**First-Principles Modelling of Solid Oxides Cell’s Electrodes**

Andrea Pizzato, Paolo Canu

Department of Industrial Engineering (University of Padua, Padua, Italy)

E-mail: andrea.pizzato.2@phd.unipd.it

Solid oxide fuel cells offer a clean and efficient alternative to conventional power generation based on fossil fuel combustion. However, their commercialization remains challenging due to various forms of polarization, primarily associated with the slow oxygen reduction reaction (ORR) rate. This study presents the development of a one-dimensional (1D) isothermal model solid oxides cells electrode, in the context of the KNOWKITE-X European Project.

The model incorporates mass balance equations for gaseous chemical species, adsorbed species and ions on electrode surfaces, and lattice species within the electrodes. It also accounts for charge and momentum conservation. At the electrodes, a microkinetic model describes species adsorption, electron transfer, and ion transfer processes for oxidation and reduction reactions. Percolation theory is employed to determine the microstructural and textural properties of the active layers, enabling the calculation of effective electrode properties.

This model bridges multiple scales, from the atomic scale, where elementary reaction steps are described, to the mesoscale, where the electrode is treated as a continuum percolating cluster, to the macroscale, which accounts for the electrode’s current output at a given overvoltage. It is used to investigate the phenomena limiting the electrode current output under various operating conditions, such as temperature, feed flow rate, composition, and applied voltage on two benchmark materials: LSCF (Lanthanum Strontium Cobalt Ferrite) as air electrode and Ni-YSZ as fuel electrode.

Another application is the rational design of the electrode itself, optimizing both electrode size and textural properties. Finally, the model can be adapted for other electrode materials and employed in the design of new mixed ionic-electronic conductor (MIEC) materials. Since a change in MIEC composition affects only the model parameters, while the governing equations remain unchanged, the model can be applied to new materials once their kinetic parameters are determined.

The structural properties of electrodes significantly influence cell performance. As an example, reducing the thickness and increasing the porosity of the LSCF cathode shifted concentration polarization to lower voltages, thereby improving performance. However, excessive porosity reduced particle contact, diminishing current output. Increasing pore formation by adding pore formers during electrode manufacturing mitigated diffusion limitations at high cell utilization but required careful balancing to maintain optimal performance and prevent mechanical failure of the electrodes. Additionally, the model assessed the impact of lattice species composition on electrodes performance.

**Keywords**: *Solid oxides, microkinetics, modelling, electrode design*