

Towards Quantification of the Reaction Product in Oxygen-Evolving Oxides by Operando Electron Energy-Loss Spectroscopy in Liquids

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The sluggish oxygen evolution reaction (OER) at the anode of the water splitting process is the bottleneck limiting the water electrolysis efficiency. In the past decades, metal oxide catalysts have been shown to exhibit exceptional activity and stability towards OER in alkaline medium [1]. Recently, the capability of probing the molecular oxygen in proximity to single-particle oxide catalysts was demonstrated using operando electron energy-loss spectroscopy (EELS) in electrochemical liquid-phase TEM (LP-TEM) [2]. The characterization framework provides possibilities to understand the active sites of single-particle catalysts such as facet dependent OER activity [3] in real-time if the evolved molecular oxygen can be reliably quantified and compared. Herein, an approach towards quantification of the molecular oxygen in a single-particle oxide by operando EELS in liquids is discussed. First, qualitative mapping of molecular oxygen evolution around an IrO₂ oxide particle based on multiple least square fitting (MLLS) is demonstrated. Then, the fitting process is extended to the quantification of a molecular oxygen bubble generated by the application of potential in a liquid-cell enclosure.

Figure 1a illustrates EELS probing of O₂ around a single IrO₂ particle, a benchmarked OER catalyst [4], in a liquid-cell enclosure under OER conditions. IrO₂ particles were dropcast on an ultra-thin Pt electrode and 0.1 M KOH solution was used as electrolyte. The liquid formed a thin-layer that wets the particles and electrodes. A constant anodic potential at 1.95 V versus RHE is applied to trigger OER. At the same time, the electron-beam was scanned across an IrO₂ particle and the O K EEL spectra were taken during the scan. The current response of chronoamperometry in Figure 1b was stabilized at ~80 nA. Figure 1c shows the O K EEL spectra taken from two different positions (that are indicated in Figure 1d ADF image). The dark green spectrum that is acquired from the position closer to the IrO₂ particle shows a notable molecular oxygen feature at 531 eV. The bright contrast in the ADF image (Figure 1d) indicates the IrO₂ particle. The center of the particle shows the relative thickness (t/λ) value as large as 2.5 while the t/λ is ~1.3 at the position close to the edge to the particle. The t/λ decreases to ~1 when the position moves farther from the particle. As the relative thickness reflects the overall thickness of the cell that is parallel to the electron-beam direction, the decreasing of its value indicates a gradient of liquid profile that is thicker at the edge of the particle.

To further understand the molecular oxygen distribution around IrO₂ under OER, the O K EEL spectra at each pixel were fitted by three standard O K EEL spectra: IrO₂, O₂, and liquid electrolyte. Prior to the MLLS fitting, the spectra were denoised by principal component analysis (PCA) to improve the fitting. Figure 1d shows the fitting coefficient maps of O₂ and liquid electrolyte. The fitting coefficient map of O₂ shows that the value is higher at the position closer to the IrO₂ particle. The fitting coefficient map of the liquid electrolyte also indicates that increased amount of the liquid at the position that is closer to the edge of the particle. The map is thus consistent with the relative thickness map. Overall, the MLLS fitting shows the capability to separate the contributions of different components in O K EEL spectra, providing qualitatively O₂ and liquid electrolyte maps.

The MLLS fitting process is further applied to quantify the amount of the components. The quantification can be fulfilled by fitting the O K edge EELS intensity using experimental scattering cross-section as standards. The areal density of each component can thus be acquired based on the fitting coefficient. As an initial system for the quantification of the amount of molecular oxygen in liquids, O₂ gas bubble was generated by the application of a high anodic potential on a Pt thin-film electrode in a liquid-cell enclosure. The quantification results indicate that the molecular oxygen and O in the liquid can be decoupled, and the areal density of the molecular oxygen can be quantified. Further validation of the quantification values and systematic studies of the quantification process will be discussed [5].

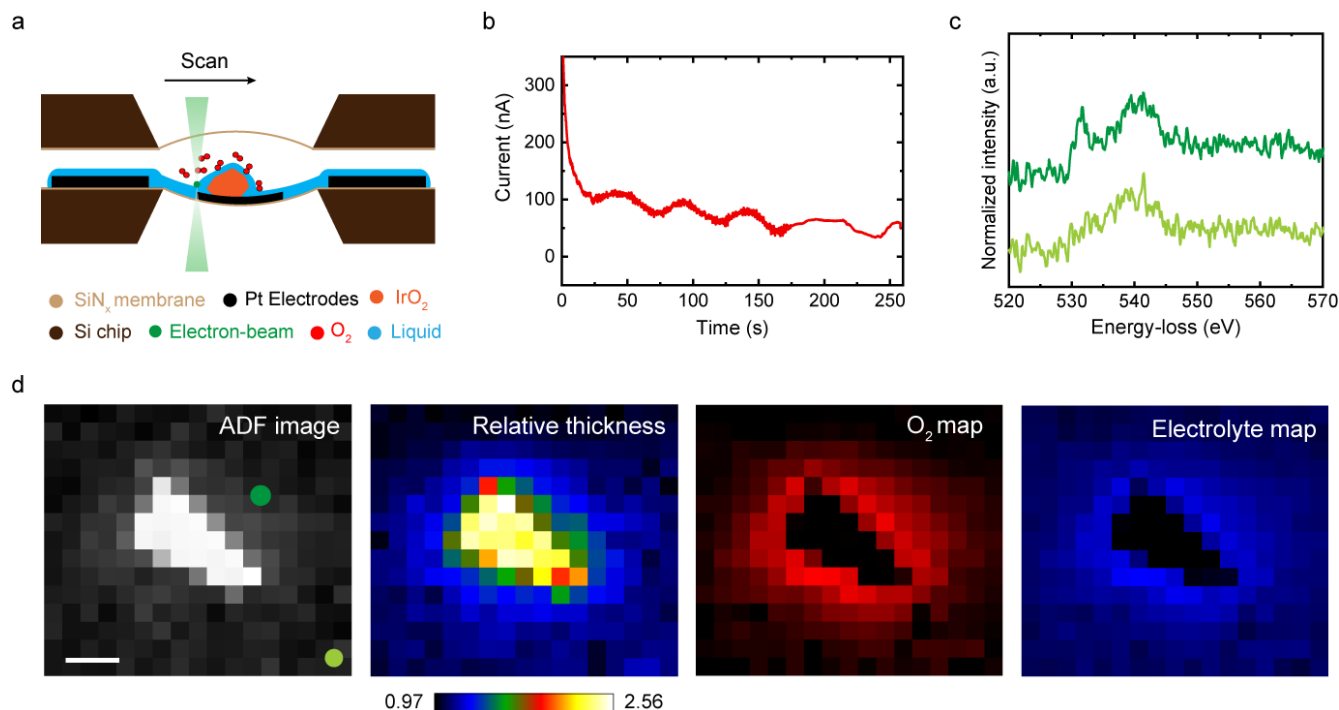


Figure 1. Probing of molecular oxygen evolution near a single IrO₂ particle. (a) A schematic illustration of probing molecular oxygen evolution near a single IrO₂ particle. Two-dimension scan was performed under the application of constant anodic potential. (b) Current response with respect to time of chronoamperometry (CA) at 1.95 V versus RHE. (c) O K EEL spectra taken from two different positions. Dark green is closer to the IrO₂ particle while the light green is further. The positions are indicated in the ADF image in d. (d) ADF image and relative thickness map of the IrO₂ particle during CA. The corresponding fitting coefficient maps of O₂ and electrolyte are shown in red and blue, respectively. Scale bar is 100 nm.

References:

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