

KINETIC ANALYSIS OF THE OXYGEN REDUCTION REACTION IN HTPEMFCS AND IDENTIFICATION OF KINETIC PARAMETERS BY MEANS OF ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

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ΠΕΡΙΛΗΨΗ

In a high temperature polymer electrolyte, (HTPEM), fuel cell, the elusive sluggish inner sphere multistep oxygen reduction reaction, (ORR), takes a major fraction of the cell's overpotential resulting in lower performance and electrical efficiency. Numerous theoretical and experimental studies have been published over several decades regarding the ORR kinetics^[1-3], but it still remains an open subject of debate and research. In this study we propose a microkinetic transition state pathway for ORR, for a HTPEM fuel cell cathodic electrode, focusing on the importance of the cathodic impedance spectrum features, in the kinetic low current density, (l_{cd}), regime of operation where ORR activation power losses are dominant. The ORR impedance spectrum usually consists of a linear high frequency part feature and one or two arcs depending on the double layer capacitance, (C_{dl}), value. The high frequency linear part of the spectrum stems from the finite ionic, (H⁺), transport resistance in the catalyst layer while the two arcs arise; 1) from the charge transfer reaction steps which all appear under the same high frequency arc, directly related to the C_{dl} of the electrochemical interface, (EI), and 2) from the low frequency arc due to the relaxation of the adsorbed surface reaction intermediates on the catalyst surface, caused by the depletion of OH_{ad} on the surface. The reaction pathway impedance was derived analytically in the l_{cd} of operation and utilized for the extraction of the relevant kinetic parameters. Figure 1 demonstrates in semi-logarithmic scale the polarization resistance with its two contributions, (charge transfer and relaxation) vs overpotential. It is evident that relaxation impedance dominates the l_{cd} in contrast to what is expected by the Butler Volmer equation, while charge transfer impedance dominates the high current density regime of operation.

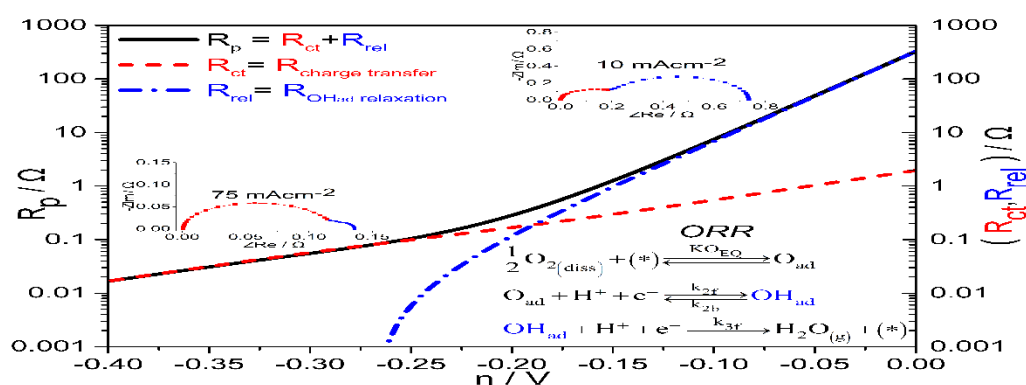


Figure 1

ΒΙΒΛΙΟΓΡΑΦΙΑ

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