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Supporting Information

Zirconium Oxycarbide: A Highly Stable Catalyst Material for Electrochemical Energy Conversion

Niusha Shakibi Nia, Daniel Hauser, Lukas Schlicker, Albert Gili, Andrew Doran, Aleksander Gurlo, Simon Penner,* and Julia Kunze-Liebhäuser*© 2019 The Authors.
Published by Wiley-VCH Verlag GmbH & Co. KGaA.
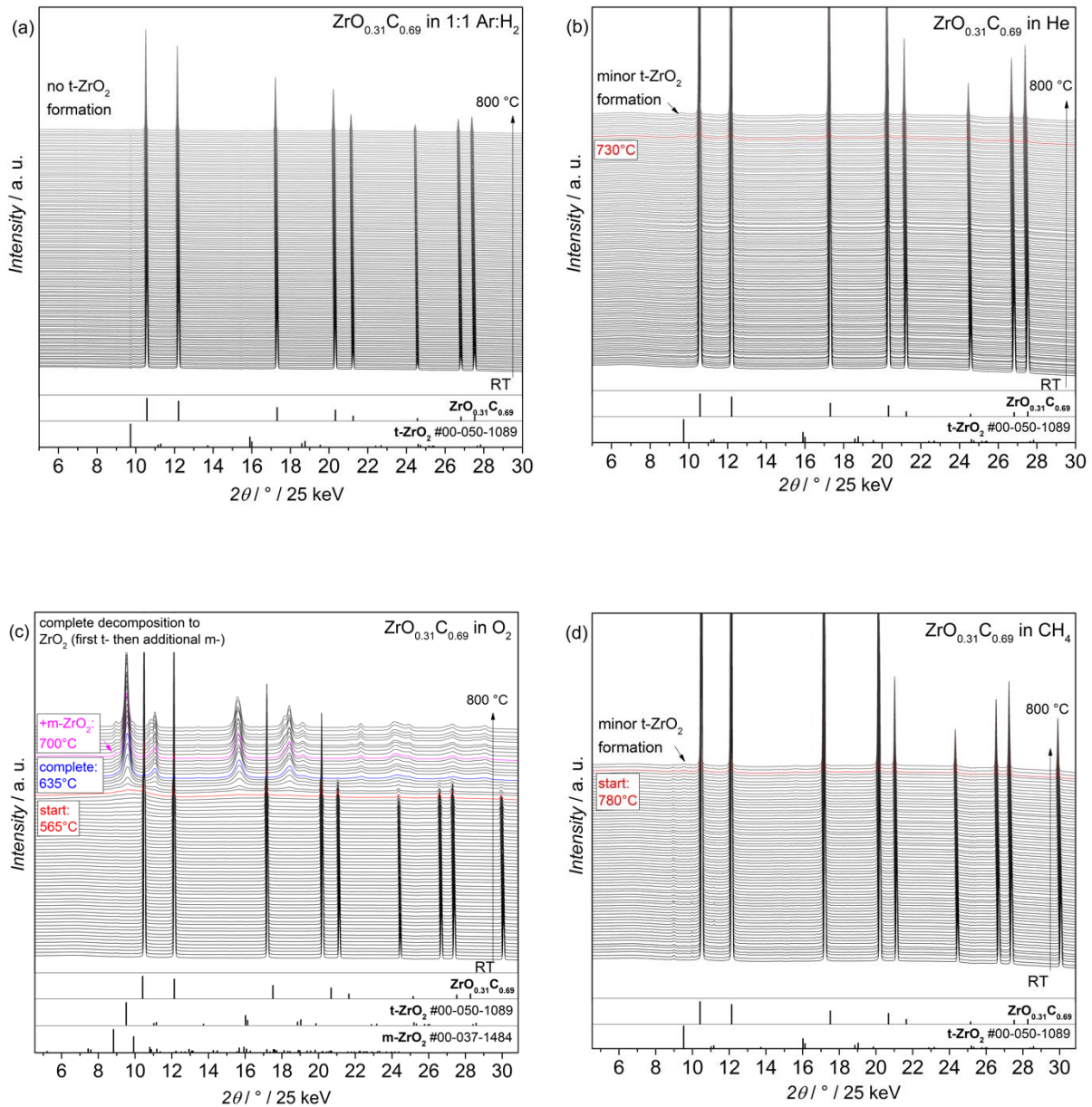An invited contribution to a Special Issue on Electrocatalysis

Supporting Information

Figure S1: *In situ* X-ray diffractograms of $ZrO_{0.31}C_{0.69}$ in different gas atmospheres. (a) 1:1 Ar:H$_2$, (b) pure He, (c) pure O$_2$ and (d) pure CH$_4$. Temperature range: from room temperature (25 °C) to 800 °C, heating ramp: 10 °C min^{-1}.

The decomposition of $ZrO_{0.31}C_{0.69}$ in different gas atmospheres is strongly influenced by the polymorphism of ZrO_2, i.e. the existence of (meta)stable monoclinic (m-ZrO_2) and tetragonal ZrO_2 (t-ZrO_2). The transformation of the latter into the thermodynamically more stable monoclinic modification is itself a strong function of the gas atmosphere. It is known, that tetragonal ZrO_2 is stabilized either by structural defects or by grain size control. In that respect, the transformation is suppressed in strongly reducing atmospheres. The more oxidizing the atmosphere, the faster the transformation. With respect to our study, we note that in O$_2$, first t-ZrO_2 appears, then very fast also

m-ZrO$_2$ is observed. In CO$_2$, a similar process is found, but with delayed transformation into m-ZrO$_2$. Nevertheless, the temperature period between the first appearance of t-ZrO$_2$ and full decomposition is about the same as in O$_2$ (start at 565 °C, end at 635 °C, i.e. 70 °C) and in CO$_2$ (start at 660 °C, end at 740 °C, i.e. 80 °C)). The crystallization of t-ZrO$_2$ itself is a kinetically determined process, where nuclei of t-ZrO$_2$ have to be formed, which then facilitate the further crystallization.
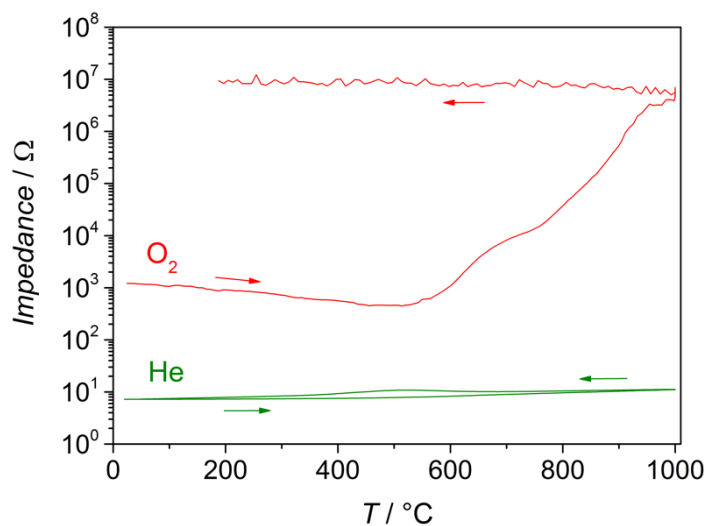
Figure S2: In situ electrical impedance spectroscopy measurements on ZrO$_{0.31}$C$_{0.69}$ in O$_2$ (red line) and in He (green line).
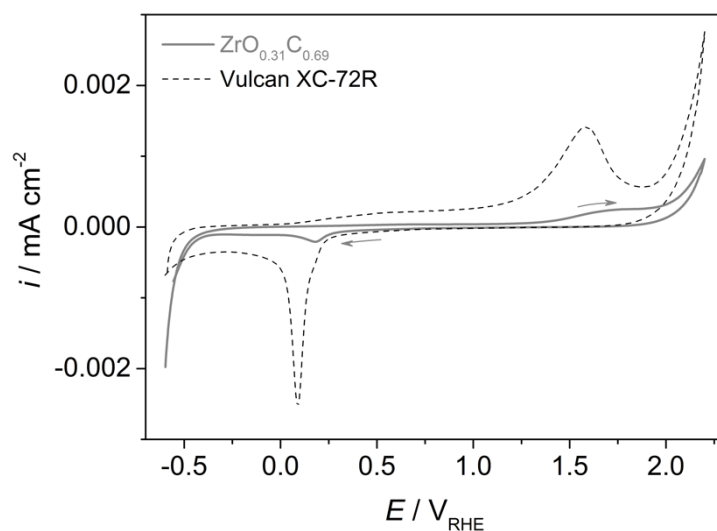

Figure S3. CVs of ZrO$_{0.31}$C$_{0.69}$ and carbon Vulcan XC-72R recorded in 0.5 M H$_2$SO$_4$ at room temperature. Scan rate: 10 mV s^{-1}. Current densities are given with respect to the BET surface areas.
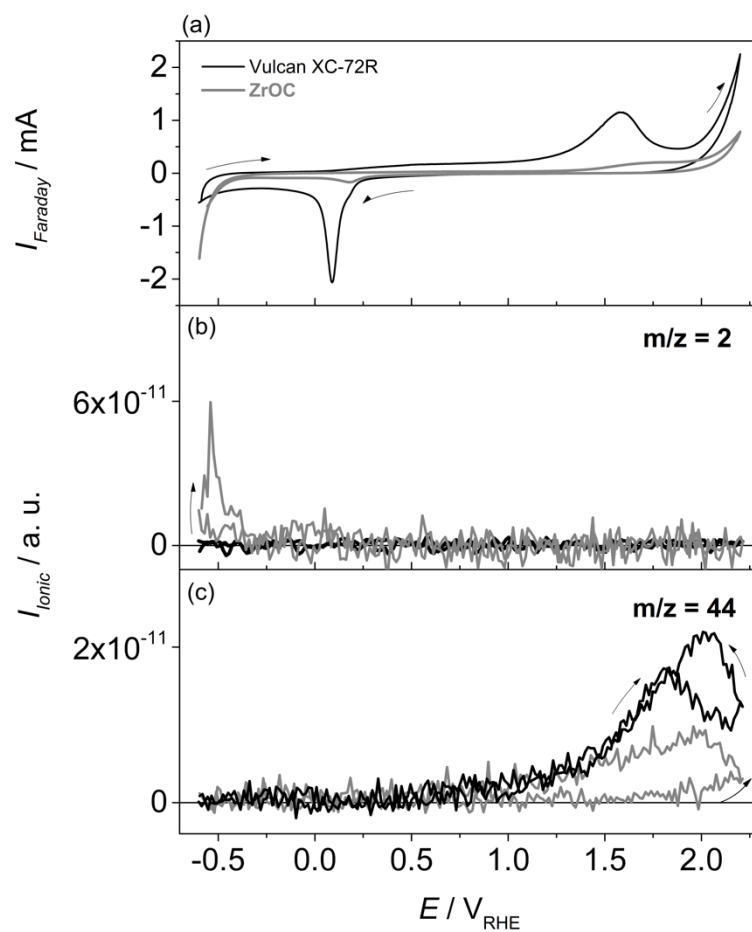
Figure S4: (a) CVs of $ZrO_{0.31}C_{0.69}$ and carbon Vulcan XC-72R recorded in 0.5 M H_2SO_4 at room temperature, (b) MSCVs for m/z = 2 and (c) MSCVs for m/z = 44. Scan rate: 10 mV s^{-1}.

DEMS calibration with Pt/C powder catalyst
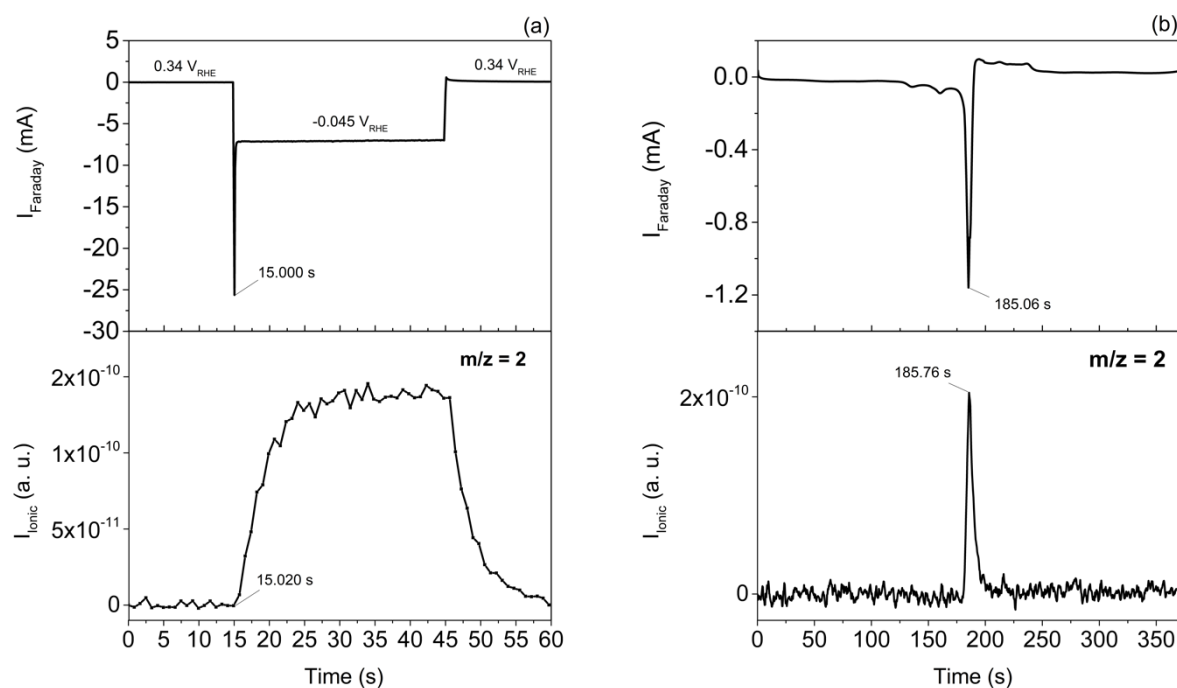
Figure S5: (a) Current transients and corresponding MSCTs at m/z = 2, (b) potentiodynamic measurements of current form 0.16 V to -0.02 V at 5 mV s^{-1} and corresponding mass spectrometric signal at m/z = 2 recorded with Pt/C catalyst in 0.5 M H_2SO_4 at room temperature.

The DEMS flow cell configuration was calibrated using Pt/C catalyst ink. To measure the current transients for hydrogen evolution at Pt/C (Figure S5a), the potential was stepped from 0.34 V to -0.045 V (vs RHE) while the mass spectrometric current transients (MSCTs) of the hydrogen signal (m/z = 2) were recorded online over time. With this technique, the delay time of hydrogen detection at m/z = 2 for potentiostatic experiments was determined as 0.02 s.

Additionally, the potential was screened between 0.16 V and -0.02 V with a scan rate of 5 mV s^{-1} (Figure S5b), from which a delay time of 0.7 s can be determined for potentiodynamic hydrogen detection. This delay time was used to correct the gas evolution onsets, determined under the same conditions, in the present manuscript.