

The Penetration Length of the Heterogeneous Electrocatalysis in Solid Oxide Fuel Cells

Antonio Bertei^{1,2*}, Enrique Ruiz-Trejo¹, Paola Carpanese³, Antonio Barbucci³, Cristiano Nicoletta², Nigel Brandon¹

1 Department of Earth Science and Engineering, Imperial College London, SW7 2AZ London, UK; 2 Dipartimento di Ingegneria Civile e Industriale, Università di Pisa, 56126 Pisa, Italia; 3 Dipartimento di Ingegneria Civile, Chimica e Ambientale, Università di Genova, 16129 Genova, Italia

**Corresponding author: antonio.bertei@for.unipi.it*

Highlights

- Modelling, 3D tomography and impedance spectroscopy for penetration length in SOFCs
- Penetration length of 250 nm in cathode by fit of different conditions and particle size
- Penetration length of 4 nm in anode from alternative approach based on fractal dimension
- Performance improvement by controlling the surface properties of electrocatalysts

1. Introduction

Solid oxide fuel cells (SOFCs) are highly efficient devices which produce electric energy from the electrochemical conversion of gaseous fuels, such as hydrogen. The electrochemical conversion of hydrogen takes place within the electrodes, which are porous composite layers consisting of randomly-dispersed electron-conducting and ion-conducting particles. More specifically, electrochemical reactions take place in the proximity of the three-phase boundary (TPB), which is the contact perimeter among the three different phases where gaseous reactants, electrons and ions coexist [1].

Both the cathodic and anodic electrochemical reactions involve the adsorption of gaseous species onto the catalytic electron-conducting phase followed by the surface diffusion of adsorbed species towards the TPB, where electron charge-transfer takes place [2-3], as shown in Figure 1. A penetration length l_δ can be identified as the characteristic length around the TPB wherein the rate-determining coupled adsorption/diffusion processes take place. Thus, the rate of reduction and oxidation reactions depend not only on the TPB length per unit volume but also on the extension of the penetration length.

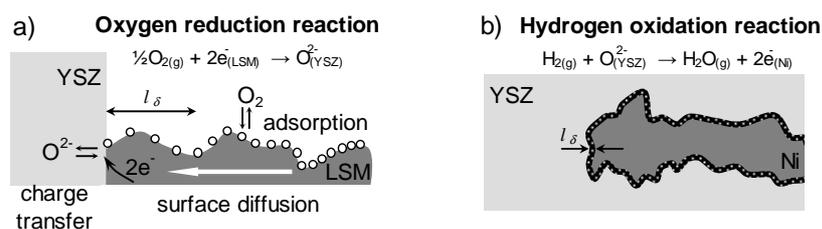


Figure 1. a) Oxygen reduction reaction in a composite cathode made of yttria-stabilised zirconia (YSZ) and lanthanum strontium manganite (LSM), lateral view; b) hydrogen oxidation reaction in a composite anode made of YSZ and nickel, top view. In both cases the penetration length l_δ identifies the extension of the reaction zone around the TPB.

2. Methods

The penetration length is quantified in both cathode and anode by using physically-based models, electrochemical impedance spectroscopy and 3D tomography. In particular, while in the cathode the penetration length can be probed by experimentally varying the particle size [2], an alternative approach based on the calculation of the TPB fractal dimension is applied in the anode [1].

3. Results and discussion

For the cathodic reaction, the penetration length is evaluated in the order of 250 nm by fitting electrochemical impedance spectroscopy data for different temperatures and oxygen partial pressures [3].

This is confirmed by varying the LSM particle size, which effectively changes the Thiele modulus of the oxygen reduction reaction. The electrode resistance scales with the calculated Thiele modulus as predicted by the kinetic model [2].

An alternative approach, shown in Figure 2, is applied for the anodic reaction [1]. The TPB length as a function of time, as extrapolated by fitting the anode resistance with a physically-based equivalent circuit, is compared with the TPB length evaluated with 3D tomography at 30 nm resolution. By resampling the microstructure for different resolutions, the fractal dimension of the TPB for the as-sintered anodes is calculated, being equal to 1.5. By comparing the extrapolated TPB length and 3D tomography data, the fractal dimension allows for the estimation of the penetration length of the hydrogen oxidation reaction, which is equal to 4 nm. Such a small penetration length could not be probed by using the conventional approach adopted for the cathode because it would be difficult to accurately control the diffusion length.

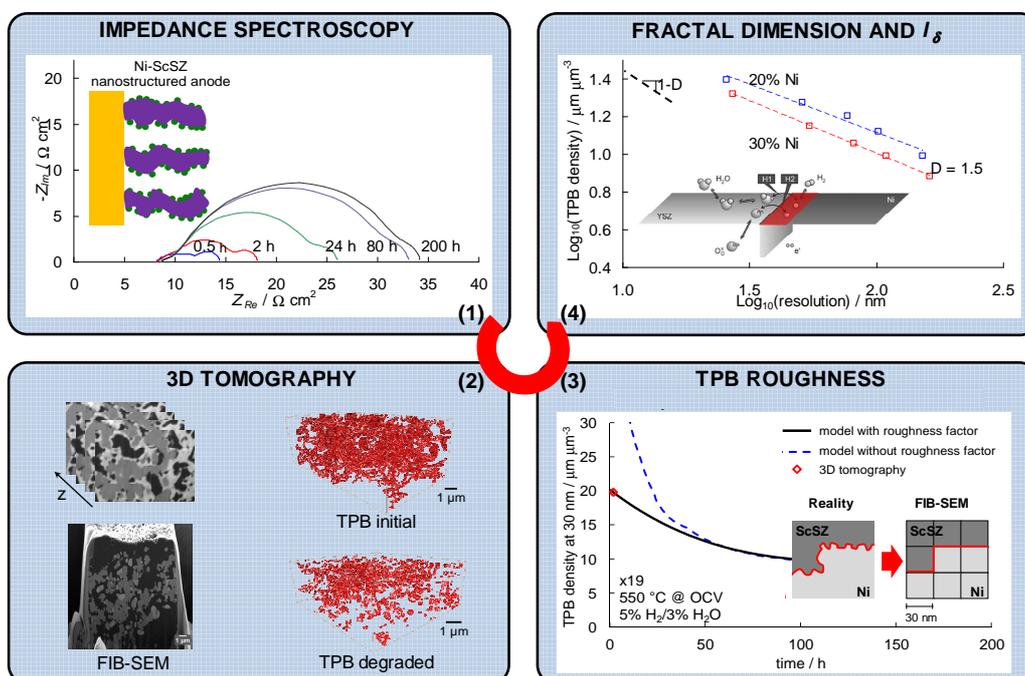


Figure 2. Novel approach for the determination of the penetration length in nanostructured SOFC anodes by using real-time impedance spectroscopy, 3D tomography and the evaluation of the TPB fractal dimension.

4. Conclusions

The penetration length of the oxygen reduction reaction in LSM/YSZ cathodes is equal to 250 nm, while it is 4 nm for the hydrogen oxidation reaction in SOFC anodes. Due to the extended reaction area, the cathode efficiency can be increased by enhancing the cathode adsorption and surface diffusion properties of the electrocatalyst rather than by increasing the TPB length per unit volume only. On the other hand, the small penetration length in nanostructured anodes (4 nm) suggests that co-infiltrating sintering inhibitors as large as 50 nm is ineffective to prevent performance degradation due to Ni coarsening, which can be limited by controlling the interfacial energy between Ni and the ionic conductor.

References

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Keywords

porous electrode; redox reaction; 3D tomography; modelling