In Situ X-Ray Spectromicroscopy Investigation of the Material Stability of SOFC Metal Interconnects in Operating Electrochemical Cells**


The present in situ study of electrochemically induced processes occurring in Cr/Ni bilayers in contact with a YSZ electrolyte aims at a molecular-level understanding of the fundamental aspects related to the durability of metallic interconnects in solid oxide fuel cells (SOFCs). The results demonstrate the potential of scanning photoelectron microscopy and imaging to follow in situ the evolution of the chemical states and lateral distributions of the constituent elements (Ni, Cr, Zr, and Y) as a function of applied cathodic potential in a cell working at 650°C in 10⁻⁵ mbar O₂ ambient conditions. The most interesting findings are the temperature-induced and potential-dependent diffusion of Ni and Cr, and the oxidation-reduction processes resulting in specific morphology-composition changes in the Ni, Cr, and YSZ areas.

Introduction

The efficiency, environmental friendliness and prospective fuel flexibility of solid oxide fuel cells (SOFCs) makes them very attractive energy generation systems. Notwithstanding the appeal, still a major concern for large-scale implementation of these complex multicomponent systems remains the stability and durability of the employed materials under typical operation conditions of high temperatures (600–1000°C) and applied potentials. Using benchmark material characterization schemes that mimic SOFC processes is not sufficient, since a real device entails multiple processes on different length scales and reacting interfaces that may be imbedded and not always accessible to analytical tools. In fact, only a limited number of in situ photoelectron spectroscopy studies under operating conditions are reported for batteries based on ion intercalation[1][2] and SOFCs using CeO₂[3] or (La,Sr)MnO₃ (LSM)[4–6] electrodes. The latter have revealed local changes in valence states of Ce and Mn as a function of applied bias and gas ambient conditions as well as transport of Mn species.

Interconnects, which provide physical separation between the air and fuel, in addition to electric connection between the anode and cathode of adjacent cells, are one of the critical components of SOFC stacks. The reduction of operating temperatures to and below approximately 750°C, has allowed the replacement of ceramic interconnects, such as perovskites [e.g., (La, Sr)-based Cr, Mn, and Co oxides][7,8] with more conventional Fe₃-, Cr₂-, and Ni-based alloys.[7,9,10] Among the alloys, ferritic stainless grades are regarded as promising, relatively cheap materials with a thermal expansion coefficient that matches the other fuel-cell stack components.[11] However, the use of this material is not devoid of drawbacks; in particular, because of the high Cr content, volatile Cr-species can poison the catalysts, and the relatively low electrical conductivity of the forming oxides build up ohmic resistance at each contact.[12] To minimize these disadvantages various protective coatings, acting as barriers for oxidation and/or Cr diffusion, have been tested.[13–15] However, Cr poisoning still remains a serious obstacle because of limited physico-chemical insights into the behaviour of the interconnects as a part of the complex multi-material system under working conditions.

Here, we address the chemical and electrochemical stability of the interfaces between the metallic interconnect, catalyst, and solid electrolyte, which is part of our current efforts for simulating real FC conditions for single FC components by the construction of model-cells in conjunction with state-of-the-art analytical measurements.[16–18] The present in situ scanning photoelectron microscopy (SPEM) study of electrochemically induced processes occurring in Cr/Ni bilayers in contact with a Y stabilized zirconia (YSZ) electrolyte at 650°C and 10⁻⁵ mbar (1 bar = 10⁵ Pa) O₂ ambient conditions aims at a molecular-level understanding of the fundamental aspects related to the durability of metallic interconnects in SOFCs. The most interesting result is the observed temperature-induced and potential-dependent diffusion of Ni and Cr away from their initial position, resulting in specific morphology-composition changes in the Ni, Cr, and YSZ areas.

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[**] SOFC: Solid-Oxide Fuel Cell.
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Results and Discussion

Model device structure

For performing in situ electrochemical SPEM measurements under controlled gas, ambient temperature, and potential conditions, we fabricated a suitable model system, sketched in Figure 1, which illustrates the main components of a real device. In the Cr/Ni/YSZ/Ni/Cr stack, Cr represents the Cr-containing interconnect, Ni the catalyst, and YSZ is the most commonly used electrolyte. It is worth noting that, as Ni is readily oxidized to NiO during the first stages of SOFC operation, we will also explore the in situ electrochemical evolution of the Ni–NiO/YSZ interface. Each Cr/Ni bilayer can act either as a working electrode (WE) or simultaneously as a reference (RE) and counter (CE) electrode. The potentials refer to the cell bias, and the possible reactions are: a) reduction of \( \text{O}_2 \) and metal oxides at the cathode, and b) oxidation of \( \text{O}^{2-} \)-species and metals at the anode. For in situ electrochemical experiments the electrochemical cell is placed inside the SPEM chamber and run under pure \( \text{O}_2 \) at 100 mbar. The temperature was raised to 650 \( ^\circ\text{C} \) at open circuit potential (OCP), and subsequently the evolution of the Cr/Ni bilayers was examined under controlled electrochemical polarization.

Elemental distribution as a function of electrochemical conditions

The SPEM images and microprobe spectra in panels a–d in Figure 2 illustrate the evolution of the initial as-fabricated state of the model device after successive heating and voltage applications. The sketches of the device in each panel summarize the events occurring under different conditions.

The SPEM images in Figure 2a, tuned to the Cr 2p\(_{3/2}\) and Ni 3p energy windows and recorded by using raster scanning of the as-fabricated cell across the photon microprobe, prove that the initial state before heating and voltage applications has well defined Cr and Ni patches on both sides of the YSZ electrolyte. The residual brightness of the Cr region in the Ni 3p map is attributable to the contribution from the Cr secondary electron emission, which is much stronger than that from the YSZ electrolyte. The single element composition of the patches with Cr and Ni (in metallic state) is confirmed by the local Cr 3s and Ni 3p spectra, taken in spots inside the Cr and Ni patches.

Figures 2b–d show the elemental lateral distribution across the cell evolving upon heating and the electrochemical polarization, elucidated from the Cr 2p and Ni 3p images and microprobe Cr 3s and Ni 3p spectra. Annealing at the working temperature of 650 \( ^\circ\text{C} \) without bias (OCP) already mobilizes the Ni and Cr atoms and the atoms start to diffuse away from their original patches. The set of spectra from the spots inside the Ni patch evidence Cr diffusion, whereas the spectrum taken on the YSZ indicates Ni diffusion. c) 650 \( ^\circ\text{C} \), bias \(-0.625 \text{ V}\) applied to the upper electrode (WE). The three spectra evidence the Ni spreading in both directions and partial Cr back-diffusion, confirmed by the Cr 2p and Ni 3p maps as well. d) Sketch of the final state of a cell held at 650 \( ^\circ\text{C} \) after alternated \(-0.625 \text{ V}\) bias applications.
the vicinity of the Ni patch, evidence Cr spreading on the Ni patch and Ni diffusion in the YSZ electrolyte. The high resolution Ni 3p and SEM images in Figures 3 a and c also reveal more details about the morphology of the Ni species diffusing in the YSZ electrolyte. They show that the spreading Ni species tend to aggregate in well-separated islands, which lose electric contact to the externally controlled electrodes and this locally affects the electrochemical reactions under applied bias. The SPEM results in Figures 2 c and 3 a show that at the cathode (WE) under applied bias, Ni diffuses also towards the Cr patch, whereas Cr partially retracts back; however, at the anode (CE) the diffusion directions of Cr and Ni preserve the OCP behaviour. Reversing the potentials and holding the cell at OCP for a prolonged time results in the spreading of Cr and Ni all over the cell, as sketched in Figure 2 d.

Chemical states as a function of electrochemical polarization under steady-state conditions

The evolution of the elemental lateral distribution is accompanied by changes in the chemical states of Ni, Cr, and YSZ, clearly evidenced by the Cr 2p, Ni 3p, Zr 3d, and Y 3d spectra, taken at different parts of the cell. Representative spectra measured under different conditions are displayed in the four panels of Figure 4. The bottom spectrum in each panel is measured under OCP conditions and all other spectra were measured after running the cell at −3 V. The dashed vertical lines indicate the binding energies corresponding to the different oxidation states of Cr, Ni, Zr, and Y. In the Cr panel the middle spectrum is taken in a spot closer to the Ni patch and the top one close to the contact. In the Ni & Cr panel the top subpanel shows two spectra measured at two spots inside YSZ, in which the spreading Ni has aggregated into isolated islands.

Figure 4. Cr 2p1/2 and 3s, Ni 3p, Zr 3d, and Y 3d spectra taken at the Cr and Ni patches of the cathode side (WE) and inside the YSZ electrolyte close to the Ni patch. The bottom spectrum in each panel is measured under OCP conditions and all other spectra were measured after running the cell at −3 V. The dashed vertical lines indicate the binding energies corresponding to the different oxidation states of Cr, Ni, Zr, and Y. In the Cr panel the middle spectrum is taken in a spot closer to the Ni patch and the top one close to the contact. In the Ni & Cr panel the top subpanel shows two spectra measured at two spots inside YSZ, in which the spreading Ni has aggregated into isolated islands.

Figure 3. SPEM and SEM images measured in two separate experiments after applying a bias of −0.625 V. a) Ni 3p image of the upper half of the cell from the WE side showing the aggregation of the Ni species spreading on the YSZ in the vicinity of the Ni patch. b) SEM image of the morphology of the Cr electrode close to the Ni patch. c) SEM image of the zone inside the YSZ electrolyte close to the Ni patch, in which Ni islands are well resolved.
present study, where a reasonable change in the spectra line-shape is observed. The top two spectra in the Cr panel, taken at two different spots, show that, as a result of the electrochemical reduction, the Cr 2p spectra are dominated by the metallic Cr$^0$ component. It is worth noting that the top spectrum in the Cr panel, which appears in the most advanced reduced state, is measured in a spot closer to the electric contact, where the overvoltage drop along the electrochemically active region is smaller. The Ni 3p spectrum measured on the Ni patch after $-3.0 \text{ V}$ biasing corresponds to a completely reduced Ni$^0$ state, and also the absence of the Cr 3s feature confirms the results reported in Figure 2c, concerning the back diffusion of Cr that has spread under OCP conditions. On the contrary, the Ni chemical state of the isolated Ni islands on YSZ remains almost unchanged, as evidenced by the two top spectra in the Ni&Cr panel in Figure 4, measured in two different spots on the YSZ electrolyte after running the cell at a $-3 \text{ V}$ bias. This peculiar result, that the NiO islands on YSZ do not undergo reduction, should be attributed to the lack of electron drain, because the islands have lost contact to the electrodes. The Zr and Y 3d spectra also evidence YSZ reduction, for which the new ‘reduced’ components correspond to a partially reduced ZrO$_2$ and metallic Y$^0$. To the best of the authors’ knowledge no reports are available on in situ electrochemical reduction using YSZ as an electrolyte, except one paper on H$_2$-reduction of NiO/YSZ to Ni/YSZ, studied by using X-ray diffraction.$^{[21]}$

Dynamic study of electrochemical Ni reduction

These experiments were performed by starting from OCP and biasing the electrode to: $-0.625$, $-1.65$ V, and $-3.0$ V. The spectra were measured inside the Ni patch, which, after being exposed to OCP conditions, was oxidized and covered by diffused Cr species. Figure 5 shows the time evolution of the Ni 3p and Cr 3s spectra at two different biases of $-0.625$ and $-1.65 \text{ V}$. As can be seen in Figure 5, at the lowest potential of $-0.625 \text{ V}$ the NiO is gradually reduced from Ni$^{2+}$ to Ni$^0$ without reaching full reduction. As reported above, the Cr chemical state remains intact (confirmed also by the Cr 2p spectra), except for a very weak loss of the Cr 3s intensity because of the back diffusion towards the Cr patch. The Ni electrochemical reduction and the Cr back-diffusion rates increase with increasing potential. Biasing at $-3.0 \text{ V}$ shows a time evolution of the spectra that is very similar to the one observed at $-1.65 \text{ V}$. However, after applying a potential of $-3.0 \text{ V}$ also Cr oxide undergoes reduction (cf., Figure 4).

After deconvolution of the sets of Ni 3p spectra, measured at $-0.625$, $-1.65$, and $-3.0$ V, we used the relative fraction of the area $A$, under the Ni$^0$ component [Eq. (1)], as a measure of the reduction rate $R$, at time $t$, to get the plots in Figure 6.

$$R = \frac{A(\text{Ni}^0)}{A(\text{Ni}^{2+}) + A(\text{Ni}^0)}$$

(1)

These plots clearly evidence a reasonable correlation between the applied potential and the electrochemical reduction rate $R$. Notably, for the lowest bias experiments, although we started with non-fully oxidized Ni, we were not able to reach complete reduction. The experimental points can be satisfactorily fitted assuming first-order kinetics and they yield the following time constants: $\tau = 149.12 \pm 38.79 \text{ min}$ for $-0.625 \text{ V}$, $\tau = 15.436 \pm 4.113 \text{ min}$ for $-1.65 \text{ V}$, and $\tau = 11.140 \pm 0.570 \text{ min}$ for $-3.0 \text{ V}$. Error bars are computed from 95% confidence intervals of $A$ estimates.

Conclusions

In this paper we report the first in situ electrochemical study carried out by using synchrotron-based SPEM on a model cell operated at high temperature, in an O$_2$ environment and with applied electrochemical bias, to shed light on the complexity

![Figure 5](image-url)  
*Figure 5. Time evolution of Cr 3s and Ni 3p spectra taken on the Ni patch at two different cathodic biases illustrating Ni reduction. In the left panel an exemplary deconvoluted spectrum (bottom) and a reference Ni 3p spectrum of metallic Ni (top) are shown.*

![Figure 6](image-url)  
*Figure 6. Reaction rate ($R$) plots obtained by calculating the relative weight of the Ni$^0$ component after deconvolution of the Ni 3p spectra taken after different reaction times for $-0.625$ V (*), $-1.65$ V (**), and $-3$ V (***).*
of the reduction–oxidation and diffusion processes occurring in SOFC devices. The results demonstrate the potential of scanning photoelectron microscopy and imaging to follow in situ the evolution of chemical states and lateral distributions of the constituent elements. The location of the metals and their oxidation states have been followed as a function of time, and electrochemical polarization. The chief results achieved are: 1) observation of the dynamic, reversible reductions of pre-oxidized Ni and Cr; 2) reversible reductions of Zr and Y; 3) surface displacements of Ni and Cr as a result of cathodic/anodic polarization and exposure to high-temperature oxidizing conditions.

The results obtained in this research contribute to: i) the rationalization of the damage mechanisms undergone by metallic materials employed in SOFCs, such as metallic interconnects; ii) the fundamental understanding of high-temperature corrosion in terms of electrochemical mechanisms; iii) the knowledge of the effects of coupling the YSZ electrolyte to corrosion in terms of electrochemical mechanisms; iv) the understanding of high-temperature oxidation processes involved in the faradaic processes. The probing depth did not exceed 4–5 monolayers.

The model electrochemical cell was mounted on a specially constructed sample holder that had the necessary heater and electrical contacts for bias applications. Before introduction into the SPEM chamber the cell was subjected to light Ar-ion sputtering and checked for surface cleanliness by Auger electron spectroscopy (AES) located in the preparation chamber attached to the SPEM. The surface cleanliness was confirmed by micro-XPS after introduction of the cell into the SPEM chamber using base pressure in the 10⁻⁶ mbar range. The electrochemical and control measurements were performed by using an AMEL 7050 system. For the in situ electrochemical SPEM experiments, pure O₂ was pumped into the chamber to maintain 10⁻⁶ mbar oxygen at ambient conditions.

More details about the cell fabrication and current measurements during polarization are given in the Supporting Information.

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