High-Rate Long Cycle-Life Li-Air Battery Aided by Bifunctional InX₃ (X = I and Br) Redox Mediators

Sina Rastegar, Zahra Hemmat, Chengji Zhang, Samuel Plunkett, Jianguo Wen, Naveen Dandu, Tomas Rojas, Leily Majidi, Saurabh N. Misal, Anh T. Ngo,* Larry A. Curtiss,* and Amin Salehi-Khojin*



ABSTRACT: Redox mediators (RMs) are solution-based additives that have been extensively used to reduce the charge potential and increase the energy efficiency of Li-oxygen (Li-O₂) batteries. However, in the presence of RMs, achieving a long cycle-life operation of Li-O₂ batteries at a high current rate is still a major challenge. In this study, we discover a novel synergy among InX₃ (X = I and Br) bifunctional RMs, molybdenum disulfide (MoS_2) nanoflakes as the air electrode, dimethyl sulfoxide/ionic liquid hybrid electrolyte, and LiTFSI as a salt to achieve long cycle-life operations of Li-O2 batteries in a dry air environment at high charge-discharge rates. Our results indicate that batteries with InI₃ operate up to 450 cycles with a current density of 0.5 A g^{-1} and 217 Capacity (mAh/g) cycles with a current density of 1 A g^{-1} at a fixed capacity of 1 A hg^{-1} . Batteries with InBr₃ operate up to 600 cycles with a current density of 1 A g^{-1} . These batteries can also operate at a higher charge rate of 2 A



 g^{-1} up to 200 cycles (for InBr₃) and 160 cycles (for InI₃). Our experimental and computational results reveal that while X_3^{-1} is the source of the redox mediator, LiX at the MoS₂ cathode, In³⁺ reacts on the lithium anode side to form a protective layer on the surface, thus acting as an effective bifunctional RM in a dry air environment. This evidence for a simultaneous improvement in the current rates and cycle life of a battery in a dry air atmosphere opens a new direction for research for advanced energy storage systems.

KEYWORDS: $Li-O_2$ battery, Li-air battery, redox mediator, redox shuttling, transition metal dichalcogenides

1. INTRODUCTION

Lithium-oxygen $(Li-O_2)$ batteries are considered a possible alternative to Li-ion batteries as the energy storage systems of the future because of their high specific energy density.^{1,2} Li-O2 batteries are conceptually different from basic Li-ion batteries in that Li ions react with reduced oxygen molecules at the cathode side to form Li-O covalent bonds rather than intercalation cathodes. Because the energy is stored in covalent bonds, these batteries can achieve much higher amounts of energy compared to intercalation-based energy storage systems.³⁻¹⁰ The theoretical energy density of Li–O₂ batteries (3500 W h/kg) is about one order of magnitude higher than that of commonly used Li-ion batteries (~400 W h/kg). However, major challenges with Li-O₂ batteries are the undesirably large charge overpotential and low rate capability of the batteries. The high charge overpotential can reduce the round trip efficiency and can cause parasitic reactions, side products, and electrolyte and cathode degradation.^{11,12} Moreover, an incomplete removal of Li2O2 during charge could passivate and clog the cathode surface, which eventually causes early failure and poor cyclability. These obstacles have prevented further development of Li-O₂ batteries so far.

To address the overpotential issue, using suitable redox mediators (RMs) is an effective way to decompose the Li_2O_2

product and lower the high charge overpotential.¹³⁻¹⁹ During charging, first, the RMs oxidize on the surface of the cathode electrochemically and the oxidized form of RMs then chemically reacts with Li2O2 to generate Li⁺ and oxygen molecules as well as regenerating the reduced form of the RM. Two of the most studied classes of RMs are organic ones such as tetrathiafulvalene (TTF),^{20,21} 5,10-dihydro-5,10-dimethyl-phenazine (DMPZ),²² and 2,2,6,6-tetramethyl-1-piperidiny-loxy (TEMPO)²³⁻²⁵ and Li-halides such as LiI²⁶⁻³³ and LiBr.^{34–36} Overall, halides are more effective than organic RMs for suppressing charge overpotentials.³⁷ However, there are two major issues with using the Li-halides as a RM. The first one is the formation of a discharge plateau because of the reduction of the (X_3^-/X^-) couple $(X^- = I^- \text{ and } Br^-)$. X_3^- is formed during the charging process and reacts to decompose Li_2O_2 . However, an excess amount of X_3^- can remain in the electrolyte, which can reduce during the next discharge to form

Received: August 24, 2020 Accepted: December 29, 2020 Published: January 22, 2021





www.acsami.org



Figure 1. Discharge/charge voltage profiles. (a) 25 mM InI₃ and a current density of 0.5 A g^{-1} . (b) 25 mM InI₃ and current density of 1 A g^{-1} . (c) 25 mM InBr₃ and a current density of 1 A g^{-1} . (d) 25 mM InBr₃ and current densities of 1 A g^{-1} discharging and 2 A g^{-1} charging. (e) Polarization gap versus number of cycles for InI₃ and InBr₃. (f) Comparison of this work with the results in the literature.^{31,32}

 X^- rather than being used for Li₂O₂ decomposition. This leads to Li₂O₂ capacity loss of the battery.³³ The second problem is the redox shutling effect during charge, which is the diffusion of the oxidized form of the RM (X₃⁻) through the electrolyte toward the Li anode and back to the cathode after it is reduced to $X^{-.38-41}$ A third problem is the reaction of LiX or LiX₃ with the anode if it is not protected.⁴²

In this study, we found that indium iodide (InI_3) and indium bromide (InBr₃) RMs are extremely effective in a system comprised of a hybrid electrolyte of dimethyl sulfoxide (DMSO) and 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM-BF₄) ionic liquid with lithium bis-(trifluoromethanesulfonic)imide (LiTFSI) salt along with a molybdenum disulfide (MoS_2) cathode that exhibit high exchange current densities during oxygen reduction and evolution reactions (ORR/OER).⁴³ Previous studies^{44,45} have used InI3 and InBr3 next to multiwalled carbon nanotube cathodes, in a pure oxygen environment. In the case of InBr₃, it was reported that the battery cycled up to 206 cycles with a small current density of 0.25 Å g^{-1} , while for the InI₃ case, only 50 and 40 cycles were achieved with current densities of 0.5 and 1 A g^{-1} , respectively. Here, we report a novel synergy with a new combination of materials that enable Li-O₂ batteries to operate in a dry air environment with a much longer cycle life and higher current densities using the indium halides (InI₃ and InBr₃). It is shown that these RMs act as bifunctional additives to simultaneously reduce the charge potential on the cathode side without the problems of loss of capacity during discharge and protect the anode surface.

2. EXPERIMENTAL SECTION

2.1. Synthesis of MOS_2 Nanoflakes (NFs). To synthesize MOS_2 NFs, a liquid-phase exfoliation technique was used by dissolving 0.3 g of MOS_2 in 60 mL of isopropyl alcohol (IPA) followed by sonication for 20 h using the probe sonicator (Vibra-Cell Sonics 130 W). Next, the MOS_2 dispersion was centrifuged at a high speed of 2000 rpm for 1 h and roughly the top 70% of the centrifuged supernatant was

collected for further experiments. Later, MoS_2 NFs were coated on a gas diffusion layer (GDL, Fuel cell etc., 25 BC) to reach the loading of 0.1 mg/cm².

2.2. Characterization Technique. 2.2.1. Transmission Electron Microscopy Measurements. A discharged cathode to 1 A h/g in a $\text{Li}-O_2$ cell was analyzed using transmission electron microscopy (TEM) (FEI Titan) to characterize the discharge product. TEM samples were prepared by sonicating the discharged cathode for 1 h in the CH₃CN solution. The resulting solution was then drop casted onto copper-supported amorphous carbon TEM grids (Ted Pella Inc.).

2.2.2. X-ray Photoelectron Spectroscopy. X-ray photoelectron spectroscopy (XPS) was performed using a Thermo Scientific ESCALAB 250Xi instrument. All spectra were calibrated based on the C-C bond binding energy located at 284.8 eV.

2.2.3. Energy-Dispersive X-ray Spectroscopy. The top-view scanning electron microscopy (SEM)—energy-dispersive X-ray spectroscopy (EDX) data were obtained using the FEI Quanta 650 ESEM in high vacuum with excellent beam stability. The system is integrated with the Oxford AZtec EDS and EBSD systems. SEM imaging was performed using an acceleration voltage (EHT) of 12 kV. The cross-sectional EDX analysis of the anode was performed using a scanning electron microscope (Hitachi S-4700-II HR-SEM). The anode was prepared by first cycling a cell at a rate of 0.1 mA/cm² to a capacity of 1000 mA h/cm² for five continuous cycles. The lithium disc was then removed from the cell and rinsed with acetonitrile in a glove box. The cross section of the lithium anode was exposed by cutting the disc using a doctor-blade, before inserting the sample into the SEM.

2.2.4. X-Ray Diffraction. X-ray diffraction (XRD) experiment was conducted using a Rigaku Smart Lab instrument operated at 45 kV and 160 mA in the 2θ range of $20-60^{\circ}$ using a scan step size of 0.03° and a scan speed of 4° min⁻¹.

3. RESULTS AND DISCUSSION

3.1. Galvanostatic Cycling Results. The battery assemblies were carried out in an Ar-filled glovebox using a custom-made Swagelok cell with MoS_2 nanoflakes (NFs) as the cathode, a Li chip as the anode, a hybrid electrolyte, and a glass microfiber filter as the separator. To synthesize MoS_2 NFs, we used our previously developed liquid phase exfoliation



Figure 2. Characterization of cathode in InI_3 based system at the rate of 1 A/g. (a,b) SEM images of cathode surface after the fifth discharge and charge cycle, respectively (scale bars: 200 nm). (c,d) Low- and high-resolution TEM images of the discharged cathode showing crystalline Li_2O_2 deposited on the MoS₂ cathode (scale bars: 100 and 10 nm, respectively). Inset shows the electron diffraction pattern of discharged product showing polycrystalline Li_2O_2 and (1,1,1) and (0,0,2) MoS₂ surfaces. (e) Raman spectroscopy of the cathode after fifth discharge and charge cycles. (f) X-ray diffraction pattern of the cathode after fifth discharge. (g) XPS of the cathode including O 1s and Li 1s regions after the fifth discharge.

technique (details of the exfoliation process are provided in the Experimental Section).^{46–48} To prepare the electrolyte, 25 mM InI₃ (InBr₃), 0.1 M LiTFSI, and a mixture of 9:1 by volume DMSO/EMIM-BF₄ were used (Section S1, Supporting Information). Cyclic voltammetry (CV) experiment was performed to find the exact oxidation and reduction peaks of the (X^{-}/X_{3}^{-}) and (X_{3}^{-}/X_{2}) redox couples in an Ar environment. (Section S2, Supporting Information).

Figure 1a,b demonstrates the battery performance containing 25 mM InI₃, 0.1 M LiTFSI, and hybrid electrolyte of DMSO/EMIM-BF₄. Figure 1a shows a stable discharge/charge at 2.75 and 3.5 V after the first cycle with a current density of 0.5 A g^{-1} . After 150 cycles, a plateau appears during discharge that is attributed to the reduction of the excess amount of nonreacted I_3^- during charge to $I^{-,33}$ The capacity loss is remarkably small (~10%) after 150 cycles and during the operation of the battery, this plateau starts moving forward resulting in a capacity loss of \sim 30% after 450 cycles. Also, after \sim 200 cycles, a second plateau during charging occurs, which is attributed to the second redox couple $(I_3^{-}/I_2)^{.33}$ This plateau gradually increases starting at \sim 300 cycles. Overall, the cell is cycled up to 450 with the cut-off potential between 2.5 and 4.0 V. Figure 1b shows the performance of the battery with the increased current density of 1 A g^{-1} . By doubling the current density, both ORR and OER potentials, respectively, show a stable trend at around 2.75 and 3.50 V after the first cycle. The cell fails after 217 cycles because of a sudden drop in the discharge potential (Figure S2). Moreover, we evaluated the fast charge of the battery with a current density of 2 A/g charge and 1 A/g discharge, which could operate up to 160 cycles (Figure S2).

In the next step, we assessed the performance of the battery with 25 mM InBr₃, 0.1 M LiTFSI, and DMSO/EMIM-BF₄

electrolytes. Figure 1c represents the voltage profiles with a current density of 1 A g^{-1} . The battery shows a stable discharge/charge at 2.75 and 3.75 V after the first cycle with no plateau. During cycling, the charge plateau becomes evident after 150 cycles meaning that the second redox couple $(Br_3^{-}/$ Br₂) appears.³⁴ The charge potential increases gradually after \sim 200 cycles because of the consumption or deactivation of InBr₃ when the voltage becomes greater than 4.0 V. However, the battery with InBr₃ still operates up to 600 cycles at a 1 A g⁻¹ discharge/charge rate compared to 200 cycles achieved using InI_3 Figure 1d shows a faster charge (2 A g⁻¹) of the battery containing InBr₃. The discharge/charge potentials are 2.75 and 3.8 V, respectively, after the first cycle. After 200 cycles, the charge potential increases to 4.1 V and the discharge potential remains constant at ~2.75. However, the battery fails after 200 cycles because of the sudden drop in the discharge potential (Figure S2). Figure 1e summarizes the polarization gap versus cycle numbers for both RMs at different rates. Our results indicate that iodide reduces the overpotential more than bromide. On the other hand, InBr₃ can cycle much better than InI₃ at high rates, but with a larger polarization gap. Figure 1f represents a comparison of this work with two other studies,44,45 indicating that the cyclability and the current density have improved significantly. For InI₃, the cycling with a current density of 0.5 and 1 A g^{-1} is, respectively, nine and four times longer compared to the earlier report.⁴⁴ For InBr₃, the achieved current density was increased by a factor of 4 along with three times higher cyclability.⁴⁵

To study the discharge products, various characterization techniques have been employed. The surface structure and morphology of the discharge product were studied using Scanning Electron Microscopy (SEM). SEM was carried out on the cathode surface after the fifth discharge and charge



Figure 3. Characterization of the Li anode in the InI₃-based system. (a) Top-view SEM image of the fresh anode (scale bar: 500 nm). (b) Top-view SEM image of the anode after the fifth discharge (scale bar: 500 nm). (c) Top-view SEM–EDX composition mapping of the anode for the Indium element (scale bar: 500 nm). (d) Cross-sectional SEM image of the anode after the fifth discharge (scale bar: 10 μ m). (e) Cross-sectional SEM–EDX composition map of the anode after the fifth discharge for the Indium (green) element showing its presence in the surface, but not in the interior (scale bar: 10 μ m). (f) XPS results of the Li anode showing indium 3d after the fifth discharge cycle. (g) Nyquist plots of the LilLi symmetric cell containing the InI₃ electrolyte after cycles at a constant current density of 0.5 mA cm⁻² with a limited capacity of 0.5 mA h cm⁻².

cycles. The SEM image after the fifth discharge cycle indicates a cloudy-like morphology (Figure 2a) of the Li_2O_2 products on the cathode surface. Subsequently, during the fifth charge cycle (Figure 2b), the discharge product is decomposed exposing the catalyst. Figure 2c,d represents TEM characterization in which low- and high-resolution imaging and electron diffraction were performed. The electron diffraction patterns obtained from the cathode (inset of Figure 2d) confirm the Li₂O₂ discharge product to be polycrystalline, and deposited on (1,1,1) and (0,0,2) MoS₂ nanoflakes. Raman spectra obtained on the cathode sample after the fifth charge and discharge cycles contain bands at 250 and 788 cm⁻¹ corresponding to the Li₂O₂ peak (Figure 2e). All other observed Raman peaks indicate the Raman modes of the exfoliated MoS₂ nanoflakes on the GDL substrate. After the fifth charge cycle, there is no Li₂O₂ peak at 250 cm⁻¹. Furthermore, the Raman signal intensity at 788 cm⁻¹, which has an overlap with the Raman peak of the pristine cathode,^{12,49} decreases as expected because of the decomposition of Li₂O₂ in the charging cycle. XRD experiment performed on the discharged cathode provides additional evidence for the Li2O2 product. The XRD patterns indicate two distinct peaks at 32 and 34° corresponding to the crystalline (100) and (101) facets of the Li₂O₂ product, respectively (Figure 2f).⁶ All other observed peaks are attributed to the catalyst and the substrate. Moreover, we used XPS to investigate the elemental composition of the products on the discharged cathode after the fifth cycle. The main peaks of Li 1s and O 1s appearing at 54.8 and 531.3 eV

confirm the formation of Li_2O_2 after the discharge process (Figure 2g).¹²

To characterize the Li anode, SEM was carried out on the pure Li anode and Li surface after the fifth discharge cycle and the images are shown in Figure 3. Figure 3a,b shows a top-view SEM image of the pristine and cycled anodes. Also, the topview SEM-EDX composition map of the indium element is shown in Figure 3c. These results indicate that a uniform layer of indium is formed on the anode surface. Also, the crosssectional SEM image of the anode is shown in Figure 3d,e. Details of the sample preparation are provided in the Experimental Section. The cross-sectional SEM-EDX composition mapping of the anode reveals the presence of ~ 26 wt % indium, shown by green color, in the surface region of the lithium (Figure S3). XPS was also carried out on the surface of the cycled Li anode to identify the chemical compositions. Figure 3f shows the distinctive peaks of the indium 3d spectrum (at 444.2 and 451.7 eV), consistent with the EDX characterization results.

Moreover, electrochemical impedance spectroscopy (EIS) measurements were performed on the fresh and cycled (5, 10, 15, and 20 cycles) anodes to measure the SEI film resistance (R_{SEI}) upon the battery cycling (Figure 3g). The plating-stripping cycling test of a symmetric LilLi cell containing the InI₃ electrolyte was performed at a constant current density of 0.5 mA cm⁻² with a limited capacity of 0.5 mA h cm⁻². Our results indicate an increase in the SEI film resistance (R_{SEI}) from 129.97 to 151.10 Ω after 20 cycles, which is attributed to

www.acsami.org



Figure 4. AIMD simulations of the Li(100) interface with the DMSO/IL electrolyte with an InX_3 molecule added to the electrolyte. (a) Initial (left) and optimized (right) structures for InI_3 , arrow indicates the initial and final positions of the In atom; (b) pair distribution function g(r) for In atoms with respect to Li atoms from the surface for InI_3 , final results (red color) indicate that In atoms are in Li; (c) initial (left) and optimized (right) structures for $InBr_3$, arrow indicates the initial and final position of In atom; and (d) pair distribution function g(r) for In atoms with respect to Li atoms from the surface for $InBr_3$; final results (red color) indicate that In atoms are in Li.

the formation of the indium layer on the Li anode surface upon cycling (Section S5, Supporting Information).

3.2. Computational Studies. The mechanism by which the InX₃ forms a layer on the lithium surface was investigated by density functional theory (DFT) using the B3LYP functional⁵⁰ and the LANL2DZ⁵¹ basis set. In this investigation, we assumed that the addition of In to the surface of the Li anode as observed in the SEM, EDX, and XPS studies predominantly occurs during the first discharge cycle. The calculated oxidation potentials of the InI₃ and InBr₃, including solvent effects, are 6.07 and 7.13 eV, respectively. This means that these species will not be oxidized at the anode during discharge, but rather chemically react as shown in the DFT calculations described below. Furthermore, the calculated reduction potentials of the InI₃ and InBr₃ (<2.6 eV) are less than the discharge potential so they will not likely be involved in the discharge process at the cathode. A possible chemical reaction between InX₃ and the chemically lithium surface is given by

$$InX_3 + Li(s) \rightarrow InLi(s) + 3LiX$$

We investigated this chemical reaction for both InI_3 and $InBr_3$, with a (100) lithium surface using DFT periodic calculations. In these calculations, the halides are in a mixed electrolyte of 18 DMSO molecules, one EMIM-BF₄ (9:1 volumetric ratio), and LiTFSI salt. All molecules were initially randomly arranged in the simulation box. The results of ab initio molecular dynamics (AIMD) simulations at the electrolyte/anode interface are shown in Figure 4. They indicate that for both InI_3 and $InBr_3$, the indium dissociates from the trihalide and moves into the Li surface with the halide ions reacting with the Li to form LiX species on the surface (Figure 4a,b). The pair distribution function g(r) for In atoms with respect to Li atoms from the surface is shown for InI_3 and

InBr₃ (Figure 4c,d). When InX₃ reacts and dissociates (shown by our DFT calculations) on the surface, In^{3+} picks up three electrons from the Li anode because indium is more electronegative than Li. Three Li from the surface can then form LiX where Li⁺ (formed by loss of the electrons to Indium) reacts with X⁻. The reaction of InX₃ with the Li surface is consistent with the experimental results from SEM, EDX, and XPS that there is indium on the lithium surface.

The mechanism by which the InX₃ additive acts as a redox mediator is that it acts as a source for LiX. The DFT calculations described above indicate that during the reaction of InI₃ and InBr₃ with the lithium surface, LiI and LiBr are likely products and, thus, a source of the redox mediator that can then act during charge at the cathode by oxidizing at the lower charge potential than required for Li₂O₂ decomposition. This results in the lower charge potential as evidenced from the voltage profiles in Figure 1 in this work. We have previously reported on DFT calculations of how LiI₃ resulting from oxidation of LiI can effectively chemically decompose Li_2O_2 during charge.⁵² The barrier for the removal of a Li⁺ cation from $\rm Li_2O_2$ was found to be ~0.5 eV. The bifunctional properties of InX₃ as an additive for both redox mediation and lithium anode protection are illustrated in the schematic in Figure 5.

4. CONCLUSIONS

In summary, we found a new combination of materials comprised of bifunctional InX_3 (X = I and Br) RMs, MoS_2 cathode material, DMSO/EMIM-BF₄ hybrid electrolyte, and LiTFSI salt that enable Li–O₂ batteries to operate in a dry air atmosphere and at a high current density of 1 A g⁻¹ with highest reported cyclability of 600 cycles for InBr₃ and 217 cycles for InI₃. The batteries can also operate at a higher charge rate of 2 A g⁻¹ up to 200 cycles for InBr₃ and 160 cycles for





Figure 5. Schematic of the InI3 additive functions in a Li–air battery: (1) reaction of InI_3 on the lithium surface, (2) formation of the In surface protection layer and generation of LiI, (3) oxidation of LiI resulting in LiI₃, (4) decomposition of Li₂O₂ on the cathode surface by LiI3, and (5) regeneration of LiI.

InI₃. Moreover, we found that the InX₃ additives serve as a redox mediator to lower the charge potential and meanwhile to protect the lithium anode. DFT calculations were used to investigate the formation mechanism of the indium protection layer on the lithium anode. This work has made significant progress in advancing the development of Li–O₂ batteries operating in the air atmosphere. Future research will be aimed at enabling efficient (low charge potential) operation of the Li–O₂ batteries with the presence of a humidity component in the atmosphere.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c15200.

Lithium-air battery cell assembly, cyclic voltammetry, battery failure test, cross-sectional SEM-EDX characterization, EIS test, and DFT calculations (PDF)

AUTHOR INFORMATION

Corresponding Authors

- Anh T. Ngo Department of Chemical Engineering, University of Illinois at Chicago, Chicago, Illinois 60607, United States; Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439, United States; Email: ango@anl.gov
- Larry A. Curtiss Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439, United States; orcid.org/0000-0001-8855-8006; Email: curtiss@ anl.gov
- Amin Salehi-Khojin Department of Mechanical and Industrial Engineering, University of Illinois at Chicago, Chicago, Illinois 60607, United States; Email: salehikh@ uic.edu

Authors

- Sina Rastegar Department of Mechanical and Industrial Engineering, University of Illinois at Chicago, Chicago, Illinois 60607, United States; o orcid.org/0000-0002-5390-2425
- Zahra Hemmat Department of Mechanical and Industrial Engineering, University of Illinois at Chicago, Chicago, Illinois 60607, United States; orcid.org/0000-0002-6463-8404

- Chengji Zhang Department of Mechanical and Industrial Engineering, University of Illinois at Chicago, Chicago, Illinois 60607, United States; Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439, United States
- Samuel Plunkett Department of Chemical Engineering, University of Illinois at Chicago, Chicago, Illinois 60607, United States; Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439, United States
- Jianguo Wen Center for Nanoscale Materials, Argonne National Laboratory, Argonne, Illinois 60439, United States; orcid.org/0000-0002-3755-0044
- Naveen Dandu Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439, United States; orcid.org/0000-0001-7122-8537
- **Tomas Rojas** Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439, United States
- Leily Majidi Department of Mechanical and Industrial Engineering, University of Illinois at Chicago, Chicago, Illinois 60607, United States
- Saurabh N. Misal Department of Mechanical and Industrial Engineering, University of Illinois at Chicago, Chicago, Illinois 60607, United States

Complete contact information is available at: https://pubs.acs.org/10.1021/acsami.0c15200

Author Contributions

A.S.-K., L.A.C., and S.R. conceived the idea for the chemistry of Li-air battery system. A.S.-K. led the battery experiments. L.A.C. led the computational studies. S.R. performed the battery tests and C.Z. helped on the analysis of results. Z.H. and S.R. performed Raman and XRD characterization. Z.H. and S.P. performed SEM and EDX characterization. S.P. performed the (S)TEM characterization. A.T.N, J.G.W., N.D., and T.R. carried out the DFT calculations. L.M. carried out XPS experiments. S.M. carried out the EIS experiments. All the authors contributed to the write up of the article.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The work of A.S.-K., S.R., C.Z., S.P., A.T.N, and L.A.C. were supported by U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Vehicle Technologies Office. The Center for Nanoscale Materials, was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Contract No. DE-AC02-06CH11357. The work of Z.H., L.M, and S.M are supported by the National Science Foundation DMREF Grant 1729420.

REFERENCES

(1) Girishkumar, G.; McCloskey, B.; Luntz, A. C.; Swanson, S.; Wilcke, W. Lithium-Air Battery: Promise and Challenges. J. Phys. Chem. Lett. 2010, 1, 2193–2203.

(2) Aurbach, D.; McCloskey, B. D.; Nazar, L. F.; Bruce, P. G. Advances in Understanding Mechanisms Underpinning Lithium-Air Batteries. *Nat. Energy* **2016**, *1*, 16128.

(3) Guo, Z.; Li, C.; Liu, J.; Wang, Y.; Xia, Y. A Long-Life Lithium– Air Battery in Ambient Air with a Polymer Electrolyte Containing a Redox Mediator. *Angew. Chem. Int. Ed.* **2017**, *56*, 7505–7509.

(4) Geng, D.; Ding, N.; Hor, T. S. A.; Chien, S. W.; Liu, Z.; Wuu, D.; Sun, X.; Zong, Y. From Lithium-Oxygen to Lithium-Air Batteries: Challenges and Opportunities. *Adv. Energy Mater.* **2016**, *6*, 1502164.

ACS Applied Materials & Interfaces

(5) Kraytsberg, A.; Ein-Eli, Y. Review on Li-Air Batteries - Opportunities, Limitations and Perspective. *J. Power Sources* 2011, 196, 886–893.

(6) Liu, T.; Vivek, J. P.; Zhao, E. W.; Lei, J.; Garcia-Araez, N.; Grey, C. P. Current Challenges and Routes Forward for Nonaqueous Lithium-Air Batteries. *Chem. Rev.* **2020**, *120*, 6558.

(7) Xie, M.; Huang, Z.; Lin, X.; Li, Y.; Huang, Z.; Yuan, L.; Shen, Y.; Huang, Y. Oxygen Selective Membrane Based on Perfluoropolyether for Li-Air Battery with Long Cycle Life. *Energy Storage Mater.* **2019**, 20, 307–314.

(8) Ruan, Y.; Yu, L.; Song, S.; Qin, X.; Sun, J.; Li, W.; Chen, B. Ambient Lithium–Air Battery Enabled by a Versatile Oxygen Electrode Based on Boron Carbide Supported Ruthenium. *Int. J. Hydrogen Energy* **2019**, *44*, 31153.

(9) Zou, X.; Lu, Q.; Zhong, Y.; Liao, K.; Zhou, W.; Shao, Z. Flexible, Flame-Resistant, and Dendrite-Impermeable Gel-Polymer Electrolyte for Li– O_2 /Air Batteries Workable Under Hurdle Conditions. *Small* **2018**, *14*, 1801798.

(10) Zou, X.; Liao, K.; Wang, D.; Lu, Q.; Zhou, C.; He, P.; Ran, R.; Zhou, W.; Jin, W.; Shao, Z. Water-Proof, Electrolyte-Nonvolatile, and Flexible Li-Air Batteries via O₂-Permeable Silica-Aerogel-Reinforced Polydimethylsiloxane External Membranes. *Energy Storage Mater.* **2020**, *27*, 297–306.

(11) Luntz, A. C.; Mccloskey, B. D. Li-Air Batteries: Importance of Singlet Oxygen. *Nat. Energy* **2017**, *2*, 17056.

(12) Asadi, M.; Sayahpour, B.; Abbasi, P.; Ngo, A. T.; Karis, K.; Jokisaari, J. R.; Liu, C.; Narayanan, B.; Gerard, M.; Yasaei, P.; Hu, X.; Mukherjee, A.; Lau, K. C.; Assary, R. S.; Khalili-Araghi, F.; Klie, R. F.; Curtiss, L. A.; Salehi-Khojin, A. A Lithium-Oxygen Battery with a Long Cycle Life in an Air-like Atmosphere. *Nature* **2018**, 555, 502– 506.

(13) Chen, Y.; Freunberger, S. A.; Peng, Z.; Fontaine, O.; Bruce, P. G. Charging a Li- O_2 Battery Using a Redox Mediator. *Nat. Chem.* 2013, 5, 489–494.

(14) Liang, Z.; Lu, Y.-C. Critical Role of Redox Mediator in Suppressing Charging Instabilities of Lithium-Oxygen Batteries. *J. Am. Chem. Soc.* **2016**, *138*, 7574–7583.

(15) Zhao, W.; Mu, X.; He, P.; Zhou, H. Advances and Challenges of Redox Mediators in Aprotic Li-O₂ Batteries. *Batteries Supercaps* **2019**, *2*, 803–819.

(16) Xu, C.; Xu, G.; Zhang, Y.; Fang, S.; Nie, P.; Wu, L.; Zhang, X. Bifunctional Redox Mediator Supported by an Anionic Surfactant for Long-Cycle Li-O₂ Batteries. *ACS Energy Lett.* **201**7, *2*, 2659–2666.

(17) Pande, V.; Viswanathan, V. Criteria and Considerations for the Selection of Redox Mediators in Nonaqueous Li-O₂ Batteries. ACS Energy Lett. **2017**, 2, 60–63.

(18) Qiao, Y.; He, Y.; Wu, S.; Jiang, K.; Li, X.; Guo, S.; He, P.; Zhou, H. MOF-Based Separator in an Li-O_2 Battery: An Effective Strategy to Restrain the Shuttling of Dual Redox Mediators. *ACS Energy Lett.* **2018**, *3*, 463–468.

(19) Kwak, W.-J.; Freunberger, S. A.; Kim, H.; Park, J.; Nguyen, T. T.; Jung, H.-G.; Byon, H. R.; Sun, Y.-K. Mutual Conservation of Redox Mediator and Singlet Oxygen Quencher in Lithium–Oxygen Batteries. *ACS Catal.* **2019**, *9*, 9914–9922.

(20) Torres, W. R.; Herrera, S. E.; Tesio, A. Y.; Pozo, M. d.; Calvo, E. J. Soluble TTF Catalyst for the Oxidation of Cathode Products in Li-Oxygen Battery: A Chemical Scavenger. *Electrochim. Acta* 2015, *182*, 1118–1123.

(21) Han, J.; Huang, G.; Ito, Y.; Guo, X.; Fujita, T.; Liu, P.; Hirata, A.; Chen, M. Full Performance Nanoporous Graphene Based Li- O_2 Batteries through Solution Phase Oxygen Reduction and Redox-Additive Mediated Li₂ O_2 Oxidation. *Adv. Energy Mater.* **2017**, *7*, 1601933.

(22) Kwak, W.-J.; Jung, H.-G.; Aurbach, D.; Sun, Y.-K. Optimized Bicompartment Two Solution Cells for Effective and Stable Operation of $\text{Li}-\text{O}_2$ Batteries. *Adv. Energy Mater.* **2017**, *7*, 1–11.

(23) Bergner, B. J.; Schürmann, A.; Peppler, K.; Garsuch, A.; Janek, J. TEMPO: A Mobile Catalyst for Rechargeable Li- O_2 Batteries. J. Am. Chem. Soc. **2014**, 136, 15054–15064.

(24) Gao, X.; Chen, Y.; Johnson, L. R.; Jovanov, Z. P.; Bruce, P. G. A Rechargeable Lithium–Oxygen Battery with Dual Mediators Stabilizing the Carbon Cathode. *Nat. Energy* **2017**, *2*, 17118.

(25) Kwak, W.-J.; Ha, S. H.; Kim, D. H.; Shin, K. H.; Sun, Y.-K.; Lee, Y. J. Synergistic Integration of Soluble Catalysts with Carbon-Free Electrodes for Li-O₂ Batteries. *ACS Catal.* **2017**, *7*, 8192–8199.

(26) Kim, B. G.; Kim, J.-S.; Min, J.; Lee, Y.-H.; Choi, J. H.; Jang, M. C.; Freunberger, S. A.; Choi, J. W. A Moisture- and Oxygen-Impermeable Separator for Aprotic Li-O₂ Batteries. *Adv. Funct. Mater.* **2016**, *26*, 1747–1756.

(27) Kwak, W.-J.; Hirshberg, D.; Sharon, D.; Shin, H.-J.; Afri, M.; Park, J.-B.; Garsuch, A.; Chesneau, F. F.; Frimer, A. A.; Aurbach, D.; Sun, Y.-K. Understanding the Behavior of Li-Oxygen Cells Containing LiI. J. Mater. Chem. A 2015, 3, 8855–8864.

(28) Lee, C. K.; Park, Y. J. CsI as Multifunctional Redox Mediator for Enhanced Li-Air Batteries. *ACS Appl. Mater. Interfaces* **2016**, *8*, 8561–8567.

(29) Qiao, Y.; Wu, S.; Sun, Y.; Guo, S.; Yi, J.; He, P.; Zhou, H. Unraveling the Complex Role of Iodide Additives in Li-O₂ Batteries. ACS Energy Lett. **2017**, 2, 1869–1878.

(30) Li, Y.; Dong, S.; Chen, B.; Lu, C.; Liu, K.; Zhang, Z.; Du, H.; Wang, X.; Chen, X.; Zhou, X.; Cui, G. Li-O2 Cell with LiI(3-Hydroxypropionitrile)₂ as a Redox Mediator: Insight into the Working Mechanism of I- during Charge in Anhydrous Systems. J. Phys. Chem. Lett. **2017**, 8, 4218–4225.

(31) Tułodziecki, M.; Leverick, G. M.; Amanchukwu, C. V.; Katayama, Y.; Kwabi, D. G.; Bardé, F.; Hammond, P. T.; Shao-Horn, Y. The Role of Iodide in the Formation of Lithium Hydroxide in Lithium-Oxygen Batteries. *Energy Environ. Sci.* **2017**, *10*, 1828– 1842.

(32) Zeng, X.; Leng, L.; Liu, F.; Wang, G.; Dong, Y.; Du, L.; Liu, L.; Liao, S. Enhanced Li-O2 Battery Performance, Using Graphene-like Nori-Derived Carbon as the Cathode and Adding LiI in the Electrolyte as a Promoter. *Electrochim. Acta* **2016**, 200, 231–238.

(33) Nakanishi, A.; Thomas, M. L.; Kwon, H.-M.; Kobayashi, Y.; Tatara, R.; Ueno, K.; Dokko, K.; Watanabe, M. Electrolyte Composition in Li-O₂ Batteries with LiI Redox Mediators: Solvation Effects on Redox Potentials and Implications for Redox Shuttling. *J. Phys. Chem.* C **2018**, *122*, 1522–1534.

(34) Kwak, W.-J.; Hirshberg, D.; Sharon, D.; Afri, M.; Frimer, A. A.; Jung, H.-G.; Aurbach, D.; Sun, Y.-K. Li-O₂ Cells with LiBr as an Electrolyte and a Redox Mediator. *Energy Environ. Sci.* **2016**, *9*, 2334–2345.

(35) Kwak, W.-J.; Park, S.-J.; Jung, H.-G.; Sun, Y.-K. Optimized Concentration of Redox Mediator and Surface Protection of Li Metal for Maintenance of High Energy Efficiency in $\text{Li}-O_2$ Batteries. *Adv. Energy Mater.* **2018**, *8*, 1702258.

(36) Xin, X.; Ito, K.; Kubo, Y. Highly Efficient Br-/NO3- Dual-Anion Electrolyte for Suppressing Charging Instabilities of Li-O_2 Batteries. ACS Appl. Mater. Interfaces **2017**, 9, 25976–25984.

(37) Zhang, C.; Dandu, N.; Rastegar, S.; Misal, S. N.; Hemmat, Z.; Ngo, A. T.; Curtiss, L. A.; Salehi-khojin, A. A Comparative Study of Redox Mediators for Improved Performance of Li – Oxygen Batteries. *Adv. Energy Mater.* **2020**, *10*, 2000201.

(38) Landa-Medrano, I.; Lozano, I.; Ortiz-Vitoriano, N.; Ruiz De Larramendi, I.; Rojo, T. Redox Mediators: A Shuttle to Efficacy in Metal-O₂ Batteries. *J. Mater. Chem. A* **2019**, *7*, 8746–8764.

(39) Togasaki, N.; Shibamura, R.; Naruse, T.; Momma, T.; Osaka, T. Prevention of Redox Shuttle Using Electropolymerized Polypyrrole Film in a Lithium-Oxygen Battery. *APL Mater.* **2018**, *6*, 047704.

(40) Zhang, W.; Shen, Y.; Sun, D.; Huang, Z.; Zhou, J.; Yan, H.; Huang, Y. Promoting Li 2 O 2 Oxidation via Solvent-Assisted Redox Shuttle Process for Low Overpotential Li-O₂ Battery. *Nano Energy* **2016**, 30, 43–51.

(41) Lacey, M. J.; Frith, J. T.; Owen, J. R. A Redox Shuttle to Facilitate Oxygen Reduction in the Lithium Air Battery. *Electrochem. commun.* 2013, 26, 74–76.

(42) Zhang, X.; Yang, Y.; Zhou, Z. Towards Practical Lithium-Metal Anodes. *Chem. Soc. Rev.* 2020, *49*, 3040.

ACS Applied Materials & Interfaces

Research Article

(43) Majidi, L.; Hemmat, Z.; Warburton, R. E.; Kumar, K.; Ahmadiparidari, A.; Hong, L.; Guo, J.; Zapol, P.; Klie, R. F.; Cabana, J.; Greeley, J.; Curtiss, L. A.; Salehi-Khojin, A. Highly Active Rhenium-, Ruthenium-, and Iridium-Based Dichalcogenide Electrocatalysts for Oxygen Reduction and Oxygen Evolution Reactions in Aprotic Media. *Chem. Mater.* **2020**, *32*, 2764–2773.

(44) Zhang, T.; Liao, K.; He, P.; Zhou, H. A Self-Defense Redox Mediator for Efficient Lithium $-O_2$ Batteries. *Energy Environ. Sci.* **2016**, *9*, 1024–1030.

(45) Liu, J.; Wu, T.; Zhang, S.; Li, D.; Wang, Y.; Xie, H.; Yang, J.; Sun, G. InBr3 as a Self-Defensed Redox Mediator for $\text{Li}-O_2$ Batteries: In Situ Construction of a Stable Indium-Rich Composite Protective Layer on the Li Anode. *J. Power Sources* **2019**, *439*, 227095.

(46) Majidi, L.; Yasaei, P.; Warburton, R. E.; Fuladi, S.; Cavin, J.; Hu, X.; Hemmat, Z.; Cho, S. B.; Abbasi, P.; Vörös, M.; Cheng, L.; Sayahpour, B.; Bolotin, I. L.; Zapol, P.; Greeley, J.; Klie, R. F.; Mishra, R.; Khalili-Araghi, F.; Curtiss, L. A.; Salehi-Khojin, A. New Class of Electrocatalysts Based on 2D Transition Metal Dichalcogenides in Ionic Liquid. *Adv. Mater.* **2019**, *31*, 1804453.

(47) Abbasi, P.; Asadi, M.; Liu, C.; Sharifi-Asl, S.; Sayahpour, B.; Behranginia, A.; Zapol, P.; Shahbazian-Yassar, R.; Curtiss, L. A.; Salehi-Khojin, A. Tailoring the Edge Structure of Molybdenum Disulfide toward Electrocatalytic Reduction of Carbon Dioxide. ACS Nano 2017, 11, 453–460.

(48) Hemmat, Z.; Cavin, J.; Ahmadiparidari, A.; Ruckel, A.; Rastegar, S.; Misal, S. N.; Majidi, L.; Kumar, K.; Wang, S.; Guo, J.; Dawood, R.; Lagunas, F.; Parajuli, P.; Ngo, A. T.; Curtiss, L. A.; Cho, S. B.; Cabana, J.; Klie, R. F.; Mishra, R.; Salehi-Khojin, A. Quasi-Binary Transition Metal Dichalcogenide Alloys: Thermodynamic Stability Prediction, Scalable Synthesis, and Application. *Adv. Mater.* **2020**, *32*, 1907041.

(49) Asadi, M.; Kumar, B.; Liu, C.; Phillips, P.; Yasaei, P.; Behranginia, A.; Zapol, P.; Klie, R. F.; Curtiss, L. A.; Salehi-Khojin, A. Cathode Based on Molybdenum Disulfide Nanoflakes for Lithium-Oxygen Batteries. *ACS Nano* **2016**, *10*, 2167–2175.

(50) Becke, A. D. A New Mixing of Hartree-Fock and Local Density-Functional Theories. *J. Chem. Phys.* **1993**, *98*, 1372–1377.

(51) Hay, P. J.; Wadt, W. R. Ab Initio Effective Core Potentials for Molecular Calculations. Potentials for the Transition Metal Atoms Sc to Hg. J. Chem. Phys. **1985**, 82, 270–283.

(52) Ahmadiparidari, A.; Fuladi, S.; Majidi, L.; Plunkett, S.; Sarnello, E.; Gholivand, H.; Hemmat, Z.; Rastegar, S.; Misal, S. N.; Jimenez, N.; Redfern, P. C.; Wen, J.; Li, T.; Ngo, A. T.; Khalili-Araghi, F.; Curtiss, L. A.; Salehi-Kojin, A. Submitted to the journal of Power sources.