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An in situ near-ambient pressure X-ray photoelectron spectroscopy study of CO_2 reduction at Cu in a SOE cell

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ABSTRACT

The cathodic behavior of a model solid oxide electrolysis cell (SOEC) has been studied by means of near-ambient pressure (NAP) X-ray Photoelectron Spectroscopy (XPS) and Near Edge X-ray Absorption Fine Structure Spectroscopy (NEXAFS), aiming at shedding light on the specific role of the metallic component in a class of cermets used as electrodes. The focus is on the surface chemistry and catalytic role of Cu, the increasingly popular metallic component in electrodes used in CO_2 electrolysis and CO_2/H_2O co-electrolysis. The NAP-XPS and NEXAFS results, obtained in situ and operando conditions and under electrochemical control, have provided important insights about the evolution of the chemical composition of the Cu surface. We have found that in dry CO_2 ambient carbon deposits are scavenged at low cathodic potential by the oxidising action of nascent O, while at high cathodic polarisations C grows due to activation of CO reduction. Instead, in CO_2/H_2O mixtures, surface deposit of C is steady over the whole investigated potential range. The presence of adsorbed CO has also been detected during electrolysis of CO_2/H_2O mixtures, while no CO is found in pure CO_2 ambient.

1. Introduction

Reduction of CO_2 to CO, a crucial step in the synthesis of hydrocarbons, is feasible by both chemical and electrochemical routes, though at high energetic costs. In the realm of electrochemistry, room- and high-temperature methodologies have been proposed, based on diverse electrolytes: aqueous, non-aqueous, molten-salt and solid oxides. In particular, CO_2 electrolysis and CO_2/H_2O co-electrolysis in solid-oxide electrolysis cells (SOECs) are attractive approaches. The high operating temperatures, typically divided in two ranges: intermediate (500–700 °C) and high (800–1000 °C), facilitate reaction kinetics, so that the use of noble metals can be avoided. Nevertheless intermediate-T operation is more desirable for durability issues as well as for the possibility of employing metallic cell supports with notably less severe brittleness problems, but still this is a field that has not been sufficiently explored.

The achievements of CO_2 electrolysis in SOECs have been the object of comprehensive recent reviews (e.g. [1–4].) as well as of a dedicated Faraday Discussion [5] and it is not necessary to repeat this information here, since our study is focused specifically on the role of metallic Cu constituent in SOECs cathodes. In order to place the role of Cu in context, it is worth recalling briefly the materials that have been used for CO_2-reduction SOECs: (i) Pt/YSZ [6–8]; (ii) Ni/YSZ [9–11]; (iii) ceria [12,13]; (iv) Ni/GDC (Gd-doped ceria) [14,15], Ni-Ru/GDC [15]; (v) Cu/YSZ [16–18]; (vi) Cu-doped La-Sr-Co-ferrite (LSCF)/CGO [19,20]; (vii) Cu/GDC [21,22]; (viii) La-Sr-Cr manganite (LSCM)-based p-type perovskites (LSCM/YSZ [11,23], LSCM/GDC [11,24]; Ni- [25] and Fe- impregnated LSCN [26]) and (ix) La-Sr titanate (LST)-based n-type perovskites, either in pure form [27] or Ni-impregnated [28]. Notwithstanding the rather extensive literature corpus, no general agreement has been reached regarding the best catalytic material for CO_2 reduction; in particular, there is still no consensus on the performance of the popular Ni-based cathodes, that are however recognized to exhibit a range of operational problems during CO_2 reduction. In this scenario Cu is gaining attention as an alternative to Ni owing to its resistance to coke formation and oxidation in hydrocarbon-fueled SOFCs [29,30], as well as for cost reasons (Cu price is 25–50% less than Ni). In fact, Cu is attractive on the one hand owing to its high current conductivity in both metallic [30] and cermet forms [31] and on the other hand for its catalytic activity towards CO_2 reduction, that has been shown to be similar to that of Ni [20,21]. However, due to its lower melting temperature compared to Ni, Cu is not suitable for

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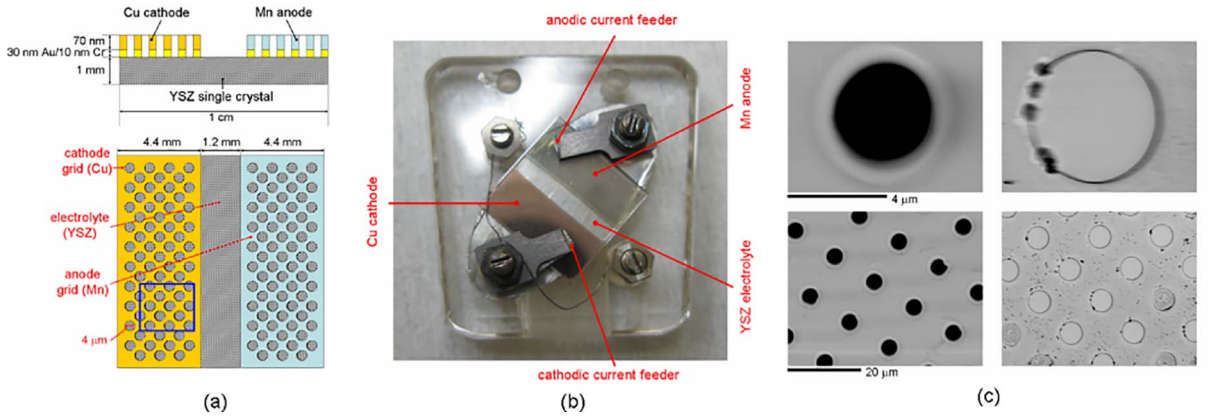

Fig. 1. (a) Sketch of the electrochemical cell: (bottom) planar view where the square indicates the area of SEM images; (top) cross-sectional view. (b) Cell mounted on sample holder and (c) Low and high resolution SEM images of a pristine cell (left) and after operation in CO_2 at 600 °C (right).

operation at temperatures higher than ca. 800 °C due to tendency to particle coarsening.

Cu cermets have been considered as anodes for hydrocarbon oxidation in SOFC, showing outstanding resistance to deactivation due to C deposition and S poisoning, as well as good catalytic activity [30,32,33], but coarsening raises durability issues. Bimetallic Cu-Ni and Cu-Co SOFC anodes have also been tested, showing improved resistance to C deposition and crack formation as well as better catalytic performance [34–37]. In particular, outstanding performance of the CH_4/air SOFC was attributed to the optimal catalytic activity of Cu/CeO_2 for CH_4 due to the combination of the redox activity of the Ce^{4+}/Ce^{3+} couple with the high electronic conductivity of Cu [36,37]. The use of Cu-containing SOFC anodes has not been restricted to applications involving C-containing fuels, but it has also been reported for H_2 oxidation [38,39].

In addition to use of Cu in SOFC systems, a few very promising reports have been published regarding CO_2 reduction. This has been first demonstrated for a peculiar SOFC configuration [19], where CO_2 reacted at the Cu-added $La_{0.58}Sr_{0.4}Co_{0.22}Fe_{0.8}O_{3-\delta}$/CGO cathode, while H_2 was oxidised at a Ni/GDC anode. The first report comparing SOEC for CO_2 reduction, operated in CO_2/CO = 1/1 at 750 °C with Cu- and Ni-based cathodes, showed improved performance and stability [21]. Post mortem Raman studies following CO_2 or H_2O electrolysis and CO_2 + H_2O co-electrolysis at 550–700 °C using Cu/$Ce_{0.8}Gd_{0.2}O_{2-\delta}$ (GDC), confirmed the suppression of C deposition [22]. Ni-Cu nanoparticles have been shown to combine the advantages of Ni and Cu, yielding a synergistic effect to maximise the current efficiencies for the direct electrolysis of CO_2 [40]. Cu/YSZ cathodes have also been used for H_2O electrolysis at 800 °C, featuring comparable performance with Ni/YSZ electrodes [16–18]. Here we should mention the recent electrochemical study of CO_2 electrolysis and CO oxidation in CO_2/CO mixtures on Ce oxide electrodes patterned on YSZ using surface sensitive near ambient pressure XPS, very relevant to our investigations [13]. Operating the cell at 600 °C the authors identified CO_3^{2-} as the key reaction intermediate, its formation being accompanied by Ce^{3+}/Ce^{4+} valence changes. It is noteworthy that no other in situ XPS work has been published so far of CO_2 electrolysis: as a result the surface chemistry of Cu-containing systems in these conditions is a fully unexplored topic, whose contribution will be crucial in clarifying mechanistic aspects related to C- deposition and durability of cathodes.

The aim of this study is to shed light on some fundamental aspects of the surface electrochemistry of Cu-based systems, in particular on the specific role of Cu in the recently proposed highly active Cu/GDC cathodes [21,22]. To this end – as a model system that as such has not been considered in actual SOEC studies – we explored the evolution of the status of Cu thin film electrodes in contact with YSZ during the CO_2 reduction reaction by near-ambient pressure (NAP) XPS and NEXAFS complemented by electrochemical measurements of two-probe linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS), operated with the method detailed in [41].

2. Experimental methods

2.1. Cell fabrication

In the present investigation, we employed planar, YSZ(100)-supported cells with lithographically defined Cu (working electrode) and Mn (counter electrode) thin-film electrodes. We used pure Cu in order to avoid the chemical complexities of cermets from which Cu particles are obtained by partial reduction (see e.g. [40]). Even though studies on planar solid-oxide cells exposed to just a single reactive gas are not identical to those on real SOECs in which the fuel and the oxidiser are separately brought into contact with optimised, highly-active working and counter electrodes, nevertheless mechanistic information gathered from this type of study is directly related to the relevant electrodic processes. The specific cell rationale, geometry, electrode fabrication and electrochemical characterisation have been detailed in a dedicated paper [41]. Over the years, we have developed lithographed planar cells for in situ micro-XPS in view of two main objectives: (i) to render the whole electrochemical system (cathode, electrolyte and anode) accessible to the X-ray beam; (ii) to confine the region exhibiting the highest electrochemical activity to the surface, to which of course XPS is uniquely sensitive. At variance with the more traditional stacked electrode configurations with porous electrodes (e.g. [42]), in our planar lithographed cells the electrochemically active triple-phase boundaries are provided by the contact lines between electrode and electrolyte, exposed to the gas ambient of the analysis chamber. The choice and behavior of the counter-electrode are detailed in [41]. Cu has been selected as the cathode in order to be able to single out the contribution of this element to the cathodic operation of the Cu-based cermets recalled in the Introduction. YSZ(100) single crystals (1 cm × 1 cm × 1 mm) were obtained from Mateck and used as cell support. The electrodes were fabricated by evaporating 70 nm thick Cu and Mn layers onto Au (30 nm) contact layers, in turn grown onto Cr adhesion buffers (10 nm): Fig. 1a shows the electrode arrangement and dimensions. In order to achieve a high surface density of triple phase boundaries (TPB) with the lithographic approach and to expose a significant length of TPB lines to the probe beam (ca. 150 μm in diameter), the electrodes were designed with a square lattice of circular holes (4 μm in diameter), giving access to the YSZ. The electrolysis cell is placed inside the XPS chamber on a suitable sapphire sample-holder (Fig. 1b) equipped with appropriate electrical connections and a laser heater, capable of reaching high temperatures.