Oxygen electrochemistry in Li-O₂ batteries probed by in situ surface-enhanced Raman spectroscopy

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Abstract
Surface-enhanced Raman spectroscopy (SERS), as a nondestructive and ultrasensitive single molecular level characterization technique, is a powerful tool to deeply understand the interfacial electrochemistry reaction mechanism involved in energy conversion and storage, especially for oxygen electrochemistry in Li-O₂ batteries with unrivaled theoretical energy density. SERS can provide precise spectroscopic identification of the reactants, intermediates and products at the electrode|electrolyte interfaces, independent of their physical states (solid and/or liquid) and crystallinity level. Furthermore, SERS's power to resolve different isotopes can be exploited to identify the mass transport limitation and reactive sites of the passivated interface. In this review, the application of in situ SERS in studying the oxygen electrochemistry, specifically in aprotic Li-O₂ batteries, is summarized. The ideas and concepts covered in this review are also extended to the perspectives of the spectroelectrochemistry in general aprotic metal-gas batteries.

KEYWORDS
in situ SERS, isotope labeling, oxygen electrochemistry, reaction mechanism, surface-enhanced Raman spectroscopy

1 | INTRODUCTION

The energy consumption via the combustion of fossil fuels is unsustainable owing to its irrevocable adverse impact on the environment. The need to accelerate the decarbonization process has urged us to speed up the search for means of more effective electric energy storage.¹,² Markedly, Lithium-ion batteries (LIBs) have achieved tremendous success in portable electronics and electric vehicles.³–⁵ However, the adherence to conventional
intercalation chemistries has limited the attainable energy density of LIBs, which lags behind the ever-growing demands. Therefore, it is of primary priority to explore other more energetic reversible electrochemical reactions as the foundation for the next-generation batteries.\(^6\),\(^7\)

The aprotic Li-O\(_2\) battery can deliver ultra-high theoretical specific energy (3500 Wh kg\(^{-1}\)) based on forming Li\(_2\)O\(_2\) as the discharge product), and hence, has received unprecedented attention as a promising alternative to LIBs.\(^6\)–\(^12\) Its high specific energy is afforded by the conversion reaction at the cathode (O\(_2^+ + 2\)Li\(^+\) + 2e\(^-\) \(\leftrightarrow\) Li\(_2\)O\(_2\), \(\theta^f = 2.96\) V vs. Li/Li\(^+\)), which abandons heavy transition metal oxides as the cathode materials in LIBs.\(^10\)–\(^12\)

Although the O\(_2\)/Li\(_2\)O\(_2\) redox chemistry appears to be simple and straightforward, the actual performance of the current Li-O\(_2\) battery is unsatisfactory and limited by several bottlenecks, that is, restricted discharge capacity, large polarization, degraded cyclability, and degradation of inactive components.\(^11\),\(^12\) To overcome these hurdles and develop a viable aprotic Li-O\(_2\) battery technology, numerous efforts have been devoted to improve the cell design, fabricate highly efficient O\(_2\) cathodes, search for stable electrolytes, and protect the Li anode from side reactions.\(^13\)

According to the studies in the last decade, it is generally accepted that the redox chemistry of O\(_2\), involving superoxide radicals and other reactive intermediates, plays a crucial role in the battery performance.\(^14\),\(^15\) Correspondingly, a fundamental understanding of the reaction mechanism is vital, which must be built upon extensive experimental evidence. Recently, researchers have made fruitful progress in this aspect including the ascertainment of O\(_2\)/Li\(_2\)O\(_2\) reaction pathways by the identification of short life-span intermediates, observation of Li\(_2\)O\(_2\) growth in operando microscopy, estimation of mass transport limitation, and exploration of cell components’ degradation mechanism.\(^14\)–\(^17\) Despite the remarkable progress in mechanistic understanding, more details need to be uncovered, in particular, the nature of transient intermediates during the operation of the Li-O\(_2\) batteries. Therefore, powerful operando analytical methods are critically needed. It is imperative to monitor chemical and/or electrochemical reactions at the three-phase (solid-liquid-gas) interfaces in real time by all methods at our disposal,\(^18\) for example, via in situ surface-enhanced Raman spectroscopy (SERS),\(^19\)–\(^22\) X-ray diffraction,\(^23\),\(^24\) ultraviolet-visible spectroscopy,\(^25\),\(^26\) differential electrochemical mass spectrometry,\(^9\),\(^27\)–\(^29\) and electron microscopy.\(^18\),\(^30\),\(^31\) These advanced in situ techniques are nondestructive and analyze the cell reactions in real time without a need to disassemble the cells. Among these techniques, in situ SERS outshines the others as an eminent method to provide spectroscopic evidence of discharge products and short life-span intermediates, indiscriminate to their physical states (solid and/or liquid) and crystallinity level (crystalline and/or amorphous).\(^18\)–\(^22\) Furthermore, once aided by isotope-labeling, in situ SERS contributes abundant information about O\(_2\) transport limitation and reactive sites.\(^22\) Thus, in situ SERS plays a vital role in revealing the mechanism of oxygen electrochemistry in Li-O\(_2\) batteries. In this review, notable recent advancements on probing the oxygen electrochemistry with in situ SERS are summarized. Our aim is not limited to an account of the relevant spectroscopic works in Li-O\(_2\) batteries but also to guide future mechanism investigations on other metal-gas batteries.

2 | A BRIEF INTRODUCTION OF IN SITU SERS IN APROTIC LI-O\(_2\) BATTERIES—THE TECHNICAL ESSENTIALS

Raman spectroscopy is based on the inelastic scattering of photons, first discovered by Raman in 1928. It probes the molecular vibrations, from which rich structural information of molecules and condensed matters can be revealed.\(^32\) However, despite the efforts of generations of scientists to upgrade the apparatus—particularly the excitation light source and high-precision detector—the improvement in detection sensitivity had not met the expectations.\(^33\) A landmark in the history of Raman spectroscopy took place in 1974, approximately 50 years after the discovery of Raman effect. Fleischmann et al.\(^34\) first observed the enormously intensified Raman scattering from adsorbed pyridine molecules on a roughened silver electrode, which was later formally termed the surface-enhanced Raman scattering effect. As an efficient and versatile mechanism to selectively amplify the normal Raman signals via the interplay of electromagnetic and chemical effects, the SERS effect overcame the intrinsic low sensitivity of typical Raman spectroscopy and opened up a new avenue for spectroscopic identification of substances in trace amount, literally down to the single molecular level.\(^35\),\(^36\) SERS critically relies on the specific optical properties and morphologies of substrates, and only coinage metals (Au, Ag, and Cu) are “SERS-active substrates” which exhibit large enhancement compared to other metallic materials. The strongest enhancements occur for surface morphology with roughness scale of 10–200 nm. Following its discovery, SERS has significantly broadened the range of Raman applications, for instance, from identifying single DNA bases, to detecting explosives and other trace materials, and to monitoring the electrochemical process in energy storage devices.\(^37\)
FIGURE 1  Configuration of the in situ SERS. (A) The Raman microspectrometry system with an inverted microscope and long-focus objective. (B) Schematic illustration of home-made spectroelectrochemical cell

Lately, in situ electrochemical SERS, among the various in situ techniques derived from SERS, was developed to dynamically monitor the formation process of solid electrolyte interphase and discharge/recharge reactions in LIBs and Li-O₂ batteries, with the primary goal of spatially and temporally resolving the intermediates and products in the bulk phase and at the interface.\textsuperscript{19–22,33} Particularly, in situ SERS in Li-O₂ battery studies allows the nondestructive detection of ongoing electrochemical processes without disassembling the cell. Moreover, unlike other scattering spectroscopy, such as in situ FTIR, in situ SERS produces sharp and distinct peaks that allow unambiguous peak assignment, not to mention its capability of resolving O-O related normal modes that FTIR fails to reveal. For example, the critical intermediate species (O⁻²⁻, LiO₂⁻) of Li⁺⁺-induced oxygen electrochemistry have been identified using in situ SERS.\textsuperscript{19–22} Hence, in situ SERS is an indispensable characterization technique for understanding the underpinning chemistry in Li-O₂ batteries.

In the typical in situ SERS studies on Li-O₂ batteries, an inverted confocal microscope system is a prerequisite, as shown in Figure 1A. A confocal Raman microscope is applied to collect the Raman signal from a single spot where the incident laser beam is focused at and block the noise signals beyond this spot, that is, from the environment and/or along the laser beam’s transmission trajectory. An inverted microscope provides an open working space above the operation platform to accommodate the electrochemistry apparatus. A specially designed inverted microscope allows the incident laser to penetrate the optical window at the bottom of spectroelectrochemical cell, as illustrated in Figure 1B, reaching the surface of working electrode. For signal collection, the scattered Raman light is also collected via this inverted objective and the beam path is reversed, and eventually projected onto the charge-coupled device detector with high sensitivity and low detection limits. Therefore, the collection efficiency of the objective lens is critical and a large NA (Numerical Aperture) value representing a high collection efficiency is desirable. Alternatively, a Raman microscope coupled with an optical fiber works well and it is more flexible than an inverted microscope setup. However, the sensitivity and signal intensity are sacrificed for flexibility. Additionally, a common fiber does not provide the optical image of the electrode surface and, thus, affords no spatial resolution. A home-made multinecked glass cell as depicted in Figure 1B is adopted for in situ measurements. The glass cell is based on a three-electrode cell design with a gas inlet and outlet for cell pressurization with oxygen. The counter electrode and reference electrode compartments are separated from the working electrode using sintered glass frits to minimize the disturbance of impurities generated there. The glass cell must be hermetically sealed to maintain the partial pressure of oxygen and block the external contaminant such as CO₂ and H₂O (PTFE ferrules are generally recommended for better durability and solvent resistance). The cylindrical working electrode is mounted vertically and the electrode surface is close to the optical window (typically sapphire and quartz), leaving a gap between the electrode surface and the window to allow mass transport of reagents and products. The gap depends on the size of the electrode and the working distance of the objective lens, typically several millimeters. Considering the thickness of the optical window and the gap, an objective lens with a long (∼7 mm) or extra-long (∼10 mm) focal length has to be used for the sample to be properly focused.

Au exhibits excellent chemical stability within the wide potential ranges of LIBs and Li-O₂ batteries and it is superior to Ag and Cu as SERS-active substrates, which both become easily oxidized at approximately 3.0 V versus Li/Li⁺⁺. Typically, a surface-roughened Au disk electrode (2 mm diameter) is utilized as a working electrode in many of the in situ SERS studies on the Li-O₂ batteries and the details of the electrochemical roughening procedure are well documented.\textsuperscript{22,38} In addition, some innovative approaches for fabricating electrodes with high SERS activity have been developed recently such as electroplating on Ni foam,\textsuperscript{39} electrodeposition with a sacrificial template,\textsuperscript{40} and sputter coating.\textsuperscript{25}

As the most common reference electrode in the studies of LIBs and Li-O₂ batteries, Li also poses some challenges on the spectroscopic study owing to its incessant side reactions with the electrolyte constituents. To circumvent this uncertainty, the partially delithiated LiFePO₄ (LFP) is sometimes selected as the alternative reference electrode.\textsuperscript{19,21,22} Compared to Li, partially delithiated LFP’s open-circuit potential is located at a relatively modest 3.45 V versus Li/Li⁺⁺,\textsuperscript{41} which largely eradicates the undesirable side reactions. The preparation procedure for LFP...
reference is akin to the general protocol for making composite cathode coating in LIBs studies. In general, the LFP reference electrode is partially oxidized (ca. 20% of total capacity) to Li$_x$FePO$_4$ ($x$ = ca. 0.8) by charging in the same electrolyte prior to use and it provides a constant potential of 3.45 V versus Li/Li$^+$ owing to its long and flat voltage plateau. Finally, a platinum wire routinely serves as the counter electrode.

### 3 APPLICATIONS OF IN SITU SERS IN OXYGEN ELECTROCHEMISTRY IN LI-O$_2$ BATTERIES

#### 3.1 Unraveling the reaction pathways of the discharge reaction (ORR)

The oxygen reduction reaction (ORR) in aprotic electrolytes has been studied for decades, and the first room-temperature Li-O$_2$ battery realized in an aprotic electrolyte was reported in 1996. However, the reaction mechanism of oxygen electrochemistry in aprotic electrolytes has yet to be thoroughly understood. In theory, the cathode of Li-O$_2$ batteries is anticipated to adopt a 2e$^-$ reduction reaction upon full discharge: O$_2$ + 2Li$^+$ + 2e$^-$ → Li$_2$O$_2$. This equation conceals the intricate step-wise reduction process that heavily depends on the electrolyte composition. Initially, the reaction mechanism of Li$^+$-induced oxygen electrochemistry was investigated by classical electrochemical methods, such as cyclic voltammetry (CV), as shown in Figure 2. The oxygen electrochemistry in CH$_3$CN electrolytes containing various amounts of Li$^+$ was conducted for comparison. In the absence of Li$^+$, a pair of reversible redox peaks assigned to the O$_2$/O$_2^-$ redox couple are observed (Equation 1). When Li salt is dissolved into the electrolyte, a new reduction peak appears at a more positive potential, approximately 2.3 V versus Li/Li$^+$ (all potentials were referred to the Li/Li$^+$ reference, hereafter, unless otherwise noted). As the concentration of Li$^+$ increases, this peak grows at the expense of the original reduction peak located at 1.8 V. The observation suggests a typical EC coupled mechanism, in which a chemical reaction follows an electron-transfer step. This subsequent chemical reaction rapidly consumes the as-formed O$_2^-$ from the E step to shift the cathodic peak potential toward the positive direction. Based on the above Li$^+$ concentration effect by CV study, the Li$^+$-induced ORR mechanism was proposed as below:

$$\text{O}_2 + \text{e}^- \rightarrow \text{O}_2^-$$  

(1)

$$\text{O}_2^- + \text{Li}^+ \rightarrow \text{LiO}_2$$  

(2)

$$\text{LiO}_2 + \text{Li}^+ + \text{e}^- \rightarrow \text{Li}_2\text{O}_2$$  

(3)

$$2\text{LiO}_2 \rightarrow \text{Li}_2\text{O}_2 + \text{O}_2$$  

(4)

O$_2$ was first reduced to O$_2^-$ via a 1e$^-$ process (Equation 1), which makes O$_2^-$ an essential intermediate in this reaction. O$_2^-$ binds with Li$^+$ to form LiO$_2$ (Equation 2), which is unstable with a short lifespan. It can be transformed into Li$_2$O$_2$ via electroreduction (Equation 3) or chemical disproportionation (Equation 4). The competition between electroreduction and disproportionation is affected by both electrolyte composition and electrode potential. Although the aforementioned ORR mechanism could be well explained by the hard-soft acid-base theory, there was no direct experimental evidence of the existence of O$_2^-$ and/or LiO$_2$ intermediates to verify it.

The pioneering study providing the direct spectroscopical evidence of the proposed reaction pathway was reported by Peng et al. in 2011. The Li$^+$-induced ORR mechanism in CH$_3$CN was investigated thoroughly by in situ SERS. SERS of the working electrode was conducted during the potentiostatic holding at several key potentials. The O$_2^-$/LiO$_2$ intermediates and the end-product Li$_2$O$_2$ were identified directly, as shown in Figure 3. The SERS spectrum was collected at the open-circuit voltage (3.2 V) prior to any electrochemical perturbation to provide a baseline and only peaks associated with CH$_3$CN were observed. Then SERS spectra were collected at 2.2 V, where ORR took place and two new peaks appeared at 1137 and 808 cm$^{-1}$, which were assigned to LiO$_2$ and Li$_2$O$_2$, respectively.
FIGURE 3: In situ SERS during O$_2$ reduction and reoxidation on Au in O$_2$-saturated 0.1 M LiClO$_4$–CH$_3$CN. Spectra collected at 2.2 V versus Li/Li$^+$ for different intervals followed by other spectra at the oxidation potentials shown. The peaks are assigned as follows: (1) C–C stretch of CH$_3$CN at 918 cm$^{-1}$, (2) O–O stretch of LiO$_2$ at 1137 cm$^{-1}$, (3) O–O stretch of Li$_2$O$_2$ at 808 cm$^{-1}$, and (4) Cl–O stretch of ClO$_4^-$ at 931 cm$^{-1}$.

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respectively. The peak of LiO$_2$ gradually shrank and vanished within several minutes while the signal of Li$_2$O$_2$ remained. This result confirms that the unstable LiO$_2$ was consumed via chemical disproportionation, which implied a reaction pathway that is constituted by Equations 1, 2, and 4. To the best of our knowledge, this was the first time that the spectroscopic evidence of the transient LiO$_2$ intermediate was provided in aprotic Li-O$_2$ batteries. Recently, it is also finally discovered that LiO$_2$ could be cryosynthesized in liquid NH$_3$ (−78°C) and it is much more reactive than the free O$_2^-$ and Li$_2$O$_2$ in a Li-O$_2$ battery.

Later studies established that LiO$_2$ can develop either on the electrode surface, denoted as LiO$_2^*$ (* denoted the adsorbed state), or in the bulk electrolyte, denoted as LiO$_2$(sol) upon the discharge, and the ratio of these two variants depends on the donor number (DN) of solvents, or specifically the solubility of Li$^+$ and O$_2^-$ in the electrolyte solvent. To shed light on the role of LiO$_2$ solubility in aprotic Li-O$_2$ batteries, the ORR mechanism was investigated in four solvents spanning a wide range of DNs from 14 to 47, as shown in Figure 4. In high-DN solvents, such as DMSO (DN = 30) and 1-methylimidazole (Me-Im, DN = 47), only O$_2^*$ and Li$_2$O$_2$ were identified during ORR by in situ SERS, but LiO$_2^*$ was not observed. At high and moderate potentials (beyond the onset potential of the second reduction process), O$_2^*$ appears within a couple of minutes, whereupon its signature peak diminishes and the peak of Li$_2$O$_2$ grows in intensity, consistent with the hypothesized disproportionation of O$_2^*$ to generate Li$_2$O$_2$. These SERS results suggest that the soluble superoxide species (LiO$_2$(sol), as loose ion pairs or clusters) evolves as a major intermediate in high-DN solvents and eventually becomes converted to Li$_2$O$_2$ through disproportionation. To further verify this theorem, Peng et al. designed a model chemical reaction to study the reaction between O$_2^-$ and Li$^+$ in the bulk electrolyte. Both experimental and theoretical evidences reveal that TMA$^+$ O$_2^-$ (one soluble O$_2^-$ source) can interact with Li$^+$ to form LiO$_2$(sol) in DMSO, which also follows the speculated disproportionation to form Li$_2$O$_2$. Therefore, the more precise ORR mechanism in high-DN solvents at high potential (low overpotential) is proposed as follows:

\[
\begin{align*}
O_2 + e^- & \rightarrow O_2^- \quad (1a) \\
O_2^- & \rightarrow * + O_2^-(sol) \quad (1b) \\
O_2^- (sol) + Li^+(sol) & \rightarrow LiO_2(sol) \quad (2a) \\
2LiO_2(sol) & \rightarrow Li_2O_2(sol) + O_2 \quad (4a)
\end{align*}
\]

The reaction at low potential (high overpotential) is more complicated. As the potential approaches the second reduction peak, the O$_2^*$ intermediate, once formed, is immediately reduced to Li$_2$O$_2$ which further passivates the electrode. As a consequence, the superoxide intermediates (O$_2^*$ or LiO$_2^*$) are difficult to discern in the SERS spectra, since SERS is sensitive to only the species in close vicinity to the electrode surface (adsorbed or within several atomic layers off the surface). To circumvent this issue, in situ SERS coupled with a fast-scan CV is adopted instead. At a sufficiently high scan rate (e.g., 20 V s$^{-1}$), only a submonolayer of Li$_2$O$_2$ is deposited on the electrode surface, leaving enough room to resolve the ORR intermediates (O$_2^*$ and/or LiO$_2^*$). Accordingly, three intermediates LiO$_2^*$, O$_2^*$, and Li$_2$O$_2^*$ were detected simultaneously at a low potential region. The concurrence of LiO$_2^*$ and Li$_2$O$_2^*$ was not originally anticipated. Because the time scale of the entire ORR is as short as milliseconds in a fast CV scan and the disproportionation of superoxide in bulk electrolyte is sluggish, the formation of Li$_2$O$_2^*$ via a solution-mediated reaction mechanism should be negligible. Therefore, Li$_2$O$_2^*$ must be formed via the LiO$_2^*$ intermediate and the surface-mediated reaction mechanism, as described below generally in low-DN solvents, should be followed. This was the first time that the surface-mediated reaction mechanism was detected in high-DN solvents (DMSO) with spectroscopic evidence. Lately, by combining in situ SERS and density functional theory calculation, it was confirmed that the discharge reaction pathway of Li$_2$O$_2$ batteries is associated with the adsorption rate of Li$_2$O$_2$ onto the electrode/electrolyte interface. Even if the system is initially operated in the regime wherein
Figure 4 Spectra collected at a gold electrode during O₂ reduction in the presence of 100 mM LiClO₄ in various aprotic solvents, recorded after different reaction times at various constant potentials indicated by the markers with matching colors in the CV curves above each stack of spectra. Vertical dotted lines with grey shading show positions of O₂⁻, LiO₂, and Li₂O₂. Insets: expanded view of the spectra outlined by the dashed circles. Spectra at the bottom were collected at the open-circuit potential (OCP). SERS demonstrates that at high voltages (low overpotentials) O₂⁻ and LiO₂ species are observed on the electrode surface after short reaction times in high- and low-DN solvents, respectively, to be replaced by Li₂O₂ over time. At low voltages (high overpotentials), Li₂O₂ is already clearly visible and dominant at the early stage. Reprinted with permission from Ref. [20]. © 2014, Nature Publishing Group.
the solution-mediated reactions are favored (e.g., low discharge current density and high-DN solvent DMSO), the solution growth would become rapidly outpaced by the surface-mediated growth once merely a minor quantity of Li₂O₂ is adsorbed onto the electrode/electrolyte interface. Therefore, the exploitation of cathode surface modification techniques to effectively retard the Li₂O₂ adsorption is arguably a promising strategy to manipulate the Li₂O₂ growth mode.

In a low-DN solvent, that is, CH₃CN (DN = 14), surface LiO₂* and Li₂O₂* are already simultaneously detected at the onset potential of ORR (the red spot in CV curve in Figure 4). However, the free superoxide species O₂−* is not identified as in high-DN solvents. Similar to the case of O₂−* intermediate in high-DN solvents, the peak of LiO₂* decreases within a few minutes (red spectra for CH₃CN in Figure 4), indicating that LiO₂* is further converted to Li₂O₂* via disproportionation or an electroreduction reaction. At low potentials (i.e., the yellow and green spots in the CV curve), electroreduction of LiO₂* is prompted. LiO₂* transforms to Li₂O₂* rapidly and only Li₂O₂* has been detected. Namely, the discharge process of Li-O₂ batteries using low-DN solvents was dominated by the surface-mediated reaction mechanism via LiO₂*. Accordingly, the ORR mechanism in low-DN solvents is proposed as below:

\[
\begin{align*}
O₂ + e^- & \rightarrow O₂^- \quad (1a) \\
O₂^- + Li^+ (sol) & \rightarrow LiO₂* \quad (2b) \\
LiO₂* + Li^+ (sol) + e^- & \rightarrow Li₂O₂* \quad (3) \\
2LiO₂* & \rightarrow Li₂O₂* + O₂ \quad (4b)
\end{align*}
\]

Although the first step (Equation 1a) is the same with the reaction in high-DN solvents, the rest of the steps are different.

In intermediate-DN solvents, that is, DME (DN 20), due to the interference of solvent peak (1100-1150 cm⁻¹), the superoxide intermediates (O₂−*/LiO₂*) cannot be unambiguously pinpointed, but the growth process of the Li₂O₂ peak provides some clue. At high potentials (red spot), the growth rate of Li₂O₂* peak in DME was slower than that in CH₃CN, but much faster than that in DMSO and Me-Im, implying a hybrid mechanism involving both solution- and surface-mediated reactions. This speculation is consistent with the cross-comparison of the morphology of the discharge products in the investigated solvents.²⁰

In summary, the Li⁺-induced ORR mechanism (both solution- and surface-mediated reaction pathways) depends on both the DN of solvent and the electrode potential. In low-DN solvents (CH₃CN, DME, etc.), the surface-mediated reaction mechanism governs the entire ORR. On the contrary, in high-DN solvents (DMSO, Me-Im, etc.), Li₂O₂ forms through solution-mediated reaction mechanism in the high potential (low overpotential) region and surface-mediated reaction mechanism otherwise (high overpotential). Overall, O₂−* (LiO₂(sol)) and LiO₂* are the pivotal SERS-sensitive intermediates of the solution- and surface-mediated reaction mechanisms, respectively.

### 3.2 Identification the reactive sites of discharge reaction

Unlike conventional LIBs, which operate by reversible intercalation/deintercalation of Li⁺ into/from the electrodes, the core of Li-O₂ battery is the reversible deposition/decomposition of Li₂O₂ during discharge/charge. The discharge product Li₂O₂ has a wide band gap and limited conductivity, and therefore, the active sites at the cathode surface of Li-O₂ batteries are doomed to be passivated by solid Li₂O₂. As such, a Li-O₂ battery only delivers a capacity far less than its theoretical promise in reality. Before a high practical specific capacity can be realized, it is crucial to understand the Li₂O₂ growth behavior at the active sites during the discharge. Although in situ electron microscopy (SEM and TEM) has been employed to study the reactive sites of Li₂O₂ growth,³⁰,³¹ the long exposure to electron beam radiation might damage Li₂O₂ and incur defects, parasitic reactions, and other artifacts. The enormous overpotential commonly resorted to in situ EM studies might distort the reaction pathway as well. Furthermore, these EM-based investigations generally only focus on the morphology changes during the electrochemically driven growth and reveal little chemical information.

By combining with isotope labeling, in situ SERS can provide both chemical and spatial information concerning the growth kinetics of Li₂O₂, particularly, the active growth sites.¹⁸O₂ and O₂ were introduced to the cell at different stages of the discharge to deliberately create an O-isotope multilayer “heterostructure” defined by the order in which Li₁₈O₂ and Li₁₆O₂ are deposited. By analyzing the distribution of Li₁₈O₂ and Li₁₆O₂ with in situ SERS, the reactive sites at the different stages of discharge can be determined. This is well exemplified by the study presented in Ref. [22]. At the beginning, an Au planar electrode was discharged to 2.0 V at a current density of 100 μA cm⁻² under O₂, and, thus, its surface was passivated by Li₁₈O₂, as detected in the red spectrum in Figure 5A. Afterwards, O₂ in the glass cell was completely replaced with ¹⁶O₂ that eventually saturated the electrolyte. The discharge process was then resumed and continued at 2.0 V under
The current decayed rapidly as shown in Figure 5B. The SERS spectra in Figure 5A shows that a new band assigned to Li$_2^{16}$O$_2$ emerges and intensifies while the existing Li$_2^{18}$O$_2$ band adjacent to it gradually vanishes at a similar pace. After 5 h, the Li$_2^{18}$O$_2$ was replaced entirely by Li$_2^{16}$O$_2$ in the spectrum (Figure 5A, top curve). Because the SERS signal is predominantly contributed by the species at the gold electrode’s surface, more specifically the Au electrode/Li$_2$O$_2$ interface in this scenario, rather than the Li$_2$O$_2$|electrolyte interface, the in situ SERS results above reflect the gradual displacement of Li$_2^{18}$O$_2$ by Li$_2^{16}$O$_2$ at the Au electrode/Li$_2$O$_2$ interface during the discharge after the O$_2$ isotope exchange. This suggests that the active redox sites of Li$^+$-induced ORR are actually located at the Au electrode/Li$_2$O$_2$ interface, where O$_2$ is reduced after penetrating the Li$_2$O$_2$ film. The failure of the Li$_2$O$_2$|electrolyte interface to compete with the Au electrode/Li$_2$O$_2$ interface is also substantiated by the sluggish transport of electrons through the Li$_2$O$_2$ film—direct conductivity measurement of Li$_2$O$_2$ film shows that its $\sigma_{\text{ion}}$ ($3.1 \times 10^{-12}$ S cm$^{-1}$) is higher than $\sigma_e$ ($2.2 \times 10^{-13}$ S cm$^{-1}$). The integration of isotope labeling into situ SERS provides a marvelous advantage for probing the reactive interface in Li$_2$O$_2$ battery and the above study has only touched a tip of the iceberg. It can be envisioned that this technique will make a substantial contribution to the understanding of not only Li$_2$O$_2$ but also other metal-O$_2$ (Na, K, Ca, etc.) batteries in the future.

3.3 Exploring the parasitic reaction mechanism of the H$^+$/H$_2$O additive

Aprotic Li-O$_2$ batteries are susceptible to parasitic reactions incurred by impurities, especially protons (H$^+$) and protic compounds (H$_2$O, etc.). Particularly, H$_2$O is an inevitable contaminant from the ambient atmosphere. So far, the effect of H$_2$O is still controversial and H$^+$/H$_2$O-mediated ORR mechanism in Li$_2$O$_2$ batteries is not entirely understood. A 2e$^-$ reaction mechanism of H$^+$-induced ORR (phenol as the H$^+$ source) was proposed by Andrieux et al.,$^{46}$ in which O$_2^–$/HO$_2^–$ and HO$_2^–$ were the intermediates and product, respectively. However, this reaction mechanism has not been validated due to the lack of spectroscopic evidence.

To fill the gap between the experiment and theory, in situ SERS was employed to comprehensively investigate the H$^+$-induced ORR mechanism in DMSO.$^{47}$ The electrolyte was 0.1 M TBAClO$_4$-DMSO containing 20 mM phenol as the proton source. SERS spectra were recorded at various potentials during one full cycle in a CV scan: cathodic scan (left column in Figure 6) and anodic scan (right column in Figure 6). During the cathodic scan, the O$_2^–$* intermediate and H$_2$O$_2^*$ products are identified. The peak of O$_2^–$* appears at 2.7 V (onset potential of H$^+$-induced ORR) and the peak of H$_2$O$_2^*$ appears at 2.5 V. During the reverse scan, the peak of O$_2^–$* gradually diminishes, yet a peak of H$_2$O$_2^*$ remains even at 3.1 V, which suggests that H$_2$O$_2^*$ is difficult to decompose. According to these observations, the H$^+$-induced ORR follows an intertwined reaction mechanism of solution and surface-mediated routes. Again, electrode potential wields substantial influence here: the solution-mediated reaction mechanism is dominant between 2.5 and 2.7 V, while the surface-mediated mechanism takes over below 2.5 V. Therein, a modified Andrieux mechanism of H$^+$-induced ORR was proposed (Equations 1a, 5, and 6), which
was also confirmed by results of density functional theory calculation.\textsuperscript{47}

\[ \text{O}_2 + \text{e}^- \rightarrow \text{O}_2^- \]  \hspace{1cm} (1a)

\[ \text{O}_2^- + \text{PhOH} \rightarrow \text{HO}_2^- + \text{PhO}^- \]  \hspace{1cm} (5)

\[ \text{HO}_2^- + \text{e}^- + \text{PhOH} \rightarrow \text{H}_2\text{O}_2^- + \text{PhO} \]  \hspace{1cm} (6)

This was one of the earliest studies that convincingly demonstrated that \( \text{O}_2^- \) and \( \text{H}_2\text{O}_2 \) appear simultaneously in an \( \text{H}^+ \)-induced ORR system. Spectroscopic evidence clearly establishes that \( \text{O}_2 \) can be directly reduced to \( \text{O}_2^- \) without coupling with a proton, even in the presence of a proton source.

In practice, even if all cell components (electrolyte, salts, membrane, electrode, etc.) in a Li-O\(_2\) cell have been thoroughly dehydrated, trace amount of H\(_2\)O remnant’s impact could still be substantial. Recently, in situ SERS was conducted to attain a profound understanding of how H\(_2\)O might interfere with Li\(^+\)-induced ORR.\textsuperscript{48} Through the spectroscopic identification of the reaction intermediates, it was discovered that H\(_2\)O could tune the Li\(_2\)O\(_2\) growth mechanism so as to affect the discharge performance of a Li-O\(_2\) battery. Beyond a critical H\(_2\)O content (threshold), Li\(_2\)O\(_2\) forms only through the solution-mediated mechanism regardless of the cathode potentials, which delays the cathode passivation and boosts the final discharge capacity. Therefore, contrary to the common notion about its generally deteriorating impact on batteries with aprotic electrolytes, H\(_2\)O can invigorate Li-O\(_2\) batteries’ capacity efficiency under certain circumstances.\textsuperscript{49–52} This has unlocked the H\(_2\)O content, routinely prohibited in the electrolyte, as an extra degree of freedom to optimize Li-O\(_2\) batteries.

### 3.4 Identification of the reactive sites of the charge reaction

Although aprotic Li-O\(_2\) batteries have an ultra-high theoretical specific energy, the round-trip efficiency is notoriously poor due to large overpotential in charging. Even for the state-of-the-art Li-O\(_2\) batteries, the charge overpotential is greater than 0.5 V, severely undermining its round-trip energy efficiency. To evaluate the possibility of attenuating this hysteresis, it is critical to understand how Li\(_2\)O\(_2\) decomposes, particularly, the nature of the reactive sites during the charge. Of special significance and interest is whether Li\(_2\)O\(_2\) decomposition is initiated at the cathode|Li\(_2\)O\(_2\) or Li\(_2\)O\(_2\)|electrolyte interface upon charging.

Built upon the Li\(_{216}\)O\(_2\)|Li\(_{218}\)O\(_2\) heterostructure created by the successive Li\(^+\)-ORR undertaken in the \(^{18}\)O\(_2\) and \(^{16}\)O\(_2\) atmosphere introduced in Section 3.2, in situ SERS can again be analogously employed to uncover the active reaction sites during the recharge.\textsuperscript{22} As illustrated in Figure 7A for the reversal SERS study, at the beginning Li\(_{216}\)O\(_2\) (red curve) naturally dominates the buried Au electrode|Li\(_2\)O\(_2\) interface, as explained in Section 3.2. The isotopically heterogeneous (along the thickness) Li\(_2\)O\(_2\) undergoes oxidation when the cell is subjected to a linear sweep voltammetry from 2.8 to 4.0 V at a rate of 2 mV s\(^{-1}\). Two oxidation peaks were observed (Figure 7B). Interestingly, in situ SERS results suggested that the decomposition of Li\(_{216}\)O\(_2\) preceded Li\(_{218}\)O\(_2\). The signal of postdeposited Li\(_{4}\)O\(_2\) continually dwindles till its full disappearance (spectra 2–4) amid the first oxidation peak (spot 2–4) and the main vibration peak of Li\(_{218}\)O\(_2\) follows it (spectra 2–4). Near the end of the first oxidation peak, Li\(_{216}\)O\(_2\) can no longer be observed while Li\(_{218}\)O\(_2\)’s characteristic peak still maintains a slight intensity, which is finally consumed once the first oxidation peak is fully traversed (spot 5 and spectrum 5). This observation confirms that the Li\(_2\)O\(_2\) at cathode|Li\(_2\)O\(_2\) interface decomposes first, following a reverse sequence compared with the discharge process. The relatively sluggish decomposition of Li\(_2\)O\(_2\) away from the electrode|Li\(_2\)O\(_2\) interface is determined by the limited electron transport across the insulating Li\(_2\)O\(_2\). The second oxidation peak (spot 6&7) is assigned to the decomposition of the remaining Li\(_2\)O\(_2\) far away from the electrode surface which requires a large overpotential to activate electrochemically. Because it is also beyond the effective detection range of SERS, its Raman signal is weak and below the detection limit.
The above inference about the location of the active decomposition sites was verified by a recent study, which conducted CVs with different cathodic cut-off potentials in 0.1 M LiClO$_4$-DMSO electrolyte saturated by $^{16}$O$_2$. The thickness of the Li$_2$O$_2$ film was controlled by the cut-off potential. It was discovered in the anodic scan that the cathodic cut-off potential only affects the second oxidation peak (at 3.6 V) but not the first oxidation peak (at 3.3 V). SERS peaks of Li$_2$O$_2$ in three samples preconditioned with progressively lower cathodic cut-off voltages (thicker Li$_2$O$_2$ deposition) always disappeared at the end of the first oxidation peak, regardless of the thickness of the Li$_2$O$_2$ film. As the SERS signal is mainly contributed by the Li$_2$O$_2$ within a delimited range (ca. 2 nm) off the electrode-Li$_2$O$_2$ interface, this observation is only consistent with a Li$^+$-induced oxygen evolution reaction (OER) initiating at the electrode-Li$_2$O$_2$ interface and gradually propagating to the Li$_2$O$_2$-electrolyte interface instead of the other way around.

This also echoes the time-resolved in situ SERS of a typical Au-Ni foam/DMSO and TEGDME battery.

Reference [43] provides further evidence about the location of the Li$^+$-induced OER with a more precise in situ SERS spectroelectrochemical investigation. In this case, a galvanostatic discharge/charge cycle was applied to deposit/decompose Li$_2$O$_2$ onto a roughened Au electrode, in contact with the 0.1 M LiClO$_4$-DMSO electrolyte initially saturated with $^{16}$O$_2$ (Figure 8A). During this cycle, SERS spectra were collected at a few key potentials (Figure 8A & B), which showed that the SERS signal of Li$_2$$^{16}$O$_2$ was clearly visible at the initial stage of the recharge (3.25 V, green curve in Figure 8B) but already faded away (blue curve in Figure 8B) at approximately 4.1 V (spot 4), even though more than half of the Li$_2$$^{16}$O$_2$ ought to remain according to the electrochemical data. By reversing the direction of the current flow at spot 4 after reaeration with
$^{18}$O$_2$, Li$_2$O$_2$ can be redeposited onto the remnant Li$_2^{16}$O$_2$. At the end of this discharge, only Li$_2^{18}$O$_2$ was identified by SERS (Figure 8B, curve 6), which confirmed that the initial reactive sites of Li$^+$-induced OER dwelled at the cathode/Li$_2$O$_2$ interface.

### 4 | CONCLUSIONS AND OUTLOOK

In situ SERS is a versatile technique for the investigation of the oxygen electrochemistry reaction mechanism in aprotic Li-O$_2$ batteries via real time, nondestructive, and ultra-sensitive analysis. Its ability to distinguish different isotopes allows it to obtain both spatial and chemical information when isotope labeling is incorporated into the design of the electrochemical reactions to tag the key interfaces. A timeline showcasing the milestones of research on oxygen electrochemistry in aprotic Li-O$_2$ batteries studied by in situ SERS is presented in Figure 9. However, the limitation of in situ SERS is also distinct, especially the stipulation to select from only a few compatible substrates (Au, Ag, and Cu). To tackle this limitation, shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS) technique, in which the Raman signal was enhanced by insulated Au nanoparticles (Au nanoparticles cores are coated with an ultrathin and pinhole-free SiO$_2$ or Al$_2$O$_3$ shell as Au/SiO$_2$ or Au/Al$_2$O$_3$ core-shell nanoparticles), can be applied as effective and powerful alternative signal magnifiers for those non-SERS active substrates such as carbon with 0D, 1D, 2D, and 3D structures. The dynamic spectroelectrochemical analysis is enabled correspondingly. Furthermore, in situ SERS can be exploited to investigate the mechanisms of other batteries involving complex precipitation/decomposition behavior at the electrode/electrolyte interfaces such as M-O$_2$ and M-sulfur batteries (M = Na, K, Ca, Mg, Zn, etc.). In the future, along with the continuous instrumentation upgrade of the spectrometer, even higher temporal and spatial resolution can be attained in the SERS characterization of the metal ion-induced oxygen electrochemistry and their detailed reaction mechanisms will eventually be revealed.

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### CONFLICT OF INTEREST

The authors declare no conflict of interest.

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