

An Agglomerate Model for the Rationalisation of MCFC Cathode Degradation

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Abstract: This paper describes the numerical modeling of a key material-stability issue within the realm of Molten Carbonate Fuel Cells (MCFC). The model describes the morphological and attending electrocatalytic evolution of porous NiO electrodes and is apt to predict electrochemical observables that can be recorded during Fuel Cell operation. The model has been validated with original experimental data measured with different laboratory-scale system.

Keywords: MCFC, reaction-diffusion PDE system, numerical simulations, cathode.

1. Introduction

Cathode degradation is a point of major concern in the development and management of commercial-scale MCFC-based power generation systems [1]. Degradation affects essentially all materials present in an MCFC – both functional and structural – and goes on through a host of different mechanisms, involving chemical, electrochemical and thermomechanical processes. Cathode materials – essentially sintered NiO, without or with Co-doping for improved stability – undergo a series of physico-chemical changes during MCFC operation, chiefly: (i) lithiation during the first few hundred hours of operation; (ii) dissolution into the molten-carbonate electrolyte and (iii) particle agglomeration on the mesoscopic scale. Process (i) leads to an improvement of electrocatalytic properties, while (ii) and (iii) cause a loss of cathode performance, principally related with the decrease of electroactive area and change in pore structure. Among these three main causes of degradation, the single most critical one seems to be particle agglomeration. More details on the problem of MCFC degradation are offered in [2] The Salento University group, in conjunction with the ENEA

group are addressing this particular issue with a combination of theoretical and experimental approaches. This particular issue in the literature, this problem has been attacked chiefly by developing novel materials [1, 3-5]) that are ideally tested under real fuel-cell operating conditions [6-11]. As far as numerical modelling is concerned, just a few papers have appeared on MCFC cathodes, describing the coupled electrochemistry and mass-transport in homogeneous and heterogeneous two-dimensional (2D) schemes (for a recent, comprehensive review, see [12]). Nevertheless, publications on the mathematical modelling of cathode degradation issues are not available in the literature, to the best of the authors' knowledge. In this paper, we attack the problem of the mathematical modelling of mesoscopic morphological changes of the cathode morphology, related to material evolution (typically: lithiation in the first stages of operation of a pristine cell) and degradation (assumed to be controlled by agglomeration of the micrometric NiO particles). In Section 2, we describe the mathematical model based on [13], in Section 3 we describe the numerical results obtained by Comsol. In Section 4 the model studied have been validated with experimental results, both original and derived from the literature.

2. The mathematical model

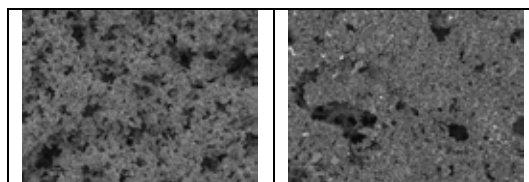


Figure 1. SEM Micrographs of a porous NiO(Li) cathod (500 \times): new (left) and after 1000 hours of working time in a laboratory MCFC (right)

On the basis of SEM observations of NiO cathodes (see Figure 1), an Agglomerate Model (AM) of the type analysed in [13] has been considered. As far as the domain is concerned, we developed and tested 2D and 3D versions of the AM with a range of particle densities (from 7 to 2432 particles in the domain). The superoxide mechanism has been considered for O₂ reduction. The mathematical model consisted in a system of coupled reaction-diffusion PDEs, corresponding to the steady state mass-balances equations for the concentrations of peroxide $c^{ox}(\mathbf{x})$ of carbon oxide $c^{cd}(\mathbf{x})$ and for the potential $\eta(\mathbf{x})$.

$$\nabla^2 c^{ox} = 0; \nabla^2 c^{cd} = 0; \nabla^2 \eta = 0; \quad \mathbf{x} \in \Omega$$

Electrochemical kinetics has been accounted for by non-linear boundary conditions (b.c.) at the electrode-electrolyte interfaces $\partial\Omega_1$, based on Butler-Volmer type relationships between local current density and overvoltage. In Table 1 we report also the b.c. given on the gas-electrolyte $\partial\Omega_2^g$ and the porous matrix-electrolyte $\partial\Omega_2^e$ interfaces, respectively.

In order to have a more precise morphology description of the agglomerate, for example to take into account the physical contact among single particles of the catalyst, we study also a 3D version of the model. The integration domain has been extruded by the 2D version (compare Figure 2 with Figure 3 below) and the catalyst particles are connected by small flat cylinders.

In Figure 2 the 3D porous matrix correspond to the *empty* part. The same Partial Differential Equation (PDE) system as in the 2D version holds, but further boundary conditions have to be considered on top, bottom and lateral sides (see $\partial\Omega_3$ in Table 1). The domain of integration and a simulation for the potential and current distributions is given in Figure 2

Our main goal is to compute concentration, current density and potential profiles over the different domains considered, as a function of the applied potential and to check for physical consistency.

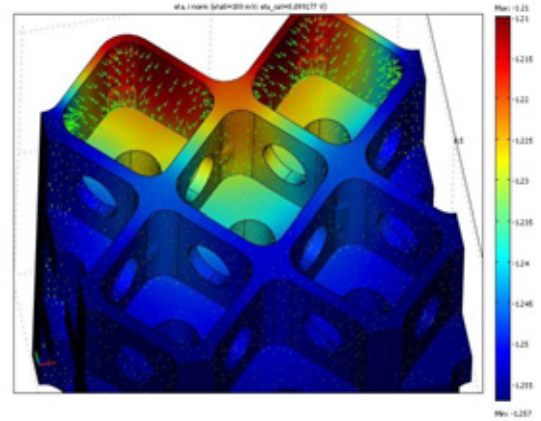


Figure 2. 3D Agglomerate model- COMSOL simulation of potential and current distribution (arrows) in the electrolyte of the MCFC cathode. The *empty* part correspond to the porous matrix.

$\partial\Omega_1$	$\partial\Omega_2^g$	$\partial\Omega_2^e$	$\partial\Omega_3$
$\nabla_N c^j = k_m g(c^{ox}, c^{cd}, \eta)$	$c^j = 1$	$\eta \equiv \eta_0$	$\nabla_N \eta = 0$
$\nabla_N \eta = k_3 g(c^{ox}, c^{cd}, \eta)$	$\nabla_N \eta = 0$	$\nabla_N c^j = 0$	$\nabla_N c^j = 0$
$j = ox, cd;$	$m=1,2$		

Table 1: Boundary conditions for the Agglomerate Model in 2D and 3D (plus last column) cases

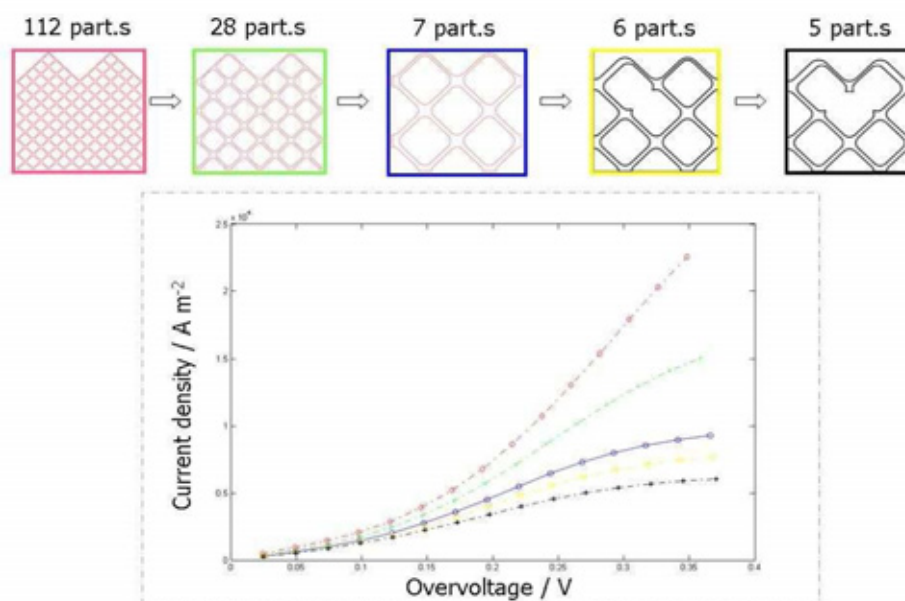


Figure 3 – Cell voltage – current density curves, computed using the integration domains shown at the top of the figure, corresponding to progressive degrees of NiO particle agglomeration.

3. Numerical simulations and results

The AM model for the different domains investigated has been implemented by using the Equation Based Modeling approach in COMSOL Multiphysics v.3.5, both in the 2D and 3D cases. The integration domains in 2D are shown at the top of the Figure 3 and, correspond to progressive degrees of NiO particle agglomeration.

The second step, based on suitable averaging procedures on the numerical results of the simulations, is to evaluate current-potential (I-V) curves corresponding to the different 2D and 3D geometries of interest. On the basis of the analysis of the computed I-V curves, reported in Figure 3, we concluded that 2D modelling – though, of course, underestimating mass-transport within the cathode – is adequate in order to track geometrical changes, descriptive of morphological changes, in terms of the integral electrochemical performance of the cathode. In particular, it was possible to follow the development of a limiting current density in estimated I-V curves, corresponding to catalyst particle agglomeration .

4. Model validation

In order to validate our model, we resorted to the use of two sets of experimental data: (i) original time-dependent I-V and Electrochemical Impedance Spectrometry (EIS) data, measured during 1000 h of operation of a pristine MCFC in the ENEA laboratories; (ii) literature cell-voltage data, recorded during long-term (up to 40,000 h [6Tanimoto 98]) MCFC operation. On the basis of electrochemical data, during experiment (i) an improvement of the cell performance has been found, resulting from lithiation of NiO during the initial 600 h, while degradation, due to particle agglomeration, can be followed in the interval 600÷1000 h. The data corresponding to experiment (ii) only describe cathode degradation. Our model proved adequate to yield - on the basis of morphological changes - the electrochemical observables corresponding to both cathode improvement and degradation. A selection of experimental and computational results are displayed in Figures 3 and 4. Time-dependent limiting c.d.s (Figure 4D) can be derived from I-V measurements (Figure 4C).

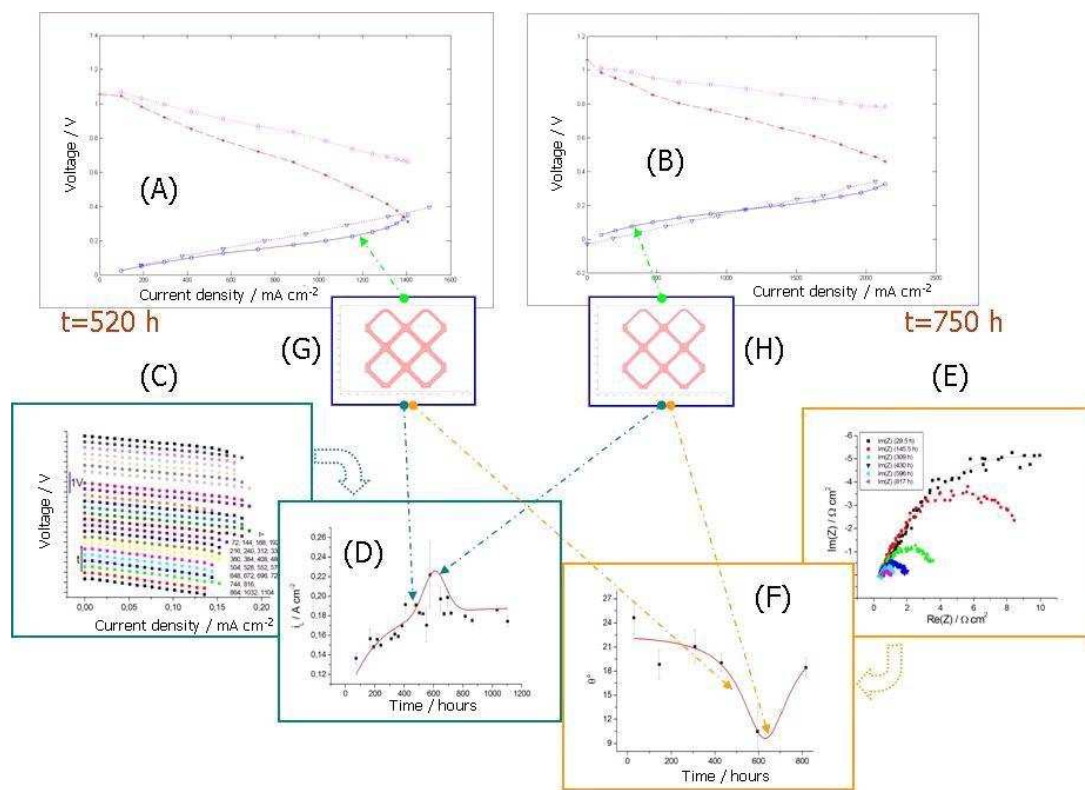


Figure 4 – Comparison of original electrochemical experimental data and numerical computations performed with the model proposed in this paper.
 (A) I-V curves corresponding to 520 h of MCFC operation: magenta, measured cell V vs current density (c.d.); red, measured anodic V vs. c.d.; blue circles: measured cathodic V vs. c.d.; blue triangles: computed cathodic V vs. c.d..
 (B) I-V curves corresponding to 750 h of MCFC operation: same colour codes as in (A).
 (C) Experimental V_{cell} -I curves measured at several MCFC operation times with fits to an electrokinetic model detailed in [12].
 (D) Limiting c.d.s corresponding to the curves shown in (C).
 (E) EIS spectra measured in the range 50 kHz÷10 mHz at several MCFC operation times with fits to an electrokinetic model detailed in [12].
 (F) Depression angles derived from the fits shown in (E).
 (G) and (H): integration domains used for the numerical computations with COMSOL.

Similarly, the temporal evolution of the EIS depression angle (Figure 4F) – diagnostic of electrode porosity – can be derived from EIS spectra (Figure 4E). Both electrochemical parameters witness an improvement of cathode behaviour during the first 600 h, followed by a decrease of performance. Lithiation gives rise to an increase of particle size accompanied by a decrease of electrolyte volume, without change of particle number. This type of geometry

change yields a modification in the computed I-V curves, that corresponds to the experimental results. Subsequent degradation can be described in terms of a decrease of particle number, with constant electrolyte volume.

In Figure 5, we show the comparison between experimental voltage evolutions and predicted voltages, corresponding to a sequence of degrees of particle agglomeration.

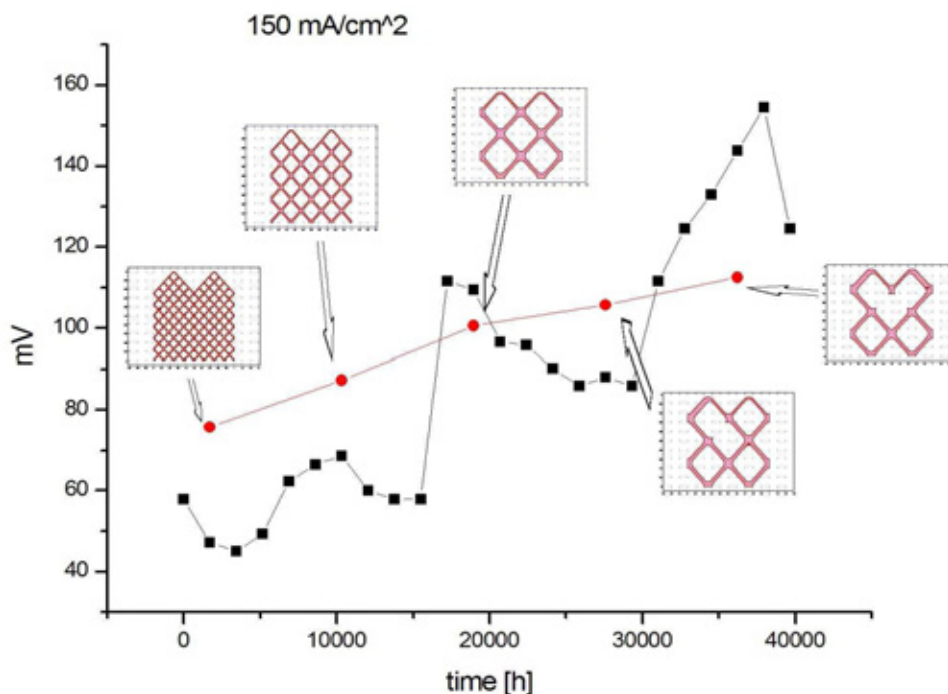


Figure 5 – Comparison of experimental (black points) and computed (red points) cathodic voltages. Time-dependent experimental data are derived from [6]. Computed results correspond to the domain geometries shown in the figure.

5. Conclusions

In this research, we have developed a numerical model – based on the literature agglomerate scheme – able to predict the changes in electrocatalytic activity brought about by lithiation (leading to an improvement of cathode performance) during the initial stages of Fuel Cell operation as well as the subsequent agglomeration (bringing about a loss of catalyst active area). The model yields local electrochemical data that can be cast into algorithms with a straightforward physical meaning able to represent integral electrokinetic quantities that can be measured during a real MCFC run. The model has been validated with original experimental data. The modular structure of our model makes it possible to extend it with the implementation of different, possibly more sophisticated, contribution to

electrode degradation, as well as to follow the evolution of anode materials.

6. References

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