrates the effect of Ru on the cathode performance in both H₂-air (Figure 2A) and DMFC (Figure 2B) operating modes, with solid lines representing initial performance of an Ru-free cathode and dashed lines representing performance after Ru had been driven across the membrane as a result of exposing the anode to a potential of 1.3 V in a driven cell mode for prolonged time. This procedure did not affect the electrochemically active surface areas of the cathode and the anode, but led to significant accumulation of ruthenium at the cathode surface (*cf.* CO stripping data, Figure 2C). As a result of ruthenium contamination, the cell suffered an approximate 25 mV penalty in hydrogen-air operation, which can solely be ascribed to lower cathode activity in oxygen reduction in the presence of Ru at the surface (Figure 2A). The performance penalty reached *ca.* 40 mV in DMFC operating mode (Figure 2B), the result that may be indicative of an additional negative effect of surface Ru on DMFC cathode’s ability to handle methanol crossover.

References

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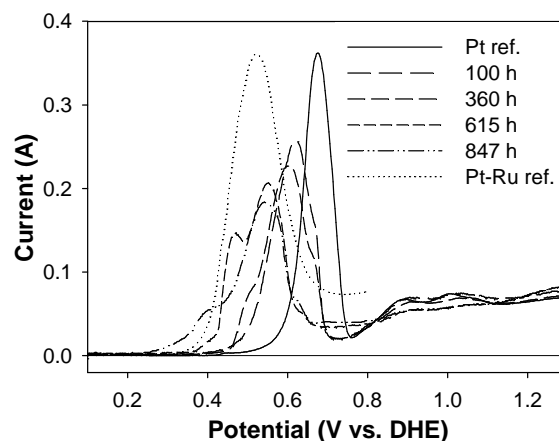


Figure 1. CO stripping from one of the cathodes in a six-cell stack at various times of a DMFC life test.

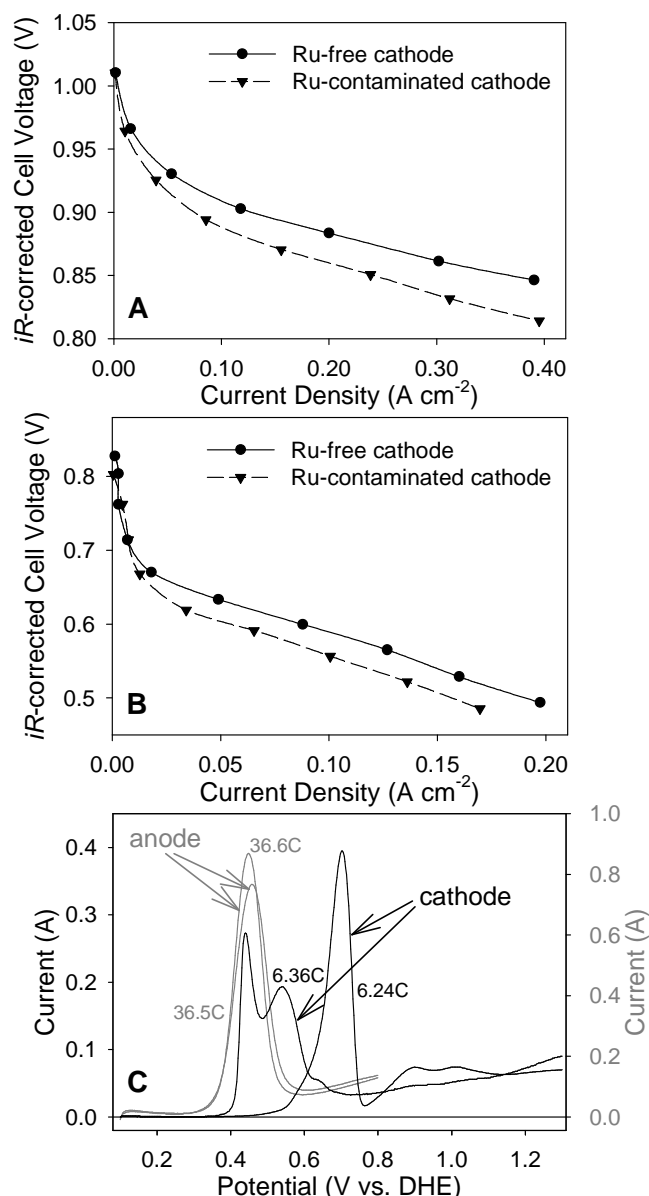


Figure 2. Impact of Ru contamination of cathode on cell performance: A – H₂-air, B – DMFC; C – cathode and anode CO stripping before and after test cathode contamination (see text).