In Situ Ambient Pressure X-ray Photoelectron Spectroscopy Studies of Lithium-Oxygen Redox Reactions

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The lack of fundamental understanding of the oxygen reduction and oxygen evolution in nonaqueous electrolytes significantly hinders the development of rechargeable lithium-air batteries. Here we employ a solid-state Li41xTi5O12/LiPON/LixV2O5 cell and examine in situ the chemistry of Li-O2 reaction products on LixV2O5 as a function of applied voltage under ultra high vacuum (UHV) and at 500 mtorr of oxygen pressure using ambient pressure X-ray photoelectron spectroscopy (APXPS). Under UHV, lithium intercalated into LixV2O5 while molecular oxygen was reduced to form lithium peroxide on LixV2O5 in the presence of oxygen upon discharge. Interestingly, the oxidation of Li2O2 began at much lower overpotentials (240 mV) than the charge overpotentials of conventional Li-O2 cells with aprotic electrolytes (1000 mV). Our study provides the first evidence of reversible lithium peroxide formation and decomposition in situ on an oxide surface using a solid-state cell, and new insights into the reaction mechanism of Li-O2 chemistry.

Electrical storage technologies are of vital importance to enable effective utilization of intermittent renewable energy sources and the creation of sustainable electric transportation. Conventional Li-ion batteries cannot meet the long-term energy storage requirements for electric vehicles, owing to their inherent gravimetric energy limitation associated with Li intercalation1–3. To increase gravimetric energy, one promising approach is to employ four-electron redox of oxygen, where Li-O2 batteries have recently shown the potential to provide gravimetric energy ~4 times that of conventional Li-ion batteries4–8. Unfortunately, little is known about the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) mechanisms in the presence of Li ions at room temperature, which has led to a number of challenges3,5 at the oxygen electrode, limiting the practical use of this technology, such as poor round-trip efficiency4, the reactivity of aprotic electrolytes with oxygen redox reaction intermediates5, and cycle life3. Improving the mechanistic understanding of oxygen reduction and evolution is critical to develop strategies to overcome these challenges.

Here we study the redox of oxygen on the surface of a mixed electronic and Li-ionic conductor, Li1xV2O5, using a specially designed, all solid-state Li-ion battery4,11, which eliminates parasitic reactions between oxygen reduction/evolution reaction intermediates and aprotic electrolytes used in conventional Li-O2 batteries reported to date. Fourier transform infrared spectroscopy9,12–14 and Raman spectroscopy15,16 have shown that carbonate solvents commonly used in Li-ion batteries are not suitable for the oxygen electrode as such as the superoxide radical ion (O2−)10,13, and yields parasitic reaction products such as Li2CO3 and lithium alkyl carbonate species. On the other hand, ether-based solvents such as dimethoxyethane (DME) are reasonably stable against O2−, where oxygen reduction leads to the formation of Li2O2 in first few cycles9,16. Unfortunately, cycling in ether-based electrolytes gradually converts Li2O2 to lithium carbonate-based species16 and Li salts used in ether-based electrolytes can react with oxygen reduction products17. Moreover, researchers have very recently reported that carbon in the oxygen electrode can react with Li2O2 to form carbones in DME18, which increases the complexity in unraveling the Li-O2 reaction mechanisms in aprotic electrolytes. Utilizing the special all solid-state cell design and ambient pressure X-ray photoelectron spectroscopy (APXPS)19–21, we directly visualize the formation and disappearance of Li-O2 reaction products (namely Li2O2) on an Li1xV2O5 surface in situ as a function of applied battery potential.
**Results**

*In situ* electrochemical APXPS measurements were conducted using a solid-state Li-O$_2$ battery$^{11}$ to probe reaction products during discharge and charge to avoid the evaporation of liquid electrolytes with low vapor pressure in the high-vacuum XPS chamber (Fig. 1). This solid-state cell consisted of lithiated lithium titanate (LLTO) as the negative electrode (having a chemical formula of Li$_{4+1_2}$Ti$_5$O$_{12}$)$^{22}$, lithium phosphorous oxynitride (LiPON) as the Li$^+$-conducting solid electrolyte ($\approx 1,000$ nm thick), and vanadium oxide (V$_2$O$_5$)$^{23}$ as the positive electrode ($\approx 23$ nm in thickness). The LLTO/LiPON/V$_2$O$_5$ cell was placed on a holder outfitted with electrical contacts to enable *in situ* electrochemical measurements in the XPS chamber (Supplementary Fig. S1)$^{24}$. The Li 1s, O 1s, C 1s and V 2p spectra were collected from the top surface of the cell, which consisted of both Li$_x$V$_2$O$_5$ and LiPON, as a function of voltage applied externally.

In *in situ* XPS evidence of reversible intercalation/de-intercalation in Li$_x$V$_2$O$_5$ under UHV. Figure 2a shows the Li 1s, O 1s and V 2p spectra as a function of potential applied across the LLTO/LiPON/Li$_x$V$_2$O$_5$ cell ($V_{\text{cell}}$) during discharge in UHV, where detailed information of fitted components is shown in Supplementary Table S1 and Fig. S3. We note that all the cell potentials ($V_{\text{cell}}$) used in this study refer to the measured open-circuit-voltage (OCV) or the applied potentials across the solid-state cell (LLTO/LiPON/Li$_x$V$_2$O$_5$). Upon discharge, the Li 1s peak position remained nearly unchanged while the peak intensity was increased slightly (up to 20% in Supplementary Fig. S3), which is due to the increasing lithium content in Li$_x$V$_2$O$_5$ as expected from Li ion migration from the LLTO to Li$_x$V$_2$O$_5$ with decreasing applied voltage from 1.8 to 0 $V_{\text{cell}}$. The Li 1s peak centered at 55.5 eV could be assigned to surface carbonate species such as Li$_2$CO$_3$ (55.5 eV)$^{25}$ that was formed upon air exposure on Li$_x$V$_2$O$_5$ and LiPON, Li$_x$V$_2$O$_5$ (55.7–55.9 eV)$^{26}$ and partially to LiPON (56.0 eV)$^{27}$. The increasing Li 1s intensity was accompanied with the broadening and gradual shift of the V 2p peak to lower binding energy, indicating lowered valence state of vanadium ions upon discharge. The V 2p peak could be fitted to three peaks at 514.5 eV, 516.0 eV, and 517.4 eV, which are attributed to V$^{3+}$, V$^{4+}$ and V$^{5+}$ in Li$_x$V$_2$O$_5$, respectively$^{27,28}$. The relative fractions of V$^{3+}$ and V$^{4+}$ ions were found to increase upon discharge while that of V$^{5+}$ decreased (Supplementary Fig. S4a), and LiPON (Fig. 1), while the battery was discharged and charged potentiostatically under ultra high vacuum (UHV, pressure $< 10^{-11}$ atm) and followed by similar testing conditions in an oxygen environment at a partial pressure of $p$(O$_2$) $= 5 \times 10^{-4}$ atm (Methods and Supplementary Fig. S2). Substantial differences in the Li 1s, O 1s and V 2p spectra were observed between UHV and oxygen conditions upon charge and discharge, which will be discussed in detail below.

**Figure 1** | Solid-state cell (LLTO/LiPON/Li$_x$V$_2$O$_5$) used for *in situ* APXPS measurements. Lithiated Li$_{4+1_2}$Ti$_5$O$_{12}$ (LLTO) of 750 nm supported on a Pt coated alumina disk, Li$_x$V$_2$O$_5$ of 23 nm and Li-ion conducting LiPON electrolyte of 1,000 nm were used as the negative electrode, positive electrodes, and electrolyte, respectively. LLTO was encapsulated by LiPON. XPS data were collected from the top surface of the cell, which consisted of both Li$_x$V$_2$O$_5$ and LiPON, as a function of voltage applied externally.

**Figure 2** | *In situ* XPS data of Li 1s, O 1s, and V 2p collected under UHV. (a) Discharge from OCV (1.85 $V_{\text{cell}}$) to 0 $V_{\text{cell}}$. (b) Charge from OCV (0.1 $V_{\text{cell}}$) to 3.0 $V_{\text{cell}}$.  

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which was used to determine the vanadium valence state of Li$_x$V$_2$O$_5$ from 4.6+ (at 1.85 V$_{cell}$) to 3.6+ (at 0 V$_{cell}$), as shown in Fig. 3a. The changes noted in the O 1s region are in agreement with lithium intercalation into Li$_x$V$_2$O$_5$. The O 1s region includes contributions from Li$_x$V$_2$O$_5$, LiPON and surface lithium carbonate species (Li$_2$CO$_3$) formed upon air exposure of LiPON and V$_2$O$_5$ (Fig. 2a). Three components centered at 530.2, 532.0 and 534.0 eV were used to describe lattice oxygen (O$^\cdot$) in Li$_x$V$_2$O$_5$, both oxygen doubly bound to phosphorus (P=O) and oxygen in Li$_2$CO$_3$, and oxygen singly bound to two phosphorus (P-O-P)$^\cdot$ in LiPON, respectively. Upon discharge, the lattice oxygen (O$^\cdot$) in Li$_x$V$_2$O$_5$ was found to be increased by 0.4 eV lower binding energy by 0.4 eV from 1.85 to 0 V$_{cell}$, which is in agreement with decreased covalency of V-O bonds with decreasing vanadium valence state.

Upon charging, the changes in the Li 1s, V 2p and O 1s upon discharge were reversed, which is indicative of reversible lithium de-intercalation in Li$_x$V$_2$O$_5$, as shown in Fig. 2b. The intensity of the Li 1s region was decreased by 40% at voltages equal to and greater than 2.0 V$_{cell}$ (Supplementary Fig. S3). This is accompanied with increased vanadium valence state upon charging from 3.6+ (0.16 mC) at 0 V$_{cell}$ to 4.6+ (3.0 V$_{cell}$) (Fig. 3a). It is interesting to note that the charge capacity of the Li 1s region was found to be increased greatly in contrast to discharge (Fig. 4b and Supplementary Fig. S6). Although the LLTO/LiPON/Li$_x$V$_2$O$_5$ cell in the presence of oxygen had a comparable discharge capacity (0.18 mC) to that in UHV (0.16 mC) (Supplementary Fig. S2), the vanadium valence state was found to decrease only slightly from 4.5+ (at 2.1 V$_{cell}$) to 4.25+ (at 0 V$_{cell}$) in Fig. 3b. The charge can be attributed largely to the formation of reaction products associated with the reduction of molecular oxygen by lithium ions on the surface of Li$_x$V$_2$O$_5$, which gradually covered the Li$_x$V$_2$O$_5$ surface upon discharge. This observation is further substantiated by the appearance and growth of a new peak centered at 531.3 eV in the O 1s region, which became dominant at the end of discharge (at 0 V$_{cell}$) (Fig. 4a). Considering the Li 1s binding energy shifts to 54.8 eV, this new species can be assigned to Li$_2$O based on the binding energies of both O 1s and Li 1s peaks of a Li$_2$O reference sample (O 1s: 531.3 eV and Li 1s: 54.7 eV) at 3.2 V versus Li/Li$_2$O (at 2.96 V Li$_2$O$^{33}$). More interestingly, a minor peak centered at 528.5 eV was found to appear and grow at voltages lower than 0.2 V$_{cell}$, indicative of Li$_2$O formation (Li$_2$O: 528.5 eV$^{34}$), where further studies are needed.

Upon charging, the intensity of Li 1s peak was decreased while that of V 2p was increased greatly in contrast to discharge (Fig. 4b and Supplementary Fig. S6). The charge capacity of the LLTO/LiPON/Li$_x$V$_2$O$_5$ cell in the presence of oxygen (Supplementary Fig. S2) can be attributed to not only lithium de-intercalation as evidenced by the increased vanadium valence state from 4.2+ (0.1 V$_{cell}$) to 4.8+ (3.0 V$_{cell}$) in Fig. 3b, but also the oxidation and removal of Li$_2$O$_x$ on the surface of Li$_x$V$_2$O$_5$. The latter is supported by the reduction of O 1s peak for Li$_2$O$_x$ centered at 531.3 eV and the shift of the Li 1s binding energy from 54.8 eV (Li$_2$O$_x$) to 55.5 eV (Li$_2$CO$_3$/Li$_x$V$_2$O$_5$) at 2.96 V Li$_2$O$^{33}$. The onset of Li$_2$O oxidation began at low applied potentials such as 1.6 V$_{cell}$, corresponding to voltages no greater than ~3.2 V versus Li$^+$/Li (V$_{Li}$), and Li$_2$O$_x$ was removed completely at the end of charge (3.0 V$_{cell}$), which re-exposed the Li$_x$V$_2$O$_5$ surface (Fig. 4b). Considering the thermodynamic reversible potential of bulk Li$_2$O at 2.96 V$_{Li}^{33}$, the oxidation of Li$_2$O$_x$ can occur at overpotentials as low as ~0.2 V$_{cell}$ (∼3.2 V$_{Li}$), which is in contrast to large charging overpotentials noted typically for Li$_2$O cells with aprotic electrolytes (~1.0 V$_{cell}$ = 4.0 V$_{Li}$)$^{33}$. 

**In situ** APXPS evidence of reversible formation and removal of Li$_2$O$_x$ on Li$_x$V$_2$O$_5$ under p(O$_2$) = 5 × 10$^{-4}$ atm. During discharge, the intensity of the Li 1s region was found to increase while that of V 2p region decreased significantly (Fig. 4a and Supplementary Fig. S6). The vanadium valence state was found to decrease only slightly from 4.5+ (at 2.1 V$_{cell}$) to 4.25+ (at 0 V$_{cell}$) in Fig. 3b. This is indicative of reversible lithium intercalation in Li$_x$V$_2$O$_5$ comparable to that reported previously from Li/Li$_x$V$_2$O$_5$ thin film batteries$^{29}$. 

![Figure 3](https://example.com/figure3.png)
Discussion

Further studies are clearly needed to elucidate the physical origin to low overpotentials of Li$_2$O$_2$ electrochemical oxidation observed in this study. We here discuss three possibilities to highlight the differences between Li$_2$O$_2$ formed in this study and those formed in Li-O$_2$ batteries with aprotic electrolytes. Li$_2$O$_2$ particles formed on the surface of Li$_x$V$_2$O$_5$ are extremely thin. Considering the volumetric capacity Li$_2$O$_2$ (9716 C/cm$^3$) and the measured capacity associated with Li$_2$O$_2$ formed on discharge (0.71 mC/cm$^2$), the average thickness of maximum Li$_2$O$_2$ coverage on the Li$_x$V$_2$O$_5$ surface was estimated to be ~0.7 nm, corresponding to ~1–2 unit cells of Li$_2$O$_2$ (Supplementary Information). This is in contrast to Li$_2$O$_2$ particles having sizes in the range of 100 to 1000 nm formed in Li-O$_2$ batteries with aprotic electrolytes. Second, the surfaces of Li$_2$O$_2$ are free of carbonate species formed on the surface of the LLTO/LiPON/Li$_x$V$_2$O$_5$ cell (no growth of the C 1s peak intensity during discharge in presence of O$_2$ in Supplementary Fig. S7), which is in contrast to the coverage of Li$_2$CO$_3$-like species on Li$_2$O$_2$ particles even with ether-based electrolytes. Third, very thin Li$_2$O$_2$ particles may have stoichiometry and electronic properties considerably different from Li$_2$O$_2$ particles. This is supported by a recent density functional theory study reporting that the reduced coordination of oxygen atoms at the surface of Li$_2$O$_2$ yields the formation of a thin metallic region localized at the surface, which may facilitate the electro-oxidation of the Li$_2$O$_2$.

This study has, for the first time, revealed reversible oxygen reduction and evolution on an oxide surface using a solid-state lithium cell using in situ APXPS, as summarized in Fig. 5. Through the direct visualization of the formation and disappearance of Li$_2$O$_2$ reaction products, this study connects the electrical potential to oxygen redox chemistry in presence of lithium ions at room temperature, and leads to numerous opportunities for exploiting in situ APXPS to gain mechanistic insights into air-based electrochemical reactions for efficient energy storage.

Methods

Negative electrode fabrication. Lithiated Li$_4$Ti$_5$O$_12$ (LLTO) thin film was used as the negative electrode in this study. Li$_4$Ti$_5$O$_12$ powder was synthesized by ball milling the stoichiometric amounts of Li$_2$CO$_3$ (Mallinckrodt – 99.5%) and TiO$_2$ (Aldrich – Anatase 99.9%), which was pressed into a 2 cm diameter disk and then fired in air at 500°C.

Figure 4 | In situ APXPS data of Li 1s, O 1s, and V 2p collected under p(O$_2$) = 5 × 10$^{-4}$ atm. (a) Discharge from OCV (2.1 V$_{cell}$) to 0 V$_{cell}$. (b) Charge from OCV (0.1 V$_{cell}$) to 3.0 V$_{cell}$.

Figure 5 | A schematic summarizing the reaction mechanism. During discharge and charge in UHV, lithium ions reversibly intercalate/de-intercalate into/from the Li$_x$V$_2$O$_5$ electrode. During discharge in p(O$_2$) = 5 × 10$^{-4}$ atm, lithium ions meet with reduced oxygen on the surface of the Li$_x$V$_2$O$_5$ electrode forming Li$_2$O$_2$, which is decomposed upon recharge in p(O$_2$) = 5 × 10$^{-4}$ atm.
and a few drops of 1.2 M LiPF$_6$ in ethylene carbonate/ethyl methyl carbonate.

a) 

1.2 V using a Maccor Battery Tester. A representative discharge profile for the solid-state cells is shown in Supplementary Fig. S8, which reveals a large plateau at $-1.53\ \text{V}$ associated with lithium intercalation into the LTO spinel structure. The Swagelok cells were disassembled in the glove box and the lithiated LTO anodes were washed for 5 min by soaking in dimethyl carbonate (Aldrich $\sim 99$% Anhydrous) to remove residual electrolyte and left to dry on filter paper in the box.

**Solid electrolyte fabrication.** The lithiated LTO electrodes were loaded into a vacuum chamber and pumped down until a base pressure below $3 \times 10^{-10}$ torr was attained. A 1 $\mu$m thick lithium phosphorus oxynitride (LiPON) solid electrolyte layer was prepared by dc magnetron sputtering of a Li$_2$PO$_4$ target in a N$_2$ atmosphere (Air Liquide – Research Grade) at an applied power of 100 W, 20 standard cubic centimeters per minute (sccm) N$_2$ flow, and a pressure of 11 mtorr.

**Positive electrode fabrication.** Vanadium oxide (V$_2$O$_5$)$_x$ thin films were prepared by dc magnetron sputtering using a vanadium target (Kurt J. Lesker $\sim 99.9$%). The films were deposited in a mixture of argon (20 sccm Air Liquide – Research Grade) and O$_2$ (4 sccm Air Liquide – Research Grade) at an applied power of 19 W and a deposition pressure of 11 mtorr. A homemade mask, cut from a stainless steel mesh, was used to add some small lines to the cathode surface. The thickness of the V$_2$O$_5$ electrode with a diameter of 0.5 cm was approximated to be 23 nm (assuming an expected deposition rate of 2.5 Å/sec for 90 seconds and on a flat surface) (corresponding to an electrode volume of 4.52 $\text{cm}^3$). The solid-state cells were stored in an Ar filled glove box and shipped in argon filled stainless steel vessels to the Lawrence Berkeley National Laboratories (LBNL) Advanced Light Sources (ALS) for in situ experiments.

**Experimental details of in situ APXPS.** XPS data of Li 1s, C 1s, O 1s and V 2p were collected from the top surface of solid-state LTO/LiPON/Li$_2$O$_x$ cells in UHV and in presence of oxygen as a function of applied cell potential at beamline 9.3.2 at BL-ALS$^\text{a}$. The cell was placed onto an insulating ceramic holder, where the Pt-coated cell was prepared by r.f. magnetron sputtering of a Li$_3$PO$_4$ target in a N$_2$ atmosphere (Air Liquide – Research Grade) at an applied power of 100 W, 20 standard cubic centimeters per minute (sccm) N$_2$ flow, and a pressure of 20 mtorr$^\text{b}$. The lithiated LTO electrodes were loaded into a vacuum chamber and pumped down until a base pressure below $3 \times 10^{-10}$ torr was attained. A 1 $\mu$m thick lithium phosphorus oxynitride (LiPON) solid electrolyte layer was prepared by dc magnetron sputtering of a Li$_2$PO$_4$ target in a N$_2$ atmosphere (Air Liquide – Research Grade) at an applied power of 100 W, 20 standard cubic centimeters per minute (sccm) N$_2$ flow, and a pressure of 20 mtorr$^\text{b}$.

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Author contributions
Y.-C.L. and E.J.C. contributed equally to this work. E.J.C., Y.-C.L., G.M.V., N.J.D. and Y.S.-H. designed the experiments. G.M.V., E.J.C., J.R.H. and L.B. fabricated the samples. Y.-C.L., E.J.C., E.M. and Z.L. collected the data. Y.-C.L., E.J.C. and Y.S.-H. performed the analysis. Y.-C.L., E.J.C. and Y.S.-H. wrote the manuscript and G.M.V., N.J.D., J.R.H. and Z.L. edited the manuscript.

Additional information
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