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Synchrotron X-ray combined technique for unravelling the catalyst degradation mechanism in CO_2 electrolysis

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Electrochemical CO_2 reduction reaction (CO_2RR) using a membrane electrode assembly (MEA)-based electrolyzer represents a promising route for the industrial conversion of CO_2 into value-added chemicals.[1] However, its scaling up for industrial applications is constrained by insufficiently elucidated mechanisms, which involve both catalyst degradation and gas-diffusion-electrode (GDE) deterioration. The single detection technique employed in earlier mechanism studies is inherently limited in pinpointing the specific origins of performance degradation, as it cannot provide a comprehensive understanding of the catalyst's dynamic multiscale structure. There is no doubt that the development of operando combined technique to concurrently capture time-resolved information, including crystalline evolution, ion distribution, particle agglomeration, etc., of catalysts in the dynamic CO_2RR process is urgent and necessary. To address this, Jakub Drnec, Brian Seger, and their collaborators developed a comprehensive X-ray characterization platform by integrating synchrotron radiation (SR) wide-angle X-ray scattering (WAXS), small-angle X-ray scattering (SAXS), and X-ray fluorescence (XRF) techniques.[2] This combined technique, with a time resolution of about ~7 min, enables operando tracking of the multiscale dynamic evolution of catalysts, ultimately elucidating the degradation mechanisms in an MEA-based CO_2 electrolyzer.[3]

They applied the combined SAXS/WAXS/XRF set-up (Figure 1A) to operando monitor the CO_2RR process in an MEA electrolyzer, whose vertical position was precisely controlled to enable periodic MEA scanning with a 5-μm step width. In their work, carbon black-supported Au or Ag nanoparticles (NPs) were spray-coated onto a commercial GDE as model cathodes; commercial sustanion X37-RT membranes as the anion-exchange membrane (AEM); Ir-based GDE was used as anode. A zero-gap MEA was successfully fabricated by sandwiching an AEM between an anode and a cathode. A focused high-energy X-ray beam parallel to the customized MEA-based reactor allows for the collection of WAXS, SAXS, and XRF data across the scanned region, providing sufficient spatial and temporal resolution to track the real-time MEA behavior. Specifically, WAXS signals from Bragg diffraction reflect the crystalline evolution and water transport within the entire MEA over a wider scan range; SAXS signals from elastic X-ray scatter-

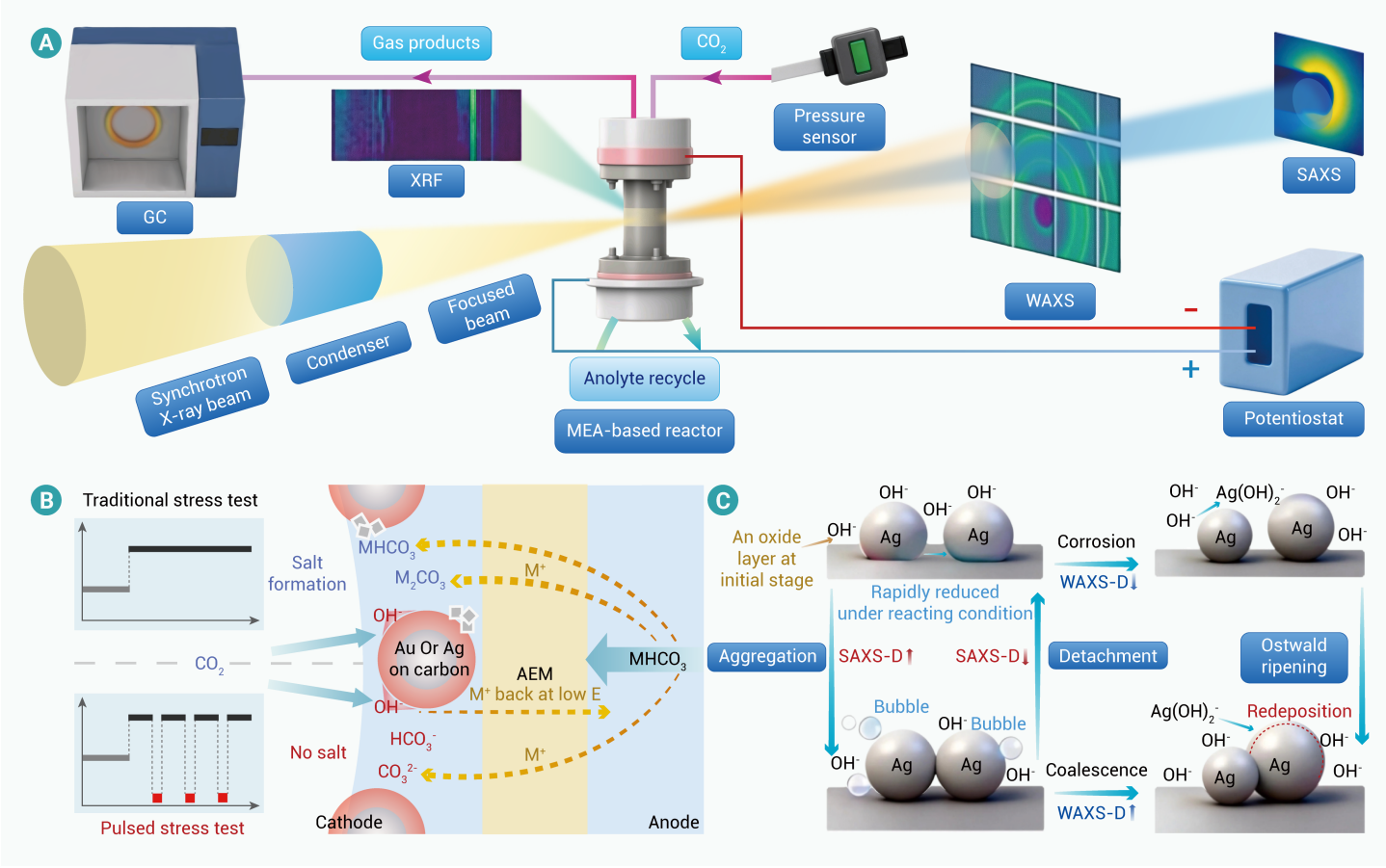

Figure 1. Schematic illustrations of the SR-based combined technique and the catalysts degradation mechanism (A) The operando SAXS/WAXS/XRF set-up for the CO_2 electrolysis measurement. (B) Revealing the pulsed AST test to prevent salt formation by comparison with the traditional stress test. (C) Structural evolution mechanisms of Ag nanoparticles during the stability test. Adapted with permission.[2] Copyright 2025, Springer Nature.

ing provide deeper insights into the overall morphological changes of nanoparticles in the catalyst layer (CL); XRF signals, generated by the ejection of core electrons upon incident X-rays, assist in identifying the elemental distribution and migration during electrolysis. A total duration of approximately 7 minutes was needed to collect 100 WAXS patterns and 50 SAXS patterns across their respective MEA scan regions, along with 150 corresponding XRF spectra. WAXS patterns confirm the face-centred cubic structure of Au and Ir in the CLs before electrochemical operation. The crystallite size of Au NPs was estimated to be ~ 9 nm via the Scherrer formula, using the full width at half maximum (FWHM) of the diffraction peaks. Au and Ir *L*-edge XRF peak intensities showed no change during electrolysis. Meanwhile, Cs *K*-edge XRF signals were present at both electrodes initially and increased significantly following 12 h of electrolysis. SAXS patterns demonstrated that the carbon-supported spherical Au NPs (~ 10 nm) catalyst displays a sloping profile featuring large form factor curvature in the middle region.

Furthermore, a pulse-electrochemistry-based accelerated stress test (AST) was established to address severe salt precipitation, allowing fast assessment of electrode durability and stability in complicated CO_2 electrolysis systems. Cations migrating across the AEM from the anolyte react with in-situ generated carbonate/bicarbonate, resulting in salt formation (Figure 1B) during prolonged electrolysis or at elevated current densities. The pulsed AST alternates between high reaction current density (i_{react}) and non-reaction potential (E_{no}), allowing periodic relaxation for accumulated ion release and salt formation prevention. A testing of the pulsed AST with an i_{react}=400 mA·cm^{-2} for 60 s and an E_{no}= 2 V for 20 s in their operando X-ray platform, clearly demonstrates that Cs intensity in the CL increased during i_{react} and decreased during E_{no}, hinting at ion back-diffusion toward the anode under the driving force of concentration gradients. This result indicates that the pulsed AST is a viable alternative to conventional AST, efficiently preventing salt precipitation and extending device longevity in CO_2 electrolysis.

The degradation of Ag and Au catalysts during the CO_2RR throughout the pulsed AST can be fully elucidated by means of operando WAXS and SAXS (Figure 1C). SAXS-derived (SAXS-D) and WAXS-derived (WAXS-D) diameters were employed for quantitative analysis of Ag/Au NPs size evolution. The former is subject to the aggregation and detachment of larger NPs, whereas the latter is influenced by chemical corrosion and crystal regrowth. During electrolysis, the SAXS-D increases with a rise in current density and decreases as it drops, while the WAXS-D exhibits a gradual increase over time. SAXS-D exhibits oscillations in the pulsed AST region, reflecting continuous changes in agglomerate size. The interplay of these processes results in complex fluctuations of SAXS-/WAXS-D in the pulsed AST. To explore the cause of structural distortions, the authors further conducted a detailed analysis of the D-ratio (SAXS-D/WAXS-D) as a useful indicator for evaluating the dispersion uniformity of crystalline NPs. Excluding the effect of Ostwald ripening-induced grain size changes, dynamic fluctuations in the D-ratio also reflect NPs adhesion strength to the substrate. Initially, the Ag catalyst with a D-ratio of 1.23 exhibits mosaicity of individual NPs. Furthermore, the elevated D-ratio in non-AST regions reflects poor Ag NPs adhesion to the substrate. By comparison, the Au catalyst shows a constant D-ratio (1.16), indicating strong interaction with the carbon substrate, suppressing aggregation and guaranteeing stable CO_2RR performance and superior durability. The adhesion discrepancy between Au and Ag catalysts is primarily governed by their intrinsic chemical and structural disparities. Concretely, the relativistic orbital contraction of Au enhances metal-substrate chemisorption, its lower surface energy enlarges interfacial contact area, and its superior lattice matching with substrates reduces interfacial strain, whereas Ag displays weaker orbital hybridization, more severe agglomeration driven by higher surface energy, and greater interfacial stress induced by lattice mismatch. Meanwhile, stability was evaluated by calculating the faradaic efficiency of CO degradation rate against the total charge passed through the cathode (% kC^{-1}), confirming the feasibility of pulsed AST for accelerating stability assessments, thus serving as a valuable tool for assessing long-term catalyst durability.

Using the customized synchrotron SAXS/WAXS/XRF combined technique and the developed pulsed AST, their work unravels the degradation mechanisms of Ag/Au catalysts in the MEA during CO_2 electrolysis, powerfully revealing that the crystalline phase stability of catalysts and the adhesion strength between NPs and the substrate are the key factors governing catalyst durability. The multiscale operando tracking capabilities and universal analytical approach can be extended to other electrocatalytic systems, providing robust guidance for the rational design and performance optimization of advanced electrocatalysts.

Despite its current notable merits, this synchrotron-based combined technique still faces certain challenges. Specifically, SAXS/WAXS/XRF alone cannot reveal the chemical states and local atomic structures that are closely associated with catalytic mechanisms due to the lack of X-ray absorption fine structure (XAFS) spectroscopy, nor can it detect micron-scale particle growth and agglomeration during salt formation due to the detection limits of SAXS and the lack of ultra-SAXS (USAXS). Therefore, those highly promising complementary combined techniques building on XAFS and USAXS, such as SAXS/WAXS/XAFS[4] and SAXS/WAXS/USAXS,[5] equipped with sample environments tailored to catalytic systems, offer dynamic multiscale insights spanning atomic, nano, and micron scales, and can solve these important questions. Besides, experimental design for such SR techniques deserves careful consideration from researchers, as the high flux and wide X-ray energy (or wavelength) ranges of SR sources, especially the fourth-generation ones, may affect the chemical or physical kinetic processes of the target system, with such effects potentially misinterpreted as 'real' results instead of radiation-influenced outcomes. To mitigate SR-induced structural damage and maximize the potential of SR-based techniques in catalysis research, it is essential to optimize beamline parameters, design protective sample environments, and leverage advanced beamline techniques like fast scanning or pulsed irradiation.

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AUTHOR CONTRIBUTIONS

Yu Kong: conceptualization, investigation, writing original draft; Zhonghua Wu: conceptualization, writing-review; Yunpeng Liu: supervision, writing-review, funding acquisition. The authors contributed to the manuscript and approved the final version.

DECLARATION OF INTERESTS

The authors declare no competing interests.