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**Electrochemical Impedance Spectroscopy analysis of Oxygen Reduction  
Reaction mechanism and energetics for Fuel Cells**P.I. Giotakos<sup>1,2</sup>, S.G. Neophytides<sup>1,\*</sup>

<sup>1</sup>*Foundation for Research and Technology Hellas, Institute of Chemical Engineering Sciences,  
26504 Stadiou Str, Platani Rion, Greece*

<sup>2</sup>*Department of Chemical Engineering University of Patras, 26504 Rio Achaia,  
[Greece\\*neoph@iceht.forth.gr](mailto:Greece*neoph@iceht.forth.gr)*

**Abstract**

High temperature polymer electrolyte (HTPEM) fuel cells, due to their high power efficiency and zero greenhouse emissions, constitute a promising candidate for green energy production. However their commercialization is severely hindered by the sluggish and energy demanding, cathodic Oxygen Reduction Reaction (ORR). Even though numerous theoretical and experimental studies have been published the last 50 years, a consensus regarding ORR kinetics is yet to be reached, especially for HTPEMFCs.

In order to elucidate and extract the ORR kinetics/energetics, a three step reaction mechanism was proposed where the first step is the chemical dissociative adsorption of  $O_{2(g)}$  on Pt catalyst, followed by two electrochemical reduction/protonation ( $e^-/H^+$ ) steps. Then we developed an analytic microkinetic transition state model for both the steady state polarization curve (IV) and the intrinsic ORR impedance spectra. We recorded the experimental data at 180°C, under differential conditions, operating the cell at the low current density activation regime, where ORR power losses are dominant and mass transport limitations negligible. For the parameter identification, we developed an in house Monte Carlo regression algorithm which was achieved a unique solution and an excellent agreement with the experimental data.

The analysis of the results demonstrated that: 1) the commonly used empirical Butler Volmer equation is inadequate to describe the experimental results, 2) the impedance spectra consist of a) a linear high frequency part caused by the finite  $H^+$  transport resistance in the CCL, b) a high frequency arc from both charge transfer reaction steps and c) a low frequency arc from ORR's "kinetic inertia" due to the relaxation of the adsorbed surface reaction intermediates on the catalyst surface. 3) Regarding energetics, the high overpotential losses of ORR stem from the combined strength of both kinetically and thermodynamically imposed barriers, specifically: a) the high bonding strength of  $O_{ads}$  on Pt surface, responsible for the high overpotential spent in the activation region and b) the rather high activation energy of the  $O_2$  adsorption step, that poses kinetic limitations retarding ORR at low and high current densities respectively.