Deciphering ORR in HT-PEMFCs

Panagiotis I. Giotakos[1,2,*] and Stylianos G. Neofytides[1]

[1]Foundation for Research and Technology Hellas, Institute of Chemical Engineering Sciences, 26504 Stadiou Str, Platani Rion, Greece

[2]Department of Chemical Engineering University of Patras, 26504 Rio Achaia, Greece

Abstract

High temperature polymer electrolyte fuel cells (HT-PEMFCs) are a promising option for green energy production with high efficiency and no carbon emissions. However, their commercialization is impeded by the energy-intensive Oxygen Reduction Reaction (ORR) whose kinetics remain elusive for more than 5 decades.

In order to elucidate and extract the ORR kinetics/energetics, the dissociative three-step/two intermediates (O_{ad} and OH_{ad}) reaction mechanism was proposed with kinetics modelled according to microkinetic transition state theory. The model was incorporated into an analytic macro-homogeneous Transmission Line Model of the Cathode Catalyst Layer (CCL) for the simulation of both the steady state polarization curve (IV) and the intrinsic ORR impedance spectra. The experimental data (EIS and IV) were recorded at 180^oC, under differential conditions, with a $4cm^2$ single serpentine cell, operating at the low current density (activation) regime, where ORR power losses are dominant and mass transport limitations negligible. For the parameter identification, an in-house Monte Carlo regression algorithm was developed achieving both 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 properly describe the experimental results, 2) ORR is kinetically limited, 3) EIS 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 large low frequency arc from ORR's **kinetic inertia**, due to the relaxation of the adsorbed surface reaction intermediates on the catalyst surface. 3) Regarding the energetics, the high ORR thermodynamic/kinetic overpotential losses stem from: a) the high bonding strength of O_{ad} on Pt(111) surface and b) the rather high activation energy of the O_2 adsorption step.

The aforementioned methodology is currently applied *in Electrolyte Supported SOFCs* in order to decipher the HOR kinetics pathway.

Acknowledgements