SUPPORTING INFORMATION

Surface Chemistry of Perovskite-Type Electrodes During High Temperature CO₂ Electrolysis Investigated by Operando Photoelectron Spectroscopy

Alexander K. Opitz a,*, Andreas Nenning a,†, Christoph Rameshan b, Markus Kubicek c, Thomas Götsch c, Raoul Blume d, Michael Hävecker d, Axel Knop-Gericke d, Günther Rupprechter b, Bernhard Klötzer c, and Jürgen Fleig a

a) Vienna University of Technology, Institute of Chemical Technologies and Analytics, Getreidemarkt 9/164-EC, 1060 Vienna, Austria
b) Vienna University of Technology, Institute of Materials Chemistry, Getreidemarkt 9/165-PC, 1060 Vienna, Austria
c) University of Innsbruck, Institute of Physical Chemistry, Innrain 80-82, 6020 Innsbruck, Austria
d) Fritz Haber Institute of the Max Planck Society, Department of Inorganic Chemistry, Faradayweg 4-6, 14195 Berlin, Germany
†) Present Address: Massachusetts Institute of Technology, Department of Materials Science and Engineering, 77 Massachusetts Avenue, Cambridge, MA, 02139, U.S.A
*) corresponding author: alexander.opitz@tuwien.ac.at
Impedance spectroscopy were measured by means of a Novocontrol Alpha-A High Performance Frequency Analyzer equipped with a POT/GAL 30V 2A interface. The typically recorded frequency range was 5 mHz – 1 MHz but was adjusted if necessary; the AC voltage was 5 mV root mean square. Impedance spectra with and without an additional DC polarization obtained on $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ (LSF) and $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.9}\text{Ni}_{0.1}\text{O}_{3-\delta}$ (LSCrNi8291) working electrodes are shown in Figures S1 and S2, respectively. All spectra consist of a high frequency intercept on the real axis – cf. Figures S1b and S2b – and an electrode feature in the medium to low frequency range. The high frequency intercept contains contributions of the ohmic resistance of ion transport in the YSZ electrolyte as well as contact and wire resistances. Since at lower temperature the electrolyte resistance is by far dominant and the relationship of ionic conductivity in YSZ and temperature is well known, it was used for temperature calibration of the employed pyrometer at 400 and 600 °C.\textsuperscript{1,2}

Without an applied DC bias the electrode features of both materials appear rather huge without reaching the real axis (see Figures S1a and S2a). Upon applying about – 1 V cathodic bias, however, the electrode feature is significantly smaller – see Figures S1b and S2b. This behavior can be understood by considering the reaction at the working electrode: \(\text{CO}_2 + 2 e^- \rightarrow \text{CO} + \text{O}_2^-\). Since without polarization virtually only CO\textsubscript{2} is present in the atmosphere the exchange rate of this reaction is extremely low; in this respect please compare also the very shallow slope at 0 V of the I-V-curve in Figure 2a. Thus the electrode resistance measured by impedance – which is inversely proportional to this exchange rate – is huge. DC bias speeds up the electrode reaction, the slope of the I-V-curve becomes larger, and the electrode’s impedance feature is thus smaller.

![Figure S1](image1.png)

**Figure S1:** (a) Impedance spectra (Nyquist plots) measured on LSF electrode at 720 °C in 0.25 mbar CO\textsubscript{2} atmosphere with and without cathodic polarization. (b) Magnification of the origin of the diagram in (a).

![Figure S2](image2.png)

**Figure S2:** (a) Impedance spectra (Nyquist plots) measured on LSCrNi8291 electrode at 720 °C in 0.25 mbar CO\textsubscript{2} atmosphere with and without cathodic polarization. (b) Magnification of the origin of the diagram in (a).
2 CURRENT-VOLTAGE CHARACTERISTICS

Current voltage curves on LSCrNi7291 and LSF were also measured at lower temperatures of 600 °C and 400 °C, respectively. The resulting Tafel diagrams are shown in Figure S3. As for the I-V-curves measured at higher temperatures the data were fitted to Equ. 6b – the resulting fit parameter $I_0$ and $\alpha$ are summarized in Table S1.

Table S1: Resulting fit parameters of Tafel Fits in Figure S3 using Equ. 6b.

| Material    | Temperature / °C | $\alpha$   | $I_0$ / mA cm$^{-2}$ |
|-------------|------------------|------------|----------------------|
| LSCrNi7291  | 600              | 0.618 ± 0.011 | $(4.3 \pm 0.2) \times 10^{-5}$ |
| LSF         | 400              | 0.700 ± 0.074 | $(3.5 \pm 1.2) \times 10^{-6}$ |

Figure S3: Tafel plots of the measured electrochemical DC current versus the applied overpotential. (a) LSCrNi7291 at 600 °C and 0.25 mbar CO$_2$. (b) LSF at 400 °C and 0.25 mbar CO$_2$.

3 SCANNING ELECTRON MICROSCOPY (SEM)

SEM images were recorded on a FEI Quanta 200 FEG. Due to preparation reasons each sample contains parts of the perovskite thin film, which are electrically not connected to the working electrode. Thus it was possible to investigate parts of the same sample with and without cathodic polarization but with the same thermal pre-history in 0.25 mbar CO$_2$ atmosphere. The SEM results for LSF and LSCrNi7291 are shown in Figure S4. On both samples cathodic polarization obviously caused evolution of small particles, which together with spectroscopic results can be regarded as exsolved metallic particles.
4 **INTERPRETATION OF XPS-DATA**

Identification of gas phase peaks was supported by suppressing them by applying a 90 V DC bias to the electron collecting nozzle of the spectrometer. This leads to a very strong broadening of the gas phase peaks, causing them virtually vanishing in the background. A comparison of C 1s spectra measured with and without the bias applied to the nozzle is shown in Figure S5.

Analysis of XPS spectra was done using the software CasaXPS. For fitting of O 1s spectra a Shirley-type background was used, whereas for C 1s spectra a combination of Shirley-type and linear background was employed. For fitting of background corrected peaks of O 1s spectra a combination of a Gaussian and Lorentzian line shape was used. In case of C 1s spectra a combination of a Gaussian and Lorentzian line shape was used for gas phase and carbonate peak, while the graphite peak was fitted with an asymmetric line shape according to literature. Binding energies obtained by the above mentioned fit routine for different XPS peaks are plotted as a function of the applied electrochemical polarization in Figure S6. These plots support the conclusion drawn from Figure 7a in the main manuscript that the carbonate is located on the oxide surface and is neither adsorbed on exsolved metal particles nor a kind of gas molecule.

**Figure S4:** SEM images of LSF electrode surfaces before (a) and after (b) cathodic polarization experiments as well as of LSCrNi7291 electrodes before (c) and after (d) cathodic polarization. In each case CO\(_2\) pressure was 0.25 mbar. After cathodic treatment formation of particles can be observed on both electrodes.

**Figure S5:** Comparison of C 1s spectra with and without 90 V DC bias at spectrometer nozzle.
Figure S6: Binding energies obtained from XPS fitting of the 232 – 233 eV O 1s shoulder (a), the 291 eV C 1s species (b), and the C 1s CO\(_2\) gas phase peak (c) – all plotted vs. the applied overpotential \(\eta\). Obviously the features of the carbonate species – (a) and (b) – directly reflect the shift of the Fermi level caused by polarization\(^\ref{footnote}\), whereas the gas phase exhibits a different behavior.
Figure S7: C 1s spectra recorded on LSF electrode in 0.5 mbar CO₂ at 720 °C. The carbon deposit forming under cathodic polarization (asymmetric peak at 284 – 285 eV) can be immediately removed by retracting the applied voltage.
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