Identical Location Scanning Transmission Electron Microscopy of Pore-Confined Copper-Based Nanoparticle Catalysts for the CO_2 Reduction

R. Zandonella[1*]; E. S. Koh[2]; A. Gunnarson[3]; P. Paciok[1]; M. Ledendecker[2]; M. Heggen[1]; F. Schüth[3]; R. Dunin-Borkowski[1]

[1] *Ernst-Ruska-Center for Microscopy and Spectroscopy with Electrons, Forschungszentrum Jülich, Jülich, Germany*

[2] *Department of Chemistry, Ernst-Berl-Institut für Technische und Makromolekulare Chemie, Technical University of Darmstadt, 64287 Darmstadt, Germany*

[3] *Max-Planck-Institut für Kohlenforschung. 45470 Mülheim an der Ruhr, Germany*

* *r.zandonella@fz-juelich.de*

Introduction

Copper-based catalysts used in the electrochemical CO_2 reduction reaction (CO2RR) bridge the gap between CO_2 removal from the atmosphere and the production of value-added molecules. For industrial applications however, catalyst stability over 100 days is a necessity for initial proton exchange membrane electrolyzer prototyping [1]. Even so, structure related degradation mechanisms are far from being well understood. In this work, copper nanoparticles confined in the porous structure of mesoporous graphitic spheres (Cu@MGS) were used to mitigate possible aggregation, dissolution and detachment and ultimately preserve electrochemically active surface area. Copper nanoparticles, attached to the surface of Vulcan XC72 (Cu@Vul) were used as a comparison standard and show the stabilizing effect of pore confinement. Identical location (scanning) transmission electron microscopy (IL-(S)TEM) was employed as a method of direct observation of identical catalyst particles pre- and post- ex-situ electrolysis, revealing the present degradation mechanisms. To circumvent experimental issues with bubble formation impeding the reaction and carbon film instabilities at potentials relevant to CO2RR, a new experimental setup (shown below) solving these issues was utilized.

Instrumentation

A Hitachi HF5000 scanning transmission electron microscopy ((S)TEM) is used as a tool to study the morphological state of a catalyst on the nanoscale. A beam of electrons is focused on a small sample area and scanned across the region of interest. Through scattering of the electrons inside the sample, contrast is generated. Dark field images (DF) show the distribution of copper nanoparticles (white) on the carbon support (dark-grey).

The Hitachi HF5000 is also equipped with a secondary electron detector (SE) providing topological information about the sample surface, highlighting the nanoparticles location on the surface (Cu@Vul) and inside the pore system (Cu@MGS).

Stabilization of Nanoparticles through Pore-Confinement

Identical Location (S)TEM (IL-(S)TEM)

IL-(S)TEM aims to investigate the same sample location bevor and after an ex-situ experiment.

The sample is deposited onto a thin carbon film on top of a TEM grid and pre-characterized using a Hitachi HF5000 scanning transmission electron microscope ((S)TEM). After pre-characterization, the grid is removed from the microscope and used as a working electrode during ex-situ electrolysis as shown below. After electrolysis, the TEM grid with the now-degraded sample is taken back to the microscope for post-characterization.

To locate the exact same sample location for pre- and post-characterization, a special finder grid featuring numbers and letters is used.

Ex-situ Electrolysis: A new experimental setup

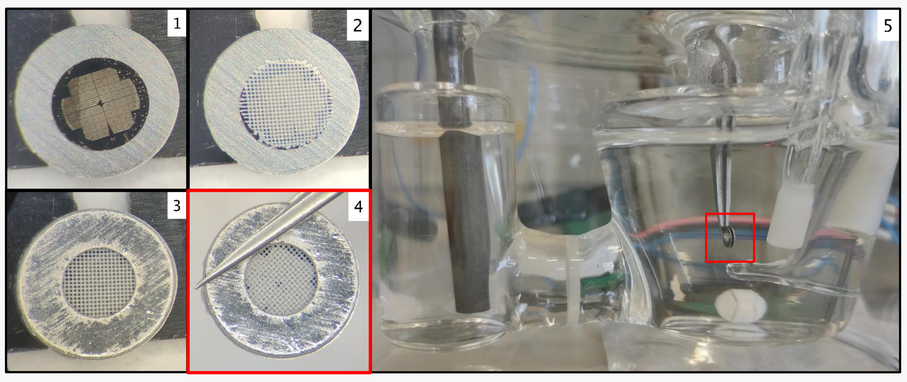
Rupture and delamination of the thin carbon film on top of the TEM finder grid leads to catastrophic sample loss when ex-situ electrolysis is performed at potentials relevant to CO2RR (V ~ 1.1 V_{RHE}).

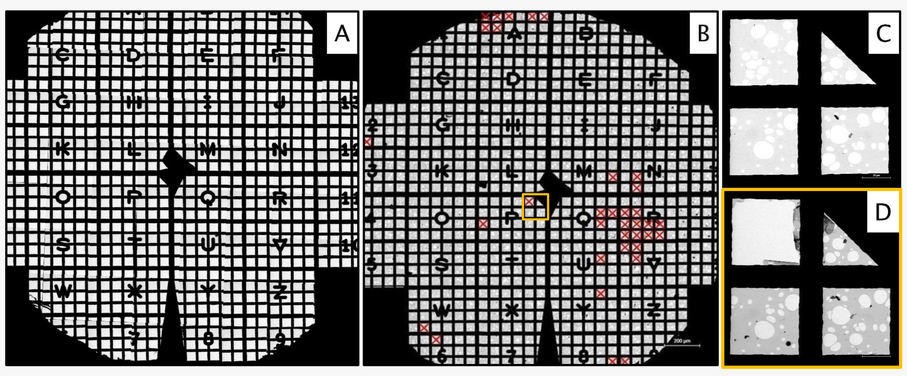
1-5) A new experimental setup using M2 washers and a nylon grid stops delamination while plasma cleaning of the components reduces bubble dwell time to a minimum. Numbers indicate the chronological order of the steps for setup assembly.

A) TEM finder grid after electrolysis at V_{RHE} = -1.1 V without the new setup showing a complete loss of the carbon film.

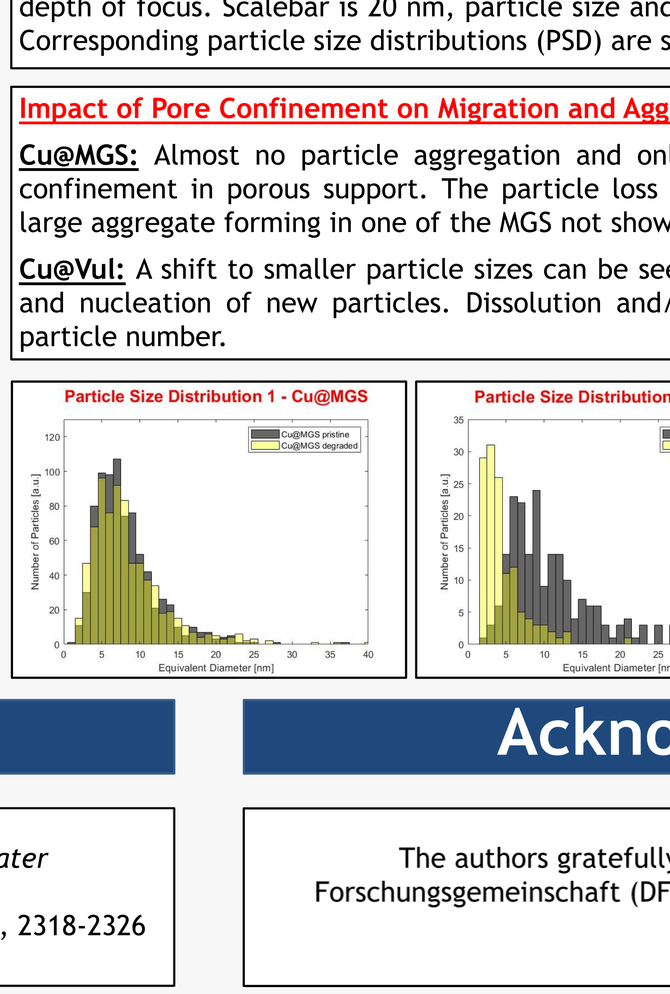
B & D) TEM finder grid after electrolysis at V_{RHE} = -1.1 V using the new experimental setup for 10 min showing minor rupture (red marks) but no delamination.

C) Pristine TEM finder grid bevor electrolysis.

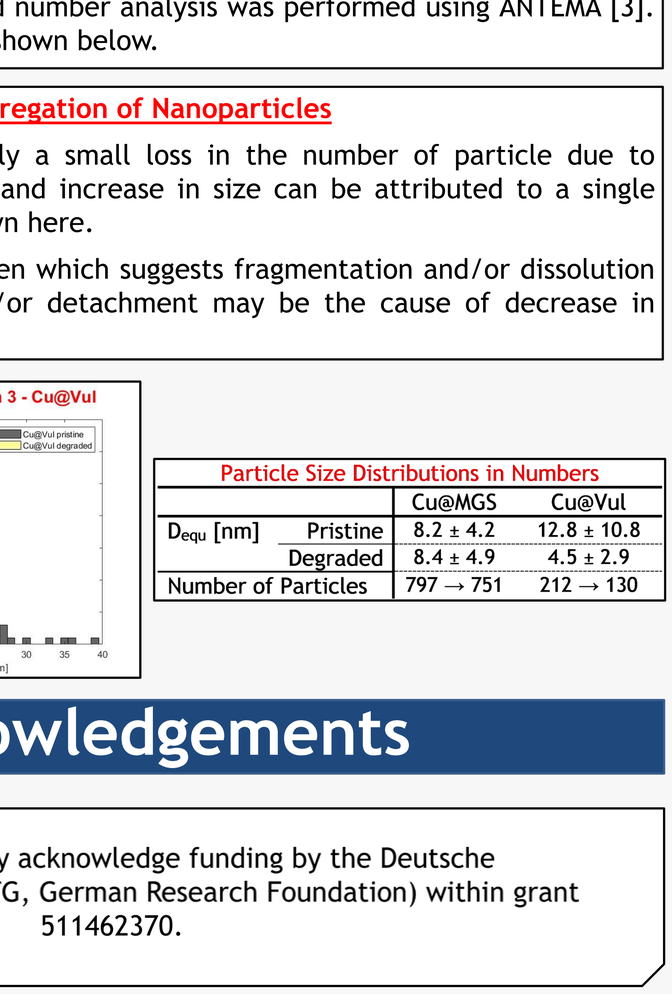




Cu@MGS (PSD 1)



Cu@Vul (PSD 3)



Figures A-B) samples in pristine form, C-D) samples in degraded form after electrolysis at -1.1 V_{RHE} for 10 minutes. Images were acquired by talking a through-focus series and z-stacking to increase the depth of focus. Scalebar is 20 nm, particle size and number analysis was performed using ANTEMA [3]. Corresponding particle size distributions (PSD) are shown below.

Impact of Pore Confinement on Migration and Aggregation of Nanoparticles

Cu@MGS: Almost no particle aggregation and only a small loss in the number of particle due to confinement in porous support. The particle loss and increase in size can be attributed to a single large aggregate forming in one of the MGS not shown here.

Cu@Vul: A shift to smaller particle sizes can be seen which suggests fragmentation and/or dissolution and nucleation of new particles. Dissolution and/or detachment may be the cause of decrease in particle number.

Particle Size Distributions in Numbers		Cu@MGS	Cu@Vul
D_{equ} [nm]	Pristine	8.2 ± 4.2	12.8 ± 10.8
	Degraded	8.4 ± 4.9	4.5 ± 2.9
Number of Particles		797 → 751	212 → 130

References

[1] H. Shin, K. U. Hansen, and F. Jiao, Nat. *Sustain* **4**, 911-919 (2021).

[2] M. Vega-Paredes, C. Scheu, and R. Aymerich-Armengol, *ACS Appl Mater Interfaces* **15**, 46895-46901 (2023).

[3] N. Gumbiowski, K. Loza, M. Heggen and M. Epple, *Nanoscale Adv.* **5**, 2318-2326 (2023).

Acknowledgements

The authors gratefully acknowledge funding by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) within grant 511462370.