A step backward for a new approach to understand and modelling LSM/YSZ composite cathodes

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EERA FCH2-SP2 WORKSHOP in frame of EIA10
Bridging experimental and numerical research: development and optimization of advanced characterization tools – Electrochemical Impedance Spectroscopy
Why this study (1) : cell type and geometries

1st we wish to check some of our data and conclusions obtained in the past with a cell geometry that does not exactly match the suggestion for reliable impedance analyses.

Reference electrode position

Electrodes misalignment


Fig. 2 Schematic (a) showing the network of ideal circuit elements electrically equivalent to a hypothetical SOFC and (b) the three-electrode configuration employed in a planar SOFC.
2nd we want to implement the experimental/theoretical studies we performed on composite cathodes [1, 2, 3], producing simulated EIS spectra on the basis of a theoretical adjustable model.

To do this we need a base of experimental data on a simplified system (no composite, no MIEC) for a validation of a theoretical model and code under study.

This code [4] is based on the

i. reconstruction of the electrode structure
ii. quantification of effective properties (diffusivity, conductivities, …)
iii. simulation of the reaction process.

Summary: mechanistic model on composite electrodes

\[ \Delta E = \eta_s = \eta_v + R_{io} i_v \]

A) For **low overpotential** we have an analytical solution using low field Butler-Volmer equation \( \eta/i = R_{ct} = RT/Fi_0 \);

B) For **medium-high overpotential** we should solve this equation numerically including the complete Butler-Volmer eq. for \( \eta \).

A) \[ \Delta E = R^s_{ct} i_s = R^v_{ct} i_v + \rho_{io} \delta i_v A_c/A \]
\[ i_{tot} = i_s A_s + i_v A_c \]
\[ i_{tot}/A = \Delta E/R_{tot} \]

\( A_c \) = reactive contact area into volume
\( A_s \) = reactive area at the surface
\( A \) = electrode area

- \( R_{ct} \) charge transfer
- \( R_{io} \) ionic resistance
- \( i_s \) surface current
- \( i_v \) volume current
(subscripts: \( S \) = surface; \( V \) = volume)
Summary: result of the model and literature

For a fast oxygen surface reaction the oxygen incorporation mainly occurs close to the three phase boundary (a); ...If the resistance of the oxygen surface reaction increases, more and more particle layers contribute to the oxygen reduction reaction (c) and for very high values of the resistance (d) the entire cathode is active."


\[ R_{tot} = R_{ct}^s \left( \frac{R_{ct}^v}{a_c \delta} + \rho_{io} \delta \right) \left( \frac{R_{ct}^v}{a_c \delta} + \rho_{io} \delta \right) \frac{A_s}{A} + R_{ct}^s \]

\[ A_c = a_c \cdot V = a_c \cdot A \cdot \delta \]

\[ A_c = \text{reactive contact area into volume} \]

\[ A_c = \text{reactive site per volume unit} \]

\[ A = \text{electrode area} \]

\[ \Delta = \text{electrode thickness} \]
Summary: Simulation of EIS and experimental (literature)

3rd Many studies have been performed on pure LSM in the past, the oxygen reduction reaction is however not clear. We believe that this is a focal point. Probably not only TPB extension has to be considered for improve electrode performance.

4th Component duration is one of the main issue for SOFC development. In heavy loads SOFC or SOEC, LSM/YSZ cathode are still considered a good solution for their high chemical stability.
Looking for reliable electrochemical EIS data
(electrolyte supported cells)

- **Electrolyte:** YSZ (TZ-8Y Tosoh) sintering 1500°C 1h. Pellets diameter 35 mm, thickness 3 mm.

- **Electrode:** Screen printed (AUR’EL 900, AUR’EL Automation S.p.A) (La$_{0.8}$Sr$_{0.20}$)MnO$_{3-x}$ (Fuelcellmaterials) (squeegee speed = 0.12 m/s: squeegee load = 4.5 kgF, sintering: 1050 °C and 1150 °C for 2h, electrode thickness 5 μm.

- High precision mask to avoid electrode misalignment.

- **Cell A:** WE-RE distance > 3 x electrolyte thickness

- **Cell B:** WE-RE distance < 3 x electrolyte thickness
- **Linearity:** the input perturbation signal small enough to keep the state of the investigated system unchanged.

- **Check of memory effects:**

- **Frequency density:** 10 point per decade

- **Correction of data for the parasitic inductance**
Results: Cell B geometry, 2 and 3 electrode configuration

Cell B at ocv:
2- and 3-electrode configurations

1. Quite good agreement in this cell geometry (CELL B) at ocv and low η

2. Quite good symmetry of the cell; equal polarisation resistance of the two opposite electrodes

3. Characteristic shape of the frequency dispersion at ocv and low η

Example of $R_{pol}$ evaluation
Results: Cell A and B geometries in comparison
(3-electrode configuration)

1. Quite good agreement in this cell geometry (CELL A and B) at ocv and low $\eta$
2. Cell A and B Deviations at higher $\eta$
Electrode sintered at 1050 or 1150 °C

Porosity $_{1050} = 49\%$
Avg particle size = 0.7 μm

Porosity $_{1150} = 34\%$
Avg particle size = 2 μm

$R_{pol}$ not normalised.
At high $\eta$ the global reaction kinetic of the two electrodes get closer
From surface to bulk transport

(activation of a second path for reaction)

(b) In the overpotential range corresponding to the reduction of the LSM (around point C in Fig. 10), oxygen vacancies are created in the electrode material according to the following global electrode equation:

\[(2Mn_{\text{Mn}} + O_{\text{YSZ}}^0) \text{LSM} + (Vo^{o}) \text{YSZ} + 2e^- \rightarrow (2Mn_{\text{Mn}} + Vo^{o}) \text{LSM} + (O_{\text{YSZ}}^0) \text{YSZ}\]  (8)

where \(Mn_{\text{Mn}}^z\) represents a \(Mn^{4+}\) on a regular manganese crystallographic site and \(Mn_{\text{Mn}}^z\) a \(Mn^{3+}\) on the same site. The peculiar behavior observed in this transition zone could be associated with a significant contribution of this reaction to the overall current.

(with dense pin shaped LSM electrode)

(with dense circular microelectrode)

H.T. Chen et al Langmuir 27 (2011) 6787
(La_{0.75}Sr_{0.25})MnO_{3-x} computational mod)
From surface to bulk, looking at electrolyte resistance

Some obtained Nyquist plots

- **800°C**
  - $p_{O_2} = 1$

- **750°C**
  - $p_{O_2} = 1$

- **700°C**
  - $p_{O_2} = 0.21$
  - OCV

Fitting analysis: Voigt type model

\[ R_1 (R_2 Q)(R_3 C) \]

Good fitting with a widely used circuit for SOFC cathode:

- \( R_1 \) electrolyte resistance
- \((R_2 Q)\) low frequency arc: to be ascribed
- \((R_3 C)\) high frequency arc: to be ascribed

F. van Heuvein, H. Bouwmeester J Electroc. Soc. 144 (1997) 144
Fitting analysis $R_1(R_2 Q)(R_3 C)$

$R_2$ (low frequency arc) shows a dependance on the applied overpotential

$\ln(1/R_3)$ shows a linear dependance on $\eta$ at medium-high overpotentials
Effective capacitance of the $R_2Q$ element

$C_{eff} \approx 2 \div 6 \times 10^{-4} \text{ F cm}^{-2}$ depends on bulk volume and values in agreement with Fleig et al.

Average $n$-CPE values 0.6

$C_{eff} = Q^n R_2^n$

Comparison between the effective and the electrostatic capacitance:

$$R_1(R_2 Q)(R_3 C)$$

capacitance decrease due to faster charged electroactive specie transport
**Reaction mechanisms**

**Overall reaction path:** \[ O_{2(gas)} + 4e^- + 2V_{O}^{\cdots} \Leftrightarrow 2O_{O}^{x} \]

**Possible reaction steps:** J. D. Kim et al. *Solid State Ionics* 143 (2001) 379

- **ads + 1\textsuperscript{st} charge transf**
  \[ O_{2(gas)} \rightarrow 2O_{ad} \quad \quad O_{ad} + e^- \rightarrow O_{ad}^- \]

- **transport**
  \[ O_{ad}^- \rightarrow O_{TPB}^- \]

- **2\textsuperscript{nd} charge transf**
  \[ O_{TPB}^- + e^- \rightarrow O_{TPB}^{\cdots} \quad \quad O_{TPB}^{\cdots} + V_{O}^{\cdots} \rightarrow O_{O}^{x} \]

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The prediction of transport properties and electrochemical performance in SOFC electrodes, is the approach we look at for helping the experimental interpretation.

Integrated microstructural–electrochemical model

Material properties → Powder characteristics → Operating conditions → Cell geometry

- Air
- Fuel

4e- + O2 → 2O2-
Spherical particles: drop-and-roll

1\textsuperscript{st}. numerical construction of the electrode structure using a sedimentation algorithm, based on data extracted from morphological observation.

Simulated procedure

1 – Drop
2 – Roll
3 – Stability
4 – Sintering
Monte Carlo random-walk

2\textsuperscript{nd} random walk Monte Carlo simulation used for calculation of effective properties (gas diffusivity, conductivities, TPB length).

\[ D_{\text{eff}} = \frac{<R^2>}{6\Delta t} \]

\[ \sigma_{\text{eff}} = \frac{<R^2>}{6\Delta t} \]

TPB length

Pore size

3rd. Application of a model able to produce simulated impedance spectra, which considers the influence of some parameters (external molar fraction of oxygen, working temperature…).
The presented analysis is still preliminary and needs further validation, possibly also by methodology based on non arbitrary choices (e.g. DIA, …).

The code for the EIS simulation is under implementation, to take into account adsorption and surface or bulk transport of the electroactive specie.

The results presented and the literature demonstrate that LSM is a complex system and we are still far to clearly understand its behaviour.

This last consideration makes us think that there is room for further improvements of LSM/YSZ electrodes, that till now have been optimised mainly looking at TPB length.
it will be great that each presentation covers points like for example:

• Current problems and challenges
• Role of the EIA for advanced characterization of catalyst/electrode and what kind of information can give for models development and validation
• What we need to improve to develop further the experimental validation using EIS as an advanced characterization technique
• Anything else that you consider relevant to discuss…
Trend of \( \ln(R_{\text{pol}})^{-1} \) versus overpotential at 800°C and \( P(O_2) = 1\text{bar} \), square sample sintered at 1050°C, circle sample sintered at 1150°C.

If activation control

B-V eq hold:

then:

\[
i = i_0 \left[ \exp \left( \frac{\alpha_c nF}{RT} \eta \right) - \exp \left( -\frac{-\alpha_c nF}{RT} \eta \right) \right]
\]

\[
R = \frac{d\eta}{di} \Rightarrow \frac{1}{R} = \frac{di}{d\eta} = -i_0 \left( -\frac{\alpha_c nF}{R_g T} \right) \exp \left( -\frac{-\alpha_c nF \eta}{R_g T} \right)
\]

\[
\ln \frac{1}{R} = \ln \frac{i_0 \alpha_c nF}{R_g T} - \frac{\alpha_c nF \eta}{R_g T} = A - B \eta
\]
Composite cathode LSM/YSZ

700 °C
750 °C
800 °C

700 °C
750 °C
800 °C

700 °C
750 °C
800 °C

700 °C
750 °C
800 °C
normalisation of raw data play a role?
800°C - 100% O\textsubscript{2} - OCV

- $Z''$ [\(\Omega \ cm^2\)]
- $Z'$ [\(\Omega \ cm^2\)]

Real
Simulation Comsol
Fitting
Simulation $R_2$
Simulation $R_3$