A Numerical Study on the Impact of Cathode Catalyst Layer Loading on the Open Circuit Voltage

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Abstract

The open-circuit voltage (OCV) is the measured potential when no current is drawn from a cell. Theoretically this potential is given by the equilibrium potential, which is determined from thermodynamics based on the operating conditions. In practice, the actual potential at zero current is measured to be approximately 300 mV lower than the theoretical value. There are a number of possible causes for the lower OCV [1,2], however the most commonly accepted is that hydrogen crossing from the anode to the cathode will react in the presence of the platinum catalyst, thereby developing a mixed potential [2,3,4]. The OCV will therefore depend on the relative kinetics of the hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR) in the cathode such that when the ORR is equal to the HOR in the cathode, the OCV is reached, see Figure 1A. The overpotential required to achieve the required ORR will determine the potential at which OCV occurs and the overpotential required will be impacted by the platinum loading in the cathode. This effect is shown experimentally, where the OCV is seen to drop significantly at loadings less than 0.05mg/cm2 , as shown in Figure 1B.

The two-dimensional, macro-homogeneous model in OpenFCST [5] is extended to allow multiple reactions in an electrode and used to study the impact of platinum loading on OCV. The model accounts for the transport of oxygen, hydrogen, water vapour and solved water, as well as the potentials of both the solid and electrolyte phases. Both the ORR and HOR are considered in the cathode, and as the hydrogen crossover rate is only of the order of 1 mA/cm2, the accuracy of the kinetic models used for the ORR and HOR are studied. Furthermore, the impact of the HOR kinetics is examined by considering recent experimental studies [7,8] that have shown the HOR is severely limited at high overpotentials by anion adsorption and oxide formation.

This work shows that the double-trap kinetic model [6] for the ORR is able to match the polarization data in the kinetic region as well as correctly predict the OCVs for platinum loadings of 0.014-0.113 mg/cm2 . The commonly used Tafel equation, in

contrast, cannot simultaneously fit both the kinetic region of the polarisation curve and the OCVs. Using a HOR model that reproduces the kinetic data showing limited activity at high overpotentials does not accurately capture the OCV and predicts that hydrogen would escape through the cathode. The impact of microscale transport is studied using the ionomer covered carbon particle (ICCP) model. A parametric study on the parameters controlling the dissolution of hydrogen into the ionomer thin film and its diffusion to the reaction site indicate that hydrogen transport is not limiting at these scales for the cell structural parameters used in this study, but may be important at higher ionomer film thicknesses. Changing the operating oxygen partial pressure shows that the double

trap model in ref. [6] does not accurately capture the change in reaction rate with the change in oxygen concentration. This work demonstrates that modeling the OCV is helpful in fitting the kinetic region of the polarisation curve, as an accurate fit here and at OCV means that the kinetic model is accurate over several orders of magnitude in current and approximately 100mV of potential.

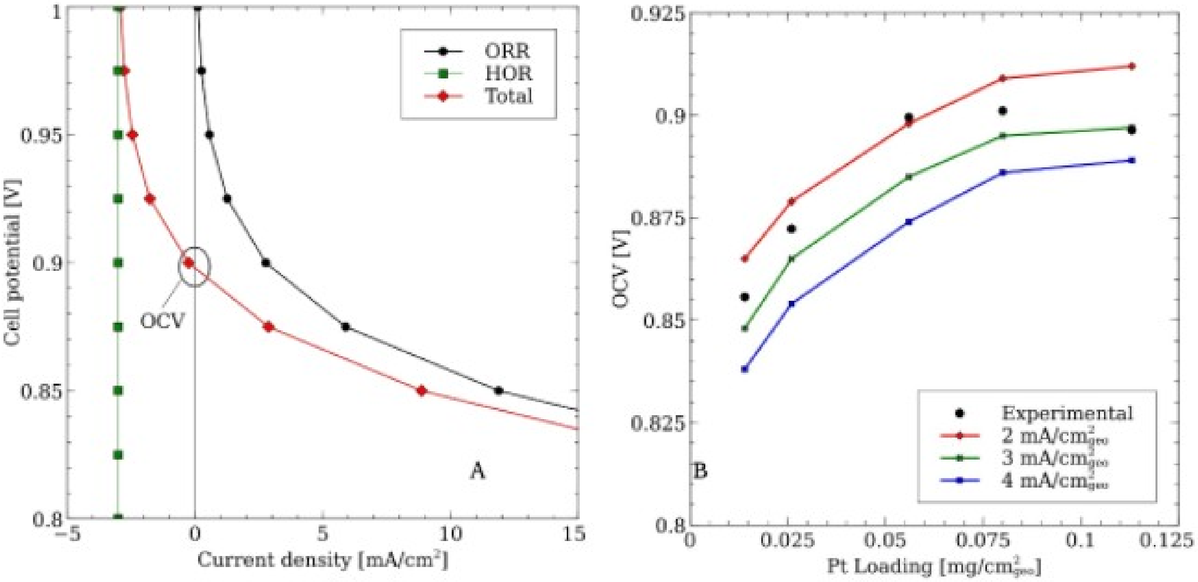

Figure 1: A) Total current in the cathode catalyst layer from the summation of the HOR and ORR, along with the location of the OCV. B) Change in OCV with platinum loading measured experimentally and determined numerically.

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