

An in situ near-ambient pressure X-ray photoelectron spectroscopy study of CO₂ reduction at Cu in a SOE cell

Benedetto Bozzini^{a,*}, Matteo Amati^b, Claudio Mele^a, Axel Knop-Gericke^c, Erik Vesseli^d

^a Dipartimento di Ingegneria dell'Innovazione, Università del Salento, via Monteroni s.n., 73100 Lecce, Italy

^b Elettra - Sincrotrone Trieste S.C.p.A., S.S. 14, km 163.5 in Area Science Park, 34149 Trieste, Basovizza, Italy

^c Abteilung Anorganische Chemie, Fritz-Haber-Institut der Max-Planck Gesellschaft, Faradayweg 4–6, 14195 Berlin, Germany

^d Department of Physics, University of Trieste, via Valerio 2, I-34127 Trieste, Italy & IOM-CNR, Laboratorio TASC, Area Science Park, S.S. 14 km 163.5, I-34149, Basovizza, Trieste, Italy

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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 CO₂ electrolysis and CO₂/H₂O 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 CO₂ 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 CO₂/H₂O 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 CO₂/H₂O mixtures, while no CO is found in pure CO₂ ambient.

1. Introduction

Reduction of CO₂ 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, CO₂ electrolysis and CO₂/H₂O 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 CO₂ 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 CO₂-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 CO₂ 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 CO₂ 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 CO₂ 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

* Corresponding author.

E-mail address: benedetto.bozzini@unisalento.it (B. Bozzini).

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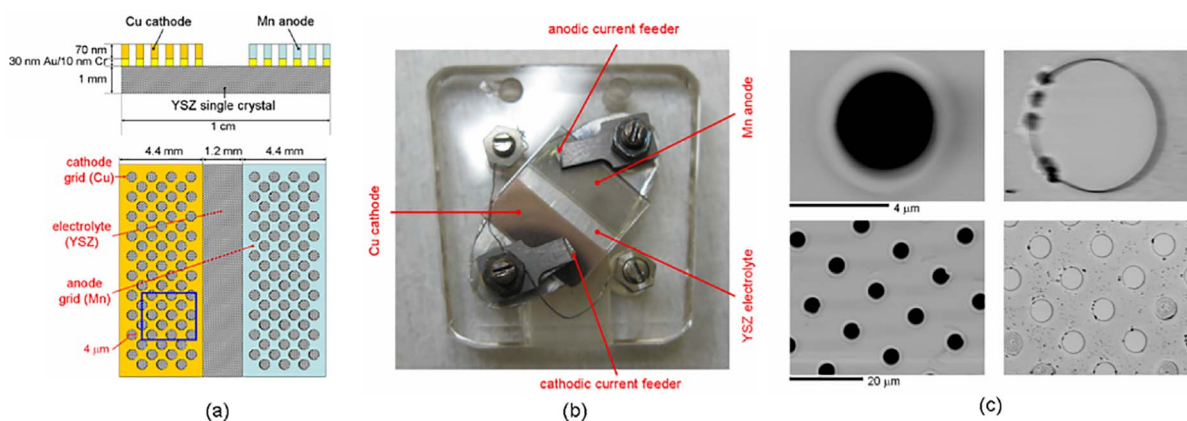


Fig. 1. (a) Sketch of the electrochemical cell: (bottom) planar view where the square indicates the area of SEM images; (top) cross-sectional view. (b) Cell mounted on sample holder and (c) Low and high resolution SEM images of a pristine cell (left) and after operation in CO_2 at 600 °C (right).

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/CeO₂ for CH_4 due to the combination of the redox activity of the $\text{Ce}^{4+}/\text{Ce}^{3+}$ 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 $\text{La}_{0.58}\text{Sr}_{0.4}\text{Co}_{0.22}\text{Fe}_{0.8}\text{O}_{3-\delta}/\text{CGO}$ cathode, while H_2 was oxidised at a Ni/GDC anode. The first report comparing SOEC for CO_2 reduction, operated in $\text{CO}_2/\text{CO} = 1/1$ 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 $\text{CO}_2 + \text{H}_2\text{O}$ co-electrolysis at 550–700 °C using Cu/Ce_{0.8}Gd_{0.2}O_{2-δ} (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 $\text{Ce}^{3+}/\text{Ce}^{4+}$ 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 electrochemical 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.

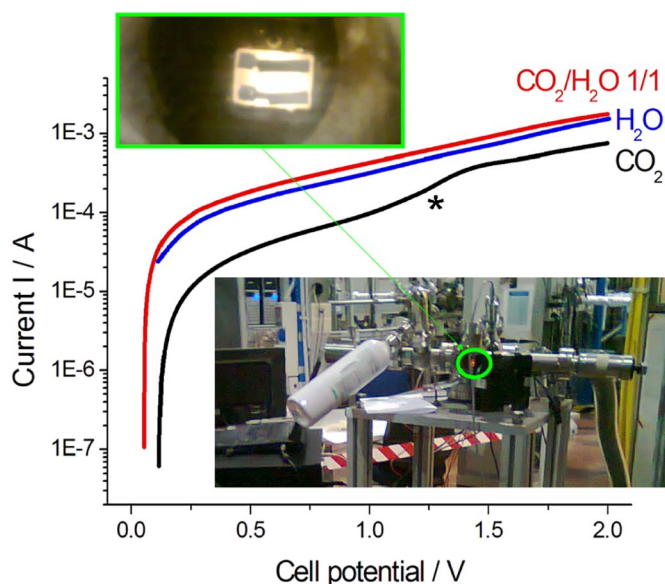


Fig. 2. Linear-sweep voltammograms of the Cu/YSZ/Mn cell, measured at 600 °C, 0.5 mbar in the indicated gas ambient. The star denotes the potential range where secondary inhibition takes place. The figure also shows: the mock-up of the analysis chamber used for off-line electrochemical experiments (below) and the operating electrochemical cell imaged through the viewport (above).

2.2. Electrochemical methods

Linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS) measurements in two-electrode configuration were performed in the analysis chamber at the working temperature in gas environment. We employed a Versastat potentiostat and data were acquired with the Versastudio software. For compactness of presentation, all through the paper, we shall refer to voltage with its absolute cell value, considering that the Cu and Mn patches have always been polarised cathodically and anodically, respectively.

2.3. Near-ambient pressure XPS and NEXAFS

Pristine cells were initially exposed to 0.5 mbar of either CO₂ or CO₂/H₂O 1:1 at room temperature and then they were brought to the operating temperature of 600 °C. Subsequently the gas environment was changed, at the same pressure, from CO₂/H₂O 1/1 ambient to CO₂/H₂O 1/2. We explored the cathodic behavior of Cu in CO₂ and CO₂/H₂O gas ambient, following the potential-dependent evolution of the Cu 2p, O 1s and C 1s core levels and Cu L-edge and O K-edge NEXAFS spectra. The experiments were carried out at the ISSS beamline of the BESSY-II Synchrotron in Berlin [43]. Since the experimental set-up using applied potentials interferes with the measurement of the sample currents as well as with the secondary electron signal, NEXAFS spectroscopy was performed by following the changes of the XPS and Auger signal while scanning the photon energy. Thus, the XPS and NEXAFS spectra probe comparable sample depths, relevant exclusively to the surface and near-surface chemical states. The XPS signal was calibrated with respect to the Au 4f reference. Peak deconvolution of the O 1s and C 1s XPS spectra was performed by least-squares fitting of the normalised and energy-calibrated signal with Doniach-Šunjić lineshapes, convoluted with a Gaussian envelope and with the addition of a linear background [44]. A non-symmetric lineshape was used also in the deconvolution of the core levels of adsorbed species at the metal surface. Indeed, at low kinetic energies the contribution of inelastic scattering processes (extrinsic losses) may significantly deviate the lineshape with respect to a pure Voigt profile, at variance with isolated atoms and molecules. Furthermore, beyond the sudden, single electron approximation, the creation of a core hole in an atomic species at a metal surface gives

origin to shake-up and shake-off features that, accompanied by unresolved vibrational losses of the adiabatic peak, may also indirectly contribute to an apparent asymmetry of the adiabatic spectroscopic line [45,46]. Energy calibration was performed with respect to the OCP value.

3. Experimental results

The potential-dependent cathodic surface electrochemistry of Cu films forming a TPB with YSZ electrolyte and a reactive gas phase was investigated by NAP XPS and NEXAFS in two representative environments of SOEC operation: CO₂ electrolysis and CO₂/H₂O co-electrolysis. Spectroscopy measurements were carried out potentiostatically. The first set of experiments studied CO₂ electrolysis, operating the cell at three cell voltages: OCP, 2 and 4 V. In the second experimental set a pristine cell was sequentially exposed to CO₂/H₂O ambient at 1/1 and 1/2 ratios and polarised at 2 V for a total period of 28 h in each case.

Fig. 1c compares SEM micrographs of the Cu electrode in pristine conditions and at the end of the experiments in CO₂ ambient. The SEM morphology of the cathode after measurements in CO₂/H₂O is essentially the same as after operation in dry CO₂. For both gas environments the main degradation forms are extensive pitting within the Cu patch and diffusion of metal into the electrolyte region, as one can notice from the compositional contrast in the YSZ regions of the pristine and aged cells. As mentioned in the Introduction, diffusion and agglomeration of Cu have been reported to be typical damaging modes of Cu-containing cermet used in both SOFCs [33,38] and SOECs [21].

3.1. Electrochemical measurements

Full details of the electrochemical measurements can be found in our previous paper [41]. Here we briefly recapitulate the essential linear sweep voltammetry (LSV) information. It is worth noting that, owing to the special nature of our TPB geometry and the reproducibility of the geometry ensured by the lithographic fabrication, it is more significant to refer to the cell current than to the current density. Fig. 2 reports LSVs measured with pristine cells. The data obtained in CO₂ indicate mixed control and a secondary inhibition process can be noticed from the feature highlighted with a star at ca. 1.2 V, the voltage required for the oxidation of C adsorbed at the Cu cathode under OCP (see also Fig. 4b below). In pure H₂O, significantly higher currents are measured due to the higher H₂O reactivity, coherently with previous results [22] showing that at a given current density steam electrolysis at Cu/GDC requires lower voltages than CO₂ reduction. The LSV behavior in CO₂/H₂O = 1/1 has contributions from both reduction reactions and no changes in slope are observed that could be related to C desorption.

3.2. In situ XPS and NEXAFS

3.2.1. CO₂ electrolysis

Fig. 3a shows Cu 2p spectra recorded in 0.5 mbar CO₂ at OCP followed by two successive cathodic polarisations of 2 and 4 V. The Cu 2p_{3/2} binding energy is centred at 931.9 eV: a peak position that is compatible with both Cu⁰ and Cu⁺ species [47]. However, the presence of the shake-up features at ca. 938 and 945 eV unambiguously indicates the formation of Cu₂O. These in-situ XPS spectra are in concert with post mortem Raman [22] and XRD [21] analyses of Cu-containing SOEC cathodes after CO₂ electrolysis, reporting the presence of Cu₂O in their Cu/GDC. The changes in the Cu 2p intensity upon switching the cell potential (Fig. 3b) are due to the variations in the C amount deposited on the surface, which, as judged from the C 1s spectra, reaches the lowest level at 2 V, as reported in Fig. 3b where the C 1s intensities are obtained from the spectra in Fig. 4b.

The O 1s spectra, shown in Fig. 4a consist of at least two distinct components. At open-circuit, two peaks can be clearly separated at

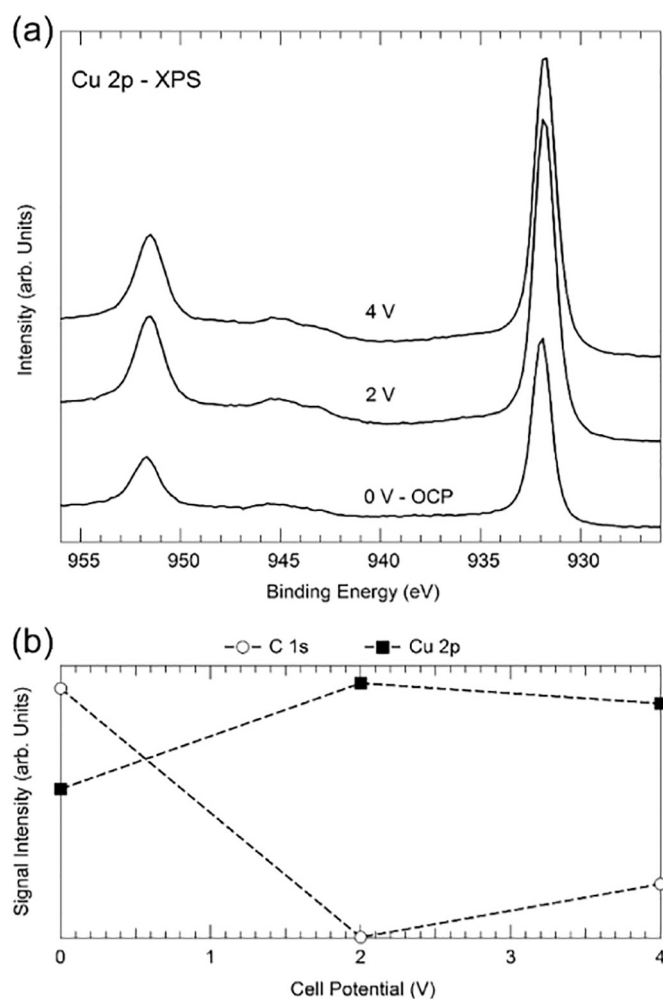


Fig. 3. (a) Cu 2p XPS spectra recorded in 0.5 mbar CO₂ at 600 °C at the indicated potentials. (b) C 1s and Cu 2p XPS signal intensities, obtained from data plotted in Figs. 4b and 3a, respectively.

530.0 ± 0.1 and 531.5 ± 0.1 eV, shifting to 529.6 ± 0.1 and 530.9 ± 0.1 eV, respectively, when applying the potential. It is worth noting that, as detailed in [41], we operated in a way that ensures that spectral shifts are not due to charging effects resulting from the application of the electrochemical polarisation. The peak at 530.9 eV is compatible with the presence of Cu₂O [47–49] and its intensity correlates with that of the Cu shake-up features of Fig. 3a. The peak at 531.5 eV present at OCP conditions could be in principle attributed also to several overlapping C-O forms like for example CO₂^{δ-} [49]. However, this latter assignment may be valid only in the case of the OCP spectrum, since it can be definitely ruled out for the biased samples due to the excessively low binding energy and to the absence of signal in the corresponding C 1s spectra (Fig. 4b), thus making the contribution from Cu₂O the most plausible interpretation. The role of hydroxyl species is also excluded since OH is not expected to be stable up to 600 °C [50], and a significant OH surface coverage may be obtained only when in equilibrium with the water gas phase (see Section 3.2.2 below). The most likely interpretation for the peak at 529.6–530.0 eV consists instead in attributing it to atomic oxygen species, either chemisorbed [47–49] or in subsurface form [48]. This scenario is coherent with the more general one recently set by XPS studies with high lateral resolution of the oxidation process of metal surfaces in reactive ambient, that has pinpointed high surface heterogeneities, typically characterised by the coexistence of different oxidation states [51]. In this framework, the shift observed between OCP conditions and after the application of the cathodic polarisation is fully compatible - both qualitatively and quantitatively - with surface reconstruction or faceting as well as with thickness variations of the oxide layer.

Fig. 4b reports the C 1s spectra. The dominant feature at 283.9 eV can be attributed to atomic or carbidic carbon [52]. Interestingly, and in line with the corresponding Cu 2p spectra (Fig. 3a), no carbidic carbon is present at 2 V, while at 4 V a carbon deposit forms, similarly to OCP conditions. Minor changes in peak position and shape between the spectra measured at OCP and at 4 V do not warrant a different spectral assignment; in fact, the C 1s line position originating from atomic carbon species is known to shift by a few tenths of eV, depending on the reaction conditions and the surrounding chemical environment. This effect, according to the literature, can be attributed to coadsorption and local restructuring phenomena, while any type of chemical bonding, a fortiori to oxygen, would yield a chemical core level shift that is larger by an order of magnitude [53]. Moreover, it is worth noting that switching back to OCP (top spectrum in panel b of

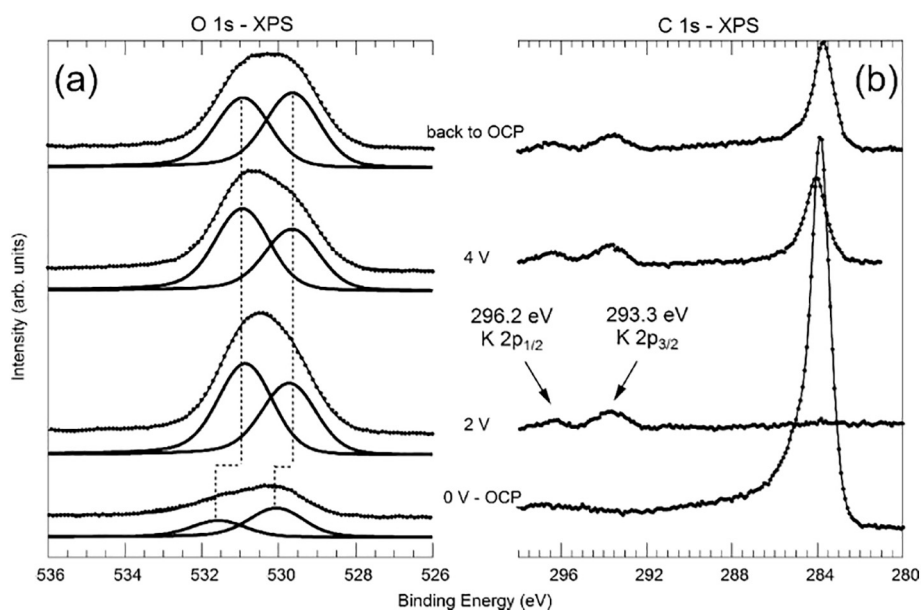


Fig. 4. (a) O 1s and (b) C 1s XPS spectra recorded in 0.5 mbar CO₂ at 600 °C at the indicated potentials. The continuous lines are the results of the fitting procedure.

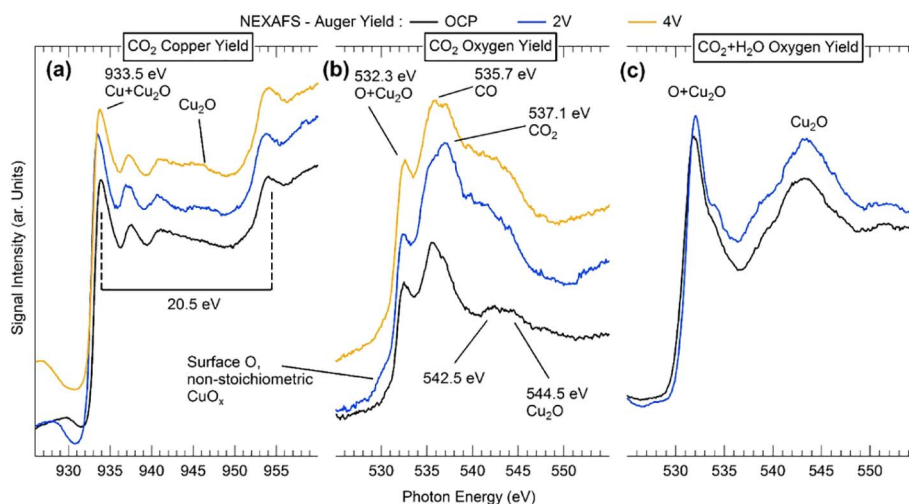


Fig. 5. NEXAFS spectra (Auger yield) at the Cu L and O K edges, recorded at 600 °C at the indicated potentials in 0.5 mbar CO₂ (Panels a and b) and CO₂ + H₂O 1/1 (Panel c).

Fig. 4) a carbon deposit is again present, even though the corresponding C 1s peak is significantly smaller with respect to the initial conditions. The absence of carbon deposits at 2 V is a result that is in keeping with [13]. Graphitic C, present at OCP, is removed under oxidising conditions due to both segregation and the direct reaction of pre-adsorbed carbon with oxygen in the supporting oxide at the electrolyte surface, while at the metal surface an electrode-cleaning procedure based on oxidation of the metal surface by CO₂ dissociation takes place. After elimination of the carbon deposit present at the initial OCP, two small features appear at 293.3 eV and 296.2 eV, assigned to K 2p_{3/2} and 2p_{1/2}, respectively. K is indeed a typical trace element of the YSZ electrolyte [54], accessible to analysis through the holes of the electrode patches (see Fig. 1). According to the interpretation above, K traces become visible upon segregation to the surface of the oxide after removal of the initial adventitious carbon contamination.

Fig. 5 shows Cu-L and O-K NEXAFS spectra obtained in the Auger yield mode. The spectra contain multiple features, that correspond to well-known species and can be readily assigned by means of a qualitative comparison with the published data [47,55–58]. For the present purpose, we reckon that it is adequate to carry out this comparison by simply marking the energy positions of the key features corresponding to the reported species. As far as the Cu L spectra are concerned, the position of the L₃ edge at 933.5 eV, together with the feature at 954.0 eV (L₂, separation of 20.5 eV) and the peak at 937.0 eV, unequivocally reveal the coexistence of Cu⁰ and Cu⁺ phases. We suppose that the metallic Cu component is present either owing to the fact that the probing depth is larger than the thickness of the thin oxide layer or because the disruption of the top oxide layer gives direct access to the underlying metallic Cu. In particular, the L₃ and L₂ features are related to the dipole transition of the Cu 2p_{3/2} and 2p_{1/2} electrons into the empty d-states and their energy separation is therefore determined by the spin-orbit coupling, which is known to be dependent on the oxidation state [55]. Concerning the O K edge the main feature at 532.3 eV indicates that the Cu₂O phase dominates [47,55] and the copper oxide phase grows further with the reaction, since the corresponding absorption features gain intensity after switching on the potential. However, the small pre-edge shoulder at ~531 eV can bear some contribution from chemisorbed O or a non-stoichiometric CuO_x phase. All O K edge spectra show a broad structure in the 535–538 eV range that can be ascribed to gas-phase CO (feature at ca. 535.7 eV) and CO₂ (feature at ca. 537.1 eV) [56–58]. This assignment is further confirmed by the data collected simultaneously in the total yield mode (not reported, for brevity), emphasizing the gas-phase contribution. Interestingly, a contribution from a subsurface oxygen species that acts as an oxide precursor has been reported to contribute in this same

range to the near-edge spectra and therefore cannot be excluded [59]. Notwithstanding these observed strong gas-phase contributions to the O K edge spectra, the features of Cu₂O can be however reliably ascertained, as reported in the previous reference.

3.2.2. CO₂/H₂O co-electrolysis

The Cu 2p XPS spectra recorded in 0.5 mbar CO₂/H₂O 1/1 and 1/2 (not reported, for brevity) are essentially the same as observed in pure CO₂ where the Cu₂O phase was found to be formed. Compared to the case of pure CO₂ the O 1s spectra are somewhat different. As can be seen in Fig. 6a, at OCP the atomic oxygen component dominates in the 529.9–530.3 eV range, shifting to higher binding energies for higher applied potential, thus indicating an increased oxidation of the surface. In parallel, a weaker feature is present at OCP at 531.5 eV, shifting up to 531.8 eV with increasing bias. Based on literature data [49], it is hardly possible to assign unequivocally this latter feature to a single chemical species. In particular, apart from the OCP spectrum, its binding energy is too high for bulk Cu oxide phases, while it may be compatible with CO₂^{δ-} and/or OH moieties. Since the intensities were normalised to the background, it is evident that keeping constant the CO₂/H₂O ratio, both components grow by increasing the applied cathodic polarisation. However, comparing the spectra of Fig. 6a with the evolution of the O 1s spectra taken in pure CO₂ ambient (Fig. 4a), it is evident that the component assigned to Cu₂O remains dominant in both cases. If the CO₂/H₂O ratio is brought to 1/2 at 2 V, the intensity ratio changes in favour of the higher-binding energy component, compatibly with a contribution to the latter from OH species.

Compared to the pure CO₂ ambient, C 1s spectra measured during CO₂ + H₂O co-electrolyses contain new components (Fig. 6b), in analogy with the O 1s region. A clear shoulder at higher binding energy with respect to the main peak can already be noticed under the initial OCP conditions. Deconvolution shows two peaks at 283.7 ± 0.1 and 285.2 ± 0.1 eV, respectively. The lower-binding energy feature corresponds to the single peak present in pure CO₂ ambient, while the higher-binding energy one can be assigned to CO [52,60]. These are the only C-containing species that can be assigned on the basis of spectroscopic data. We cannot exclude that other products form, but surely they do not contribute to the surface composition, that is the scope of this work. It is worth noting that it is customary in NAP-XPS studies of high-surface area catalysts, to monitor the gas phase of the analysis chamber by mass spectrometry: in the present case this was not possible owing to the fact that the low active surface of our planar, lithographed electrodes did not allow to achieve an appropriate signal-to-noise ratio for meaningful speciation. It is apparent that the dependence of carbon coverage on the potential is profoundly affected by the presence of H₂O:

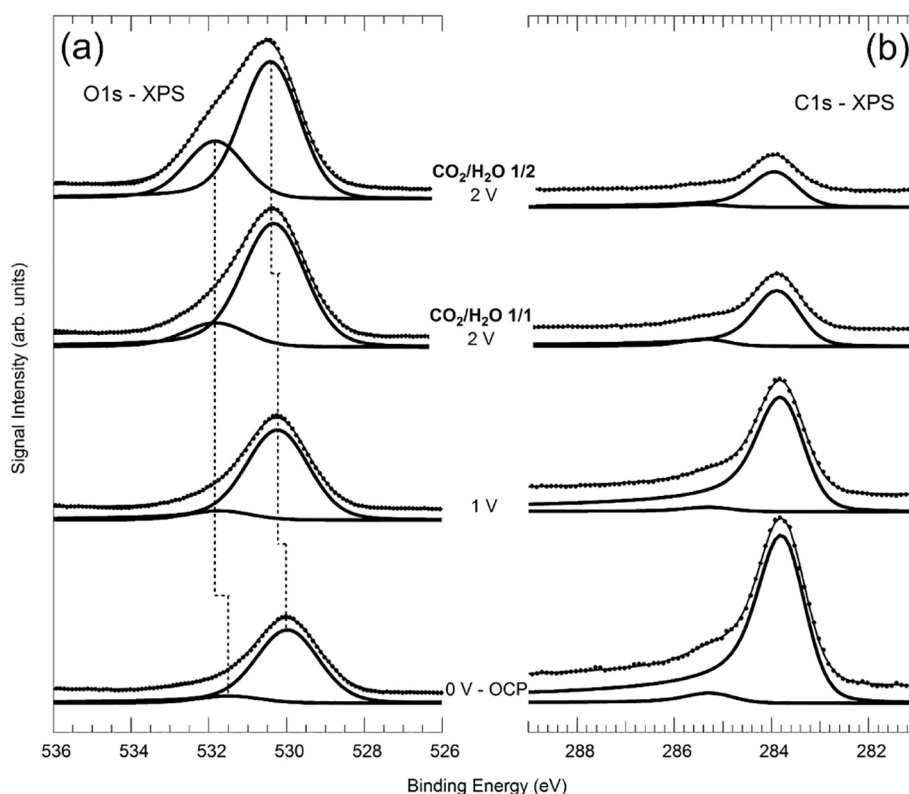


Fig. 6. (a) O 1s and (b) C 1s XPS spectra recorded in 0.5 mbar $\text{CO}_2/\text{H}_2\text{O}$ 1/1 and 1/2 (see figure) at 600 °C at the indicated potentials. The continuous lines are the results of the fitting procedure.

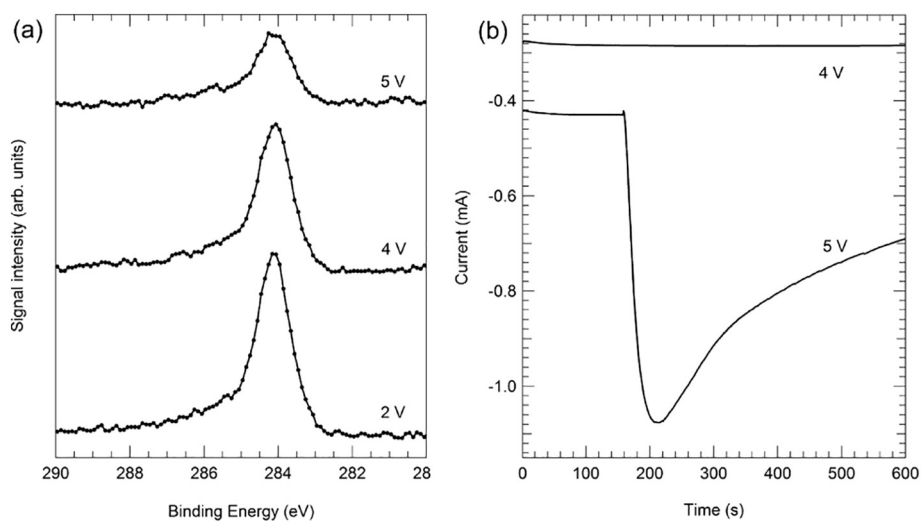


Fig. 7. Reductive C removal experiment in 0.5 mbar H_2O at 600 °C at the Cu cathode. Electrode previously polarised potentiostatically at 2 V in 0.5 mbar $\text{CO}_2/\text{H}_2\text{O}$, as detailed in the text. (a) C 1s XPS spectra recorded at the indicated potentials: each potential has been applied for 5 min. (b) Potentiostatic transients recorded as a result of the application of the indicated cell polarisation, during the measurements of the C 1s XPS spectra shown in Panel (a).

while in pure CO_2 the initial carbon contamination (0 V – OCP) disappears at 2 V, when the Cu electrode is exposed to the reactant mixture ($\text{CO}_2/\text{H}_2\text{O}$) the C 1s peak is still present and it decreases with the applied voltage. It is worth noting that the intensity of the higher-binding energy shoulder is notably less affected by the applied potential and it remains almost constant. Essentially the same scenario is found for both the investigated $\text{CO}_2/\text{H}_2\text{O}$ ratios. As discussed below, this should be ascribed to a process involving a water/hydrogen-assisted mechanism that efficiently promotes the fast decomposition of carbon dioxide at the surface of the electrode either as a result of H_2 formation from H_2O decomposition or by direct reaction with H_2O [60]. At the end of the experiment, C removal was attempted in pure H_2O ambient

at 0.5 mbar, performing a series of potentiostatic experiments by increasing the cell voltage in steps of 1 V and holding the potential for 5 min, until a significant reduction of the C 1s peak intensity was observed at 5 V. Fig. 7 reports the potential dependent C 1s spectra and a representative selection of potentiostatic transients, showing a straightforward correlation between the cell current and the amount of adsorbed C. It can be clearly seen that at 5 V, a distinct increase of cell current is recorded, corresponding to the reductive desorption of C from the cathode, correlated with a clear decrease of the C 1s peak intensity.

NEXAFS spectra at the Cu L and O K edges, measured under $\text{CO}_2 + \text{H}_2\text{O}$ co-electrolysis (Fig. 5b) do not add qualitatively new

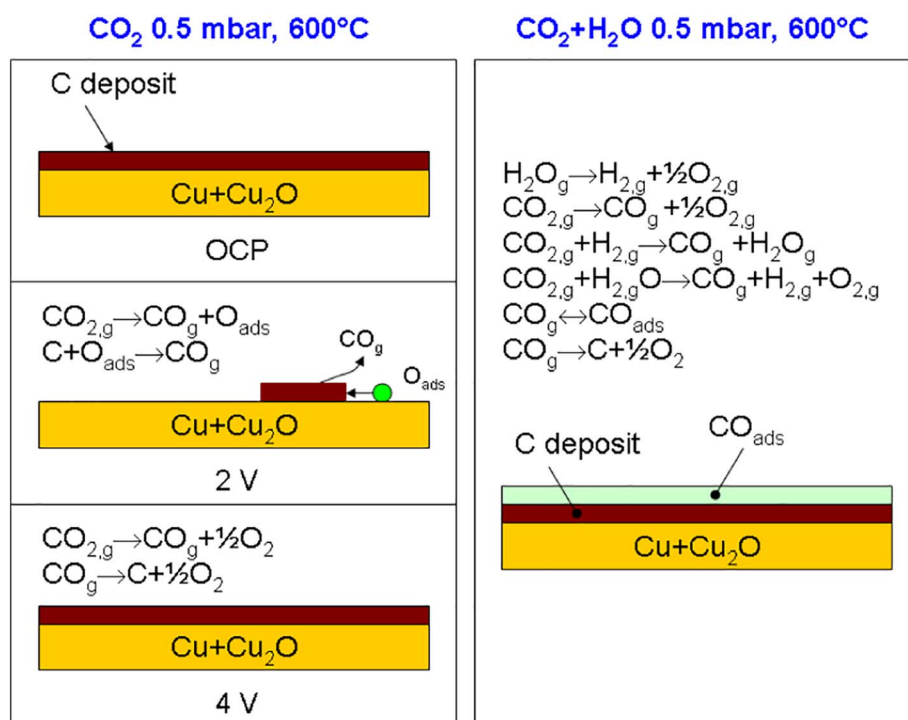


Fig. 8. Scheme of the reaction scenarios prevailing in the investigated gas environments under electrochemical polarisation.

information since the same characteristic features were found as in CO₂ ambient. The Cu L spectra are identical to those measured in CO₂ (Fig. 5a) and have been omitted for brevity, while the O K ones (Fig. 5c) simply indicate a more strongly oxidised surface, coherently with the foregoing discussion.

4. Discussion

4.1. CO₂ electrolysis

Our in situ results regarding CO₂ electrolysis suggest the reaction scenario detailed below and marshalled into Fig. 8. The Cu electrode surface in the initial conditions (0 V – OCP) is fairly oxidised and covered with adventitious carbon. When a cathodic polarisation of 2 V is applied, CO₂ decomposition sets in, yielding CO + O. During this reaction, that is an oxidising one [29], the produced atomic oxygen at the electrode surface reacts: (i) with the initially pre-adsorbed carbidic species to CO, as evidenced by the disappearance of the C 1s peak of the atomic carbon species when switching the potential from OCP to 2 V and (ii) with the electrode surface, yielding Cu₂O, as witnessed by the growth of the oxide-related features observed in the Cu and O NEXAFS and XPS spectra. It is known that, in order to dissociate CO₂ on copper, a barrier of 1.5–1.7 eV has to be overcome [61], while CO decomposition requires a higher energy (about 2.5 eV). Apparently at 2 V the CO dissociation cannot compete with the low-barrier CO desorption, favoured at the operating cell temperature of 600 °C. Thus at 2 V the electrode surface is already oxidised and carbon cannot accumulate. However, when the potential is increased to 4 V, also CO dissociation becomes feasible and carbon accumulation at the surface occurs. No signal from adsorbed species (carbonate, carbon monoxide, carbon dioxide) is observed and it is in fact not expected due to the high surface temperature (600 °C) at which the residence time of both reactants and products is known to be very short, thus yielding negligible surface coverage values. For completeness, it is worth reporting here that the joint analysis of the C 1s and O 1s peaks recorded at 600 °C in CO₂ 0.5 mbar at ceria cathodes in [13] has been explained with the presence of carbonate - with possibly some contribution to the O 1s spectrum

from the SiO₂ support - in a wide range of electrochemical conditions. The adsorption of CO_x species at ceria [62,63], ceria/copper and Cu [64] had been previously reported to be unstable above ambient temperature.

4.2. CO₂/H₂O co-electrolysis

The presence of a surface CO peak in the C 1s XPS spectra measured during the CO₂ + H₂O co-electrolysis can be explained with the fact that water reduction, that occurs at significantly lower voltages than CO₂ reduction on Cu (see e.g. [22]), yields hydrogen that may assist CO₂ reduction to CO. In addition, even at OCP conditions, direct interaction between CO₂ and water molecules at the catalyst surface can also lower the CO₂ decomposition barrier, as previously observed under both model and near-ambient pressure conditions [52,60]. Indeed, a hydrogen-assisted mechanism can lower the energy barrier for the CO₂ dissociation into CO and O so as to make it a fast process even at very low temperature [60]. Further reduction of CO, enabled by the increased rate of hydrogen production resulting from the applied cathodic polarisation, stabilises the surface coverage with carbidic carbon also at 2 V, where C is instead oxidised in pure CO₂ ambient. This scenario is further supported by the intensity changes of the O 1s peak measured with applied polarisation.

5. Conclusions

In this paper we have studied in situ and operando the surface chemistry of a Cu cathode under CO₂ electrolysis and CO₂/H₂O co-electrolysis conditions by near ambient pressure XPS and NEXAFS in a model SOEC at 600 °C. Our key findings are that in dry CO₂, pre-existing C deposits are scavenged at lower cathodic potential (cell voltage of 2 V) by the oxidising action of nascent oxygen resulting from CO₂ reduction, while C forms at the cathode surface at higher cathodic polarisations (cell voltage of 4 V) as a result of the reduction of CO, which is not activated at the lower voltages. In dry CO₂ no surface C-O species are found, while in CO₂/H₂O adsorbed CO is present as a result of CO₂ reduction favoured by H₂ formation, resulting from H₂O

decomposition or by direct reaction with water. Under co-electrolysis conditions, due to the presence of adsorbed CO, C deposits are stabilised and can be reacted off only at significantly more reducing potentials.

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