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COMMENTARY

Revealing electrochemical interface dynamics at the atomic level

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The electrochemical electrode-electrolyte interface is critical to a number of vital applications, from batteries to electrocatalysis, but unveiling their complex dynamics is stymied due to the inherently buried nature of this interface. By using a novel polymer electrochemical liquid-cell, Prof. Haimei Zheng and her team were able to use transmission electron microscopy (TEM) to observe these interfaces in real-time during electrocatalytic reactions.[1] The unprecedented spatial resolutions this new concept enabled revealed a dynamic, liquid-like interphase formed at the interface during operation.

They applied their new technique to diagnosing the interfacial evolution of a copper nanorod catalyst suitable for electrocatalytic CO_2 reduction (ECR). Transforming CO_2 into useful fuels and chemicals will help industries reduce their carbon emissions by making CO_2 a valuable resource instead of a waste product, thereby providing a financial incentive for carbon-intensive industries to invest in carbon capture. A promising route to this goal is through harnessing ECR, which uses green renewable energy to convert CO_2 into more useful substances. Copper-based ECR catalysts appear to be unique in that only they can produce the more complex and valuable C_{2+} products. However, an outstanding question is the role of the copper oxidation state (Cu^0, Cu^+, $Cu^{\delta+}$), how this valence evolves during the reaction,[2] and its link with the resulting products.[3] This necessitates in situ study, as simply comparing catalysts before and after the reaction is potentially confounded by the oxidation of Cu in air. Ideally, this would also be locally resolved, allowing for explicitly linking this oxidation state to the evolving catalyst surface, rather than being limited to an average measurement of the whole catalyst.

Operando electrochemical TEM would, in theory, be an ideal technique to crack this problem, as it offers high spatial and temporal resolutions, a variety of imaging contrast mechanisms, and a powerful spatially-localized spectroscopic probing capability in electron energy loss spectroscopy (EELS). This combination of capabilities allows for detailed observation and analysis of electrochemical processes at the atomic level, providing insights into the mechanisms that govern these reactions. However, prior to this work, there was an unfortunate trade-off between the different operando electrochemical TEM techniques – between high spatial resolution, control of the electrolyte selection, and the ability to bias – which meant that diagnosing these systems remained out of reach for TEM (see Figure 1).

A so-called "open-cell" approach, where a low vapor pressure ionic liquid is used as the electrolyte to ensure compatibility with the TEM's high vacuum, is able to realize high spatial resolution imaging of the interface and allow for the application of a bias. This method is advantageous because it maintains the integrity of the high vacuum environment necessary for TEM operation. However, the ionic liquids required for this method are often not suited to probing particular electrochemistry questions; often the question is heavily contingent on using a particular type of electrolyte that is not necessarily an ionic liquid. The ECR is one such area; if we want to understand the processes during ECR, such as evolution of the catalyst surface, we must replicate the reaction conditions, and therefore the electrolyte should typically be aqueous. Ionic liquids are currently seldom employed for ECR, and may yield different catalyst behaviors during operation to aqueous electrolytes, where attributes such as local pH variation and hydrogen evolution side-reactions may contribute.[4] Thus an in situ approach that allows for aqueous electrolytes is desirable.

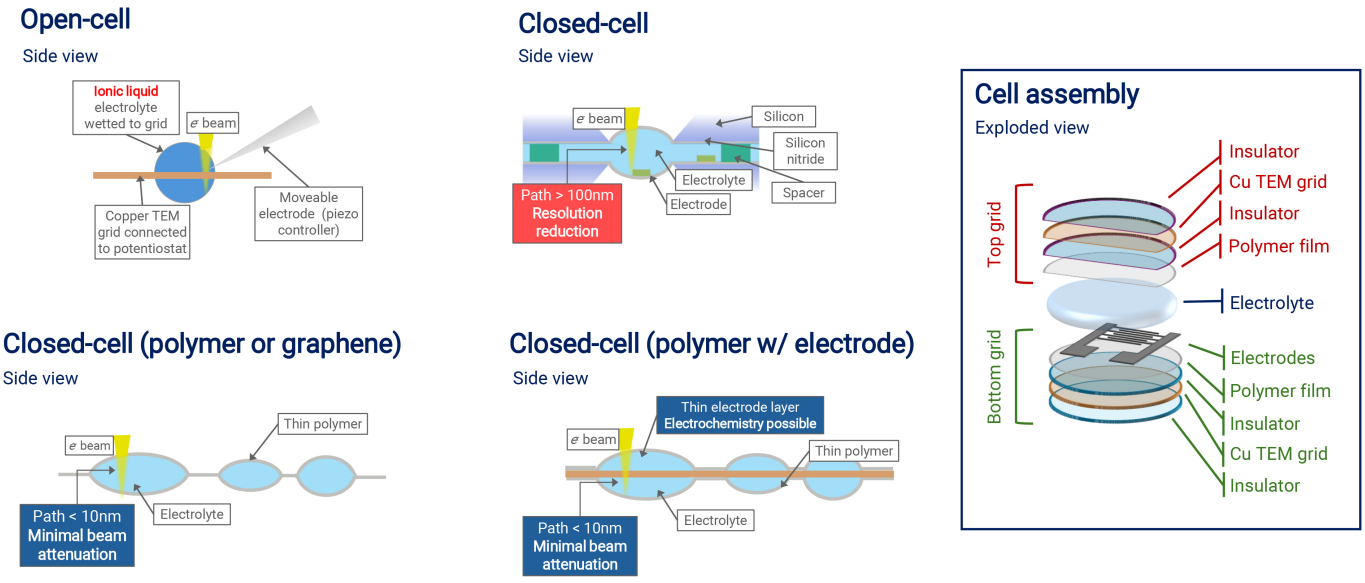

Figure 1. Side-view/cross-section illustrations comparing the different approaches for imaging a liquid inside the vacuum of a TEM The open-cell consists of a low vapor pressure ionic liquid wicked to a standard copper TEM grid, which is connected to an external potentiostat, with the second electrode a ultrafine metal tip that is maneuvered inside the TEM via a piezo-stage to assemble a circuit. The traditional closed-cell approach assembles a cell from silicon chips with inset silicon nitride windows, allowing for patterned electrodes and arbitrary electrolyte selection, but at the drawback of limited resolution. An ultrathin carbon membrane can be used instead, along with much smaller amounts of electrolyte, to improve the resolution drastically, at the cost of an inability to supply a bias voltage to an electrode. The cell developed by Zheng et al., an exploded view of which is shown on the right, overcomes this limitation by introducing a micropatterned electrode assembly into the polymer (formvar film) closed cell, allowing for high resolution imaging of electrochemical interfaces.

Fortunately, a "closed-cell" approach allows for virtually any electrolyte to be studied, including aqueous, providing a more versatile environment for observing electrochemical processes. This method involves sealing the electrolyte within a cell, typically using amorphous thin-films of silicon nitride as the cell windows. These windows are embedded in larger silicon chips, and

have the advantage of being a suitable substrate to permit the patterning of microelectrodes, thus allowing for electrochemical reactions to be instigated inside the cell. However, the relatively thick cell windows, combined with the thick liquid layer enclosed within the cell, preclude high-resolution imaging due to scattering and attenuation of the electron beam as it transmits through the cell.

The limit to spatial resolution with closed-cell approaches has been shown to be surmountable by employing ultra-thin films as the window material, such as graphene or amorphous carbon.[5] Such materials are thinner and lighter than silicon nitride membranes, thereby lessening the scattering and attenuation of the electron beam. Additionally, this approach minimizes the volume of the liquid sealed between the two films, further improving beam transmission and imaging resolution. However, this improvement comes at the cost of losing the ability to supply a biasing voltage, as it is not possible to pattern electrodes on the carbon/graphene membranes. Without the ability to apply a bias it is not possible to study electrochemical interfaces.

The work of Zheng et al. overcame this technical limit for the first time by integrating an additional thin layer of micropatterned platinum to act as a set of interdigitated electrodes, sandwiched between insulating layers of aluminum oxide to ensure electrical isolation from the encapsulating membranes (see right box in Figure 1). Copper nanowires were simply drop-cast on to the electrode layer on the pre-assembled bottom grid, exactly as when preparing a standard TEM grid, before an electrolyte droplet was introduced by wetting and then sealed between the two assembled grids. The top grid is a partial circle, so as to allow a gap for the contact pads of the bottom grid's electrode layer to be accessed for connection to the TEM holder electrical contacts. As a result, they were able to image the electrochemical interface at the copper nanowire as it was biased in a CO_2 saturated $KHCO_3$ electrolyte, revealing the atomic level structural changes. The system was also compatible with cryo-freezing, as the cell can be disassembled back into the two grids and the bottom grid characterized as per a normal TEM grid, thus allowing for the preservation of the copper nanowire electrochemical interface for post-experiment analysis by high signal-to-noise EELS.

The unprecedented resolution of their in situ imaging revealed that the interface underwent reconstruction, leading to the formation of an amorphous interphase layer between the electrolyte and electrode. This interphase was observed to be highly dynamic, flowing across the electrode and continually reconstructing across the crystalline electrode beneath. Such interphase mediated restructuring of the electrode surface was studied at atomic detail, and coupled with density functional theory (DFT) calculations. Copper atomic vacancies continually formed and refilled at the electrode interface, with vacancies observed to favor forming along step edges, as supported by DFT, and with the DFT further suggesting this was promoted by application of a bias. This is used as the basis for their theoretical framework for explaining the formation of this amorphous interphase, as these surface copper atoms are 'activated'.

The authors model that application of a bias leads to the electron doping density of the copper surface increases, activating them. These surface copper atoms are more prone to form quasi-liquid structures with nearby adsorbed or solvated carbons present in the electrolyte, for instance CO formed from the ECR. This interphase is therefore a dynamic mixture of Cu^0 and Cu^{1+}, as copper atoms undergo dissolution, formation of solvation complexes with carbon molecules, and redeposition back on the electrode surface. This contention of the interphase being a mixture of Cu^0 and Cu^{1+} was supported by EELS probing of the interphase, which was achieved by cryo-freezing the bottom grid after the in situ experiments. Performing subsequent EELS experiments on the grid at cryogenic temperature minimizes beam damage and ensures preservation of the interphase layer. By comparison of the L edges from the EELS the local Cu oxidation state was able to be determined, which revealed the presence of both Cu^0 and Cu^{1+}. Other elements, such as C and O, are likely also present in the interphase layer, however cannot be easily distinguished by EELS or energy dispersive X-ray spectroscopy (EDS) mapping as the same elements would also be present in the underlying formvar polymer films of the TEM grid.

Their work goes on to suggest that this amorphous interphase mechanism is a generalized concept, extending beyond just the case of the copper ECR catalyst, with other experiments suggesting similar behavior in other metallic element interfaces when biased. The generality of their results could have important implications for the informed design of catalyst interfaces, and stimulates an appreciation of the nature of these systems as dynamic and evolving during the reaction itself. The technique they present is also of great significance, as it presents the ability to study electrochemical reactions at high spatial imaging resolution by TEM for the first time, overcoming the fundamental hurdles that existed with in situ TEM to-date.

For future developments of in situ electrochemical TEM, as well as dealing with the perennial issue of controlling and accounting for the effect of the electron beam, it would be desirable to be able to flow the electrolyte in this system while biasing. A drawback of studying small liquid volumes is the rapid depopulation of the ionic species dissolved within it, and the concomitant saturation with product species as the reaction proceeds, which would be remedied by employing the continuous replenishment of the electrolyte with a flow system.

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DECLARATION OF INTERESTS

The author declares no competing interests.