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In-situ photoelectron microspectroscopy during the operation of a single-chamber SOFC

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ABSTRACT

This paper reports the first in-situ synchrotron-based scanning photoelectron microscopy study of an operating YSZ-supported single-chamber SOFC with Au–MnO_2 composite cathode and NiO anode, fed with 10^{-5} mbar 1:1 mixture of CH_4 fuel and O_2 at 650 °C. We employed a YSZ-supported cell with Au–MnO_2 composite cathode and NiO anode. The chemical imaging and micro-XPS results were complemented with simultaneous electrochemical measurements, open circuit potential, potentiostatic and impedance spectrometry. The cell was operated under two conditions: (i) with fully oxidized electrodes and (ii) after in-situ reductive activation of the anode. The current delivered by the cell after in-situ reduction was about one order of magnitude higher. The chemical states of Ni and Mn were affected by the in-situ reduction process but they were not modified by the fuel-cell operation. Notwithstanding the absence of chemical state transformations of the electrode materials during the prolonged fuel-cell operation, cell aging brings about morphological change, accompanied by a decrease of the extracted current.

1. Introduction

The study of SOFC-related materials and systems with state-of-the-art surface analytical tools is gaining momentum. In particular, space-resolved photoelectron spectroscopy has proved rewarding, since it yields a wealth of unique chemical and structural information despite its vacuum requirements constrain the range of accessible systems. In this respect, a number of in-situ electrochemical studies with model half cells, driven by external power sources rather than by the Gibbs free energy of the fuel oxidation reaction, have already shed light on various processes that can occur in operating SOFCs [1–6]. However, a major breakthrough in understanding the dynamic interactions in the SOFCs will be achieved driving the real electrochemistry of a whole cell and here we report the first results obtained in such configuration. Although with the present experimental set-up spatially separated delivery of fuel and oxidant is still not achievable, it is possible to use a mixture and to separate the fuel and oxidant action by fine-tuning of the electrocatalytic properties. The present Single-Chamber SOFC (SC-SOFC) concept is relevant to (i) development and fabrication of rugged, low-cost devices with simple fuel-handling facilities and (ii) using cheap fuels without a gas-purification step, such as naturally produced biogas, containing CH_4 mixed with air [7–9]. Using SC-SOFC with both electrodes accessible to analysis, with scanning photoelectron microscopy (SPEM) we obtained the first results during the operation, featuring simultaneously the real anodic and cathodic reactions using actual fuel (CH_4) and oxidizer (O_2).

2. Materials and methods

For our previous in-situ electrochemical SPEM studies, performed in 10^{-6} mbar O_2 [1,2] or C_2H_4/H_2O 1:1 mixture [3], we developed planar YSZ(100)-supported cells with Ni/Cr and Ni/Cu/Cr layers. The YSZ single-crystal electrolyte is mechanically and thermally stable for lithography and fully compatible with SPEM experiments [10,11]. We used the same approach for fabricating the present planar SC-SOFCs, schematically shown in Fig. 1a. Based on the literature, we selected Au–MnO_2 [12] and NiO [8] as cathodic and anodic materials. The electrodes were fabricated by evaporating 100 nm thick metal layers, the Au–MnO_2 precursor was a Au–Mn bi-layer grown onto a thin Cr adhesion buffer (see the SEM micrographs in Fig. 1d.1, d.3). All experiments were carried out using SPEM at the ESCAmicroscopy beamline at Elettra laboratory in Italy. The SPEM operates in imaging and spectroscopic modes with spectral resolution of 0.18 eV and lateral resolution down to 100 nm [13]. The lateral distribution of each element is mapped by collecting core level photoelectrons emitted within the relevant kinetic energy window while raster-scanning the specimen with respect to the microprobe. Electrochemical measurements were run with a PAR potentiostat. Impedance

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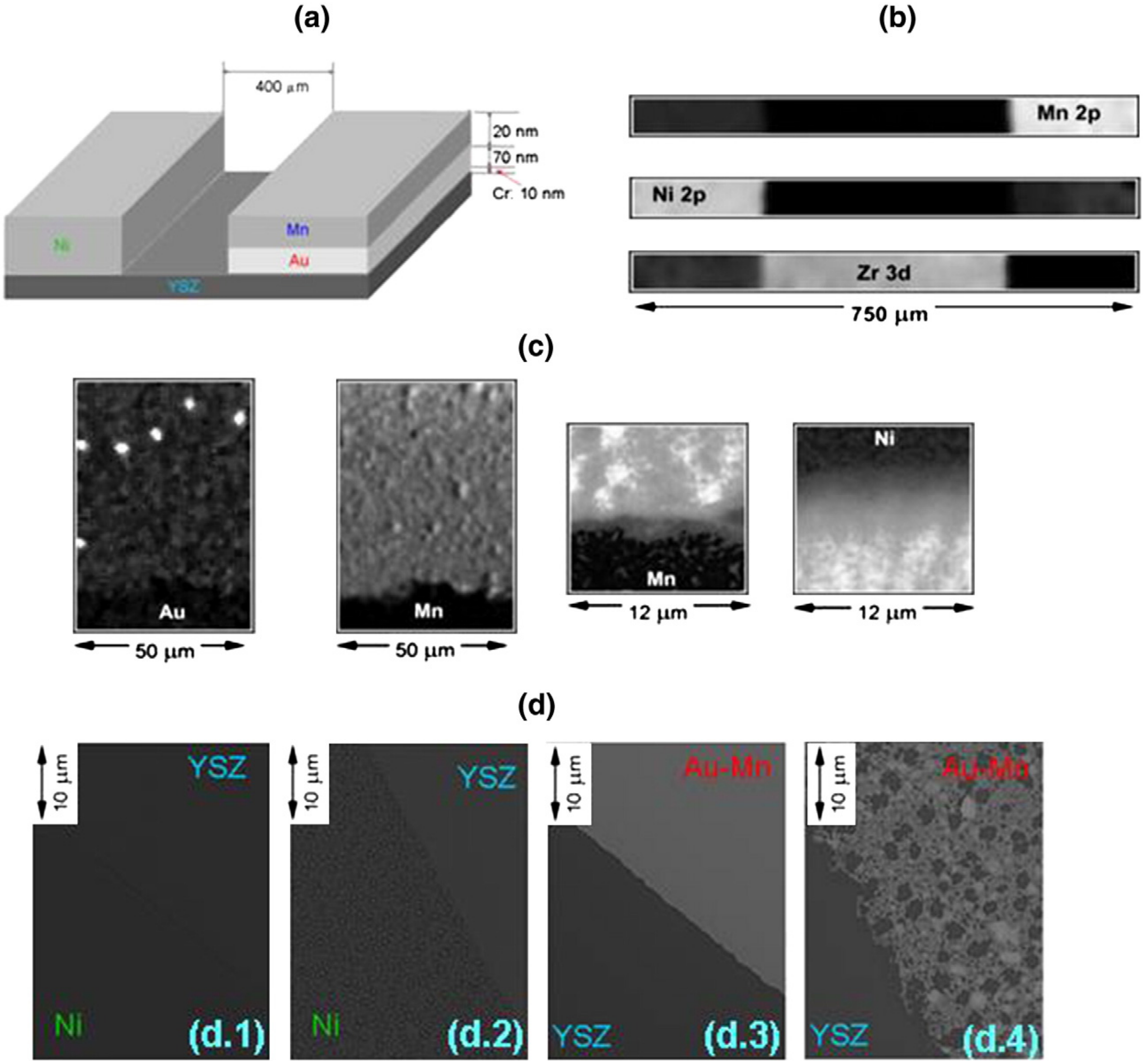

Fig. 1. (a) Scheme of the planar SC-SOFC for in-situ electrochemical SPEM measurements. (b) Ni 2p, Mn 2p and Zr 3d SPEM images of the pristine cell, where the bright areas with sharp edges correspond to the Ni, Au–Mn electrodes and the YSZ electrolyte. (c) SPEM Au 4f, Mn 2p and Ni 2p maps taken after long operation of the cell, showing the developed island-like morphology due to restructuring and aggregation within the electrodes and migration of Ni and Mn onto the electrolyte. (d) SEM micrographs of the Ni/YSZ and Au–Mn/YSZ interfaces confirming the restructuring of pristine cell (d.1, d.3) after long operation (d.2, d.4).

spectrometry was carried out with a signal of 10 mV_{pp} in the frequency range of 1 MHz–1 mHz.

3. Results and discussion

The SC-SOFC introduced in the SPEM station was Ar ion-sputtered to remove contaminant layers introduced during fabrication and then it was annealed in 10^{-6} mbar of O_2 at 650 °C. This resulted in Mn and Ni oxidation, evidenced by the Ni and Mn 2p photoelectron spectra in Fig. 2a and b and minor morphology changes (not shown) compared to the ones observed after the following cell operation.

In-operando studies were performed at 650 °C in 10^{-5} mbar 1:1 CH_4:O_2 mixture in two conditions: (i) with fully pre-oxidized electrodes and (ii) after reduction of NiO by applying external cathodic polarization of −1 V with respect to the Au–Mn electrode, apt to offset the chemical action of the gas [1–3]. Such partial reduction is also recommended in ref. [14] for optimal SC-SOFC operation. SPEM images and micro-spot XPS spectra (see Figs. 1 and 2), measured systematically at open circuit potential (OCP) and during operation at 75 mV, have evidenced the evolution of morphology and chemical state of the anode and cathode. In both conditions, we initially measured the steady-state OCP (Fig. 3a) and electrochemical impedance spectra (EIS) at OCP (Fig. 3c). Subsequently, the cell voltage was set to 75 mV and the extracted current time-series (Fig. 3b) and EIS (Fig. 3d) were measured. The OCPs in the pre-oxidized and reduced conditions were 163.6 ± 0.4 and 407.1 ± 8.8 mV, respectively: such low values can be attributed to the small inter-electrode gap dimensions [15]. The corresponding EIS spectra show one charge-transfer loop, followed by an unclosed arc, whose accurate mechanistic explanation is beyond the scope of this letter, but nevertheless yields notable diagnostic insight. In particular, the apparent quantitative changes between OCP and operation with pre-oxidized or in-situ reduced anodes witness that the SOFC electrochemistry was fully under control during the SPEM measurements. After cathodic activation of Ni-based anode, the current is increased by ca. one order of magnitude. The improvement of cell efficiency as a result of the anode activation could be observed notwithstanding the cell aging due to previous operation with the NiO anode. It is worth noting that in