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Development of the Li-O₂ battery as a practical energy storage technology has been underpinned by the lack of a stable electrolyte to enable reversible conversion between O₂ and Li₂O₂, given that previous applied organic electrolytes all show reactivity toward reactive oxygen species. Wang and colleagues show that this issue can be solved with a water-in-salt electrolyte that contains no organic solvent molecules. The net result is a highly effective electrolyte that enables stable Li-O₂ battery operations up to 300 cycles.
Article

Cathodically Stable Li-O2 Battery Operations Using Water-in-Salt Electrolyte

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SUMMARY
Development of the Li-O2 battery into a practical technology hinges on the availability of a stable electrolyte. Because of the high reactivity of oxygen species in the system, no known organic electrolytes meet the stability requirements. The search for a suitable electrolyte system remains an outstanding challenge in Li-O2 battery research. Here, we show that the issue can be solved with the use of a water-in-salt electrolyte system that involves no organic solvents. In essence, the electrolyte consists of super-concentrated LiTFSI (lithium bis(trifluoromethanesulfonyl)imide), in which H2O molecules are locked to the ions and exhibit little reactivity toward Li2O2 or other oxygen species. The net result is a highly effective electrolyte that permits stable Li-O2 battery operations on the cathode with superior cycle lifetimes. A new door to practical Li-O2 batteries with high performance is opened up.

INTRODUCTION
Compared with other electrochemical energy storage technologies (e.g., Li-S and Li-ion), the Li-O2 battery promises the highest theoretical energy density and has therefore attracted significant research attention.1–11 Development of the Li-O2 battery into a practical technology, however, has been undermined by severe issues regarding parasitic chemical reactions.12 In particular, the ubiquitous presence of reactive oxygen species has proven an outstanding challenge because various cell components, including the cathode, the electrolyte, and the Li anode, all show reactivity toward oxygen species.12,13 Numerous approaches have been proposed to address the issue, and varying degrees of success have been demonstrated. For example, it has been shown that replacing the carbon cathode with non-carbon ones greatly improves the cyclability.14–19 The issues regarding Li anode reactivity could be addressed by covering the Li metal with artificial solid-electrolyte-interface layers or by replacing the Li metal anode with other materials.20–25 The latter approach (replacing Li metal) would reduce the achievable capacities.26 The most significant issue regarding parasitic chemical reactions with the electrolyte, however, remains outstanding (Figure 1A).12,27,28 Some ideas have been proposed and tested, such as modifying the molecular structure of the existing organic solvents or using solid electrolytes to replace the liquid ones.29–32 Although promising preliminary results have been reported, further research is needed to fully evaluate the effect of these approaches in stabilizing practical Li-O2 battery operations. To date, Li-O2 batteries with long cycle lifetime and stable electrolyte as supported by rigorous product detection are still rare.

Careful examination of the issues associated with electrolyte stability reveals that reactivity toward organic solvent molecules lies at the heart of the problem.33–36
These molecules are necessary because they provide the desired physical properties, such as ionic mobility and O₂ solubility, to support Li-O₂ battery operations. It is, therefore, conceivable to address the issue by replacing organic solvent molecules. The challenge would be how to maintain the high ionic mobility without the supporting organic solvent. This goal became possible recently with a report on a unique mixture of water and salt, which has proven effective in improving the performance of Li-ion batteries.³⁷–³⁹ The electrolyte has been referred to as water-in-salt (WiS).³⁸,⁴⁰–⁴³ In essence, WiS takes advantage of the strong solvation effect of super-concentrated LiTFSI (lithium bis(trifluoromethanesulfonyl)imide). Li⁺ is known to be strongly solvated by H₂O molecules. At high concentrations (21 mol/1 kg of H₂O or 21 M), TFSI⁻ was also found to exist in the solvation sheath. The net result is that all H₂O molecules in WiS strongly solvate both ions (Li⁺ and TFSI⁻), leaving few free H₂O molecules to behave like bulk H₂O. As such, the chemical reactivity characteristic of bulk H₂O is greatly suppressed, whereas good ionic conductivity (~10 mS/cm) is maintained to serve as an electrolyte.³⁸ Indeed, previous research has shown that the operation potential window of WiS can be significantly increased.
in comparison with typical aqueous electrolytes (from 2.63–3.86 V in aqueous solution to 1.9–4.9 V in WiS; unless noted, all potentials reported in this article are relative to Li+/Li). More importantly, the limited protons in the WiS electrolyte have been shown to be strongly solvated and thus exhibit little reactivity toward nucleophiles such as polysulfide species, by which a high performance aqueous Li-ion/S battery has been demonstrated. Inspired by these results, in this work we explore whether such an electrolyte system is suitable for Li-O2 battery operations. Our idea is to take advantage of the fact that there are no organic solvents in WiS electrolyte. We expect that the known electrolyte decomposition pathways in typical Li-O2 batteries would be inaccessible (Figure 1B). Consequently, by-product formation is expected to be greatly suppressed. Indeed, our results support that the WiS system is stable under Li-O2 battery operation conditions. Most importantly, we prove that the battery discharges and charges through reversible conversion between O2 and Li2O2, but not reactions with H2O. As a result, significantly longer cycle lifetime (over 70 cycles) can be achieved with a carbon cathode including WiS electrolyte than with that including organic electrolytes (e.g., 16 cycles in 1,2-dimethoxyethane [DME]). When the carbon cathode is replaced by a stable non-carbon one, over 300 cycles of reversible Li-O2 battery operations can be measured.

RESULTS

Electrochemical Performance of Li-O2 Cells Using Water-in-Salt Electrolyte

The first and most important concern we addressed was whether H2O in the WiS electrolyte dominated the electrochemical behavior. That is, it is of critical importance to understand whether the WiS electrolyte enables reversible aprotic conversion between O2 and Li2O2. For this purpose, we carried out electrochemical experiments in the WiS electrolyte and compared the cyclic voltammograms (CVs) with those obtained in two organic electrolytes (Figure 1C). Specifically, we chose to compare the WiS electrolyte with 0.1 M LiTFSI in N,N-dimethylacetamide (DMA), which was predicted to be stable against nucleophilic attack by superoxide, and 0.1 M LiTFSI in DME, which exhibits one of the best stabilities and therefore has been the most commonly used electrolyte for Li-O2 research. As shown in Figure 1C, the reduction wave is turned on at ca. 2.7 V, corresponding to O2 → Li2O2. On the reverse scan, the oxidation wave is turned on at ca. 3.0 V, corresponding to Li2O2 → O2. These redox features closely resemble those in DME and DMA (Figure 1C, inset) but are missing in the CV where O2 is absent. Moreover, these electrochemical features are distinctly different from those obtained in 1 M LiTFSI in H2O (1 mol/1 kg, denoted as salt-in-water [SiW]), where the Li2O2 oxidation wave is missing (Figure S1). This is because the O2 reduction product in a normal aqueous electrolyte is expected to interact strongly with H2O (especially H+ in H2O) to undergo disproportionation. The results shown in Figure 1C suggest that the electrochemical processes in WiS within the measurement potential window are dominated by Li2O2 ↔ O2 conversion but not the electrolyte decomposition (such as H2O splitting).

Next, we performed galvanostatic characterization of the WiS electrolyte, and the purpose was to study whether the electrolyte supports repeated Li2O2 ↔ O2 conversion under pseudo-operation conditions. For these experiments, we used Vulcan carbon as the cathode (see Supplemental Information for preparation details). Li is not suitable as an anode for these tests because it would react with H2O in WiS (the stability window of WiS is 1.9–4.9 V versus Li+/Li). To eliminate possible complications due to parasitic chemical reactions on the Li anode, we used LiFePO4 (LFP) as a pseudo anode for this portion of the study. LFP has been used as a pseudo
anode material for Li-O₂ battery operations and has proven reliable; it has also been tested in a WiS system previously. Nonetheless, it is noted that this approach might not be suitable for practical Li-O₂ battery implementations because the utilization of LFP as the anode would not only decrease the overall cell voltage but also undermine the gravimetric energy density. The true value of doing so lies in the knowledge generated by presenting a study platform where confounding factors such as parasitic chemical reactions at the Li anode are eliminated. In addition to serving as the pseudo anode, a second piece of delithiated LFP was used as a reference electrode (Figures S2–S4). A potential has been converted to be relative to Li⁺/Li. Important to our purposes, no measurable parasitic chemical reactions or catalytic effects were observed in this part of the study when the LFP pseudo anode and reference electrode were used.

As shown in Figure 1D, significantly longer cycling numbers were achieved in WiS (70 cycles) than in DME (16 cycles) before the discharge potential reached the 2.3 V cutoff. DMA (8 cycles) exhibited slightly worse performance than DME. In all three electrolyte systems, an obvious decrease in the discharge potentials was observed toward the end of the cycling experiments. The phenomenon has been previously ascribed to the degrading catalytic activities of the carbon cathode as a result of parasitic chemical reactions on the surface. The voltage-capacity curves of selective cycles (Figure S5) support this understanding. The relatively stable recharge potential of the WiS system toward the end of the cycling test, however, is distinct from that in DME or DMA, where a rapid increase of the recharge potential was also observed (Figure 1D). Previously, such an increase has been ascribed to the presence of by-products (e.g., organic carbonates due to electrolyte decomposition or carbon cathode decomposition or both). That we do not observe this increase in WiS suggests the decomposition of the WiS electrolyte is minimal. Lastly, we note that high capacity was also measured in the WiS electrolyte, and the discharge capacity ranged from ca. 3,500 to 1,500 mAh/gcarbon for current densities of 50–400 mA/gcarbon, respectively (Figures S6 and S7). The values are comparable with those reported in the literature under similar test conditions.

Detection of Li₂O₂ as the Discharge Product

We then used X-ray diffraction (XRD) to examine the discharge products. Upon deep discharge (with the capacity reaching 2,500 mAh/gcarbon), the most prominent diffraction peaks at 2θ = 32.8°, 34.9°, and 40.6° were unambiguously assigned to Li₂O₂ (Figure 2A). The low-intensity peaks at 2θ = 31.7° and 37.1° are close to the standard peaks of Li₂CO₃, whose presence is commonly observed as a result of the reactivity of the carbon cathode under deep discharge conditions. As discussed below, Li₂CO₃ is unlikely a result of electrolyte decomposition. The morphology of the deep discharge products was studied by scanning electron microscopy (SEM; Figure 2E) and transmission electron microscopy (TEM; Figure 2F). A representative toroidal structure was observed, consistent with literature reports where fast kinetics favors toroid formation (e.g., when H₂O impurities were present in the organic electrolytes). TEM micrographs and electron energy loss spectroscopy (EELS) spectra (Figure S8) prove that the toroid is indeed Li₂O₂, consistent with previous studies. We next characterized the test cell ex situ under pseudo-operation conditions (cycled at 500 mAh/gcarbon) to study the reversibility of the product formation and decomposition. The XRD patterns shown in Figure 2B were consistent with those of the deep discharge, albeit at lower intensities. No other major diffraction peaks were observed. The Raman spectra shown in Figure 2C provide additional support that Li₂O₂ is the product of discharge, which can be
reversibly decomposed upon recharge. Similar to the XRD studies, the Raman spectra were collected without sample exposure to ambient air. We used X-ray photoelectron spectroscopy (XPS) to study the Li 1s electron-binding energies, and the spectra are plotted in Figure 2D. Note that for the XPS experiment, the samples were briefly exposed to ambient air during sample transfer because of instrumentation limitations. That is why we see contributions from Li2CO3 in the deconvoluted peak compositions. Nevertheless, consistent with other literature reports, the main composition of the discharge product was indeed Li2O2. Importantly, we saw no measurable Li2CO3 contribution in the recharged sample (Figures 2D and S9), further supporting that the observed Li2CO3 by XPS in the discharged state is due to exposure to ambient air but not inherent to the discharge process. This behavior (Figure 2D) needs to be distinguished from that of deep discharge (Figure 2A), where carbon cathode degradation may become measurable because of the high capacities and the low cutoff potentials. We applied Fourier-transform infrared spectroscopy (FTIR) to confirm that Li2O2 was the discharge product and could be fully decomposed (Figure S10). Importantly, no LiOH was detected by FTIR. Additional SEM micrographs also revealed that Li2O2 formed upon discharge could be completely removed after recharge (Figure S11). The toroidal morphology of Li2O2 was consistently observed for a discharge
rate \leq 200 \text{ mA/g}_\text{carbon}, above which less regularly shaped products started to appear (Figure S12). No LiOH was observed in this part of the product analysis. The result provides strong support that the WiS electrolyte enables aprotic O\textsubscript{2} \leftrightarrow Li\textsubscript{2}O\textsubscript{2} conversion but not O\textsubscript{2} \leftrightarrow LiOH, which would be expected from common aqueous Li-O\textsubscript{2} systems and is undesired for the present study.\textsuperscript{4,56}

The selectivity is most likely due to limited H\textsubscript{2}O reactivity and mobility toward nucleophiles such as Li\textsubscript{2}O\textsubscript{2}. Similarly low reactivity toward polysulfides in the WiS electrolyte has been reported by both experimental and theoretical studies.\textsuperscript{43}

**Quantitative Product Analysis**

Quantitative analysis of the product was conducted next, and the purpose was to establish that the measured charges in electrochemical characterization corresponded to Li\textsubscript{2}O\textsubscript{2} formation and decomposition. In other words, our goal was to prove that the faradic efficiency was high. We first explored the iodometric titration technique developed by McCloskey et al.\textsuperscript{55} For the WiS electrolyte, we obtained a yield of 85.0%. The yield for DME was 79.4%, and that for DMA was 79.1% (Figures 3A and S13). As has been discussed by McCloskey et al., the titration yield is sensitive to several factors such as the type of cathode materials used,
the loading amount, and the discharge capacity, as well as the extent to which impurities are removed. The yields we obtained are in line with the literature reports, although slightly lower than the best reported values (see Table S1). That we measured the highest yields in WiS strongly supports that a lower amount of by-product was formed in WiS than in DME or DMA. The unaccounted products by the titration method (ca. 15%) could be dissolved species (e.g., \( \text{H}_2\text{O}_2 \) and \( \text{LiOH} \)) and non-\( \text{Li}_2\text{O}_2 \) solid species (e.g., carbonates), as well as the result of system errors inherent to the titration method. To study whether any products could be dissolved in the electrolyte as a result of a strong solvation effect or parasitic reactions, we compared the titration results with and without the electrolytes in Figure 3B and observed no significant differences. The result suggests that no measurable contribution of the measured capacity comes from \( \text{H}_2\text{O}_2 \) as possible by-products, further supporting the suitability of WiS as a stable electrolyte system for \( \text{Li}_2\text{O}_2 \) battery operations. To characterize the recharge products, we used isotopically labeled \( \text{H}_2^{18}\text{O} \) in the WiS electrolyte. Only at high recharge potentials (over ca. 4.6 V versus \( \text{Li}^+/\text{Li} \)) did we observe detectable \( ^{36}\text{O}_2 \) (ca. 4%) as an indication of electrolyte oxidation (Figure 3C). Importantly, no measurable \( \text{CO}_2 \) evolution was detected throughout the recharge process, in stark contrast to when organic electrolytes were used. The gas evolution result lends strong support that WiS electrolyte is more stable against decomposition during recharge (Figures S14 and S15). To further prove that the electrolyte was stable upon cycling, we examined the electrolytes after five cycles of repeated discharge and recharge (in the discharged state) by using nuclear magnetic resonance (NMR) spectroscopy. The spectra (Figures 3D, S16, and S17) clearly show that a small amount of \( \text{LiCO}_2\text{H} \) as by-product was present with DME and DMA electrolytes but was by and large absent with the WiS electrolyte. Lastly, we also monitored the pressure during the first ten cycles of the test cell featuring the WiS electrolyte. The calculated pressure recovery efficiency \( (\frac{\Delta P_{\text{discharge}}}{\Delta P_{\text{recharge}}} ) \) was ca. 100% throughout the process (Figure S18). Taken as a whole, the quantitative analysis presented in this section strongly supports that the WiS electrolyte enables reversible \( \text{Li}_2\text{O}_2 \) conversion with minimum decomposition reactions commonly observed in other organic electrolyte systems.

### Cycling Performance of Li-O2 Cells Using Carbon-free Cathode

It has been reported that the parasitic chemical reactions within the electrolyte and on the carbon cathode exhibit a synergistic effect. For instance, the susceptibility of carbon to reactive oxygen species leads to the formation of carbonates on carbon cathode surfaces, which increases the need for applied potentials, especially during recharge. The high applied potentials are an important reason for electrolyte decomposition, which in turn increases carbonate deposition on the carbon support, exacerbating the situation. Thus, the use of carbon as a cathode makes it difficult to fully realize the promises enabled by the WiS electrolyte. Indeed, we attributed the loss of yield for WiS electrolyte as shown in Figure 3A to possible parasitic chemical reactions with the carbon cathode, which was supported by spectroscopic characterization of the cycled carbon electrodes (Figures S19–S21). To better take advantage of the stability offered by WiS electrolyte, we next investigated a carbon-free cathode material developed by us previously, TiSi2 nanonets decorated with Ru nanoparticles. The idea was to understand the true potentials enabled by WiS without confounding factors connected to either the Li metal anode (by replacing it with LFP) or the carbon cathode (by replacing it with Ru/TiSi2). Indeed, remarkable performance in terms of cyclability was obtained. At a discharge depth of 1,000 mAh/gRu (or 500 mAh/gRu+TiSi2), over 300 cycles of repeated discharge and recharge was measured (Figure 4A). An average round-trip energy efficiency (based
on the measured voltage of the cathode) of ca. 62% was achieved (Figure 4B). This cyclability is among the highest reported in the literature at that capacity. The product was further characterized by XPS, Raman spectroscopy, and SEM to be only Li₂O₂ (Figures S22–S24), and the results are consistent with those shown in Figure 2 (obtained on the carbon cathode).

We note that the Ru/TiSi₂ cathode is not yet optimized. For instance, the catalytic activity of Ru in WiS for the oxygen evolution reactions (OER) may be different from that in organic electrolyte systems, although the discharge and recharge characteristics of Ru/TiSi₂ in WiS (Figure 4A) are similar to those of Ru/TiSi₂ in DME from our previous results. Such different catalytic activity is most likely due to different solvation effects between H₂O and DME. Moreover, the activities of Ru/TiSi₂ in catalyzing O₂ reduction and evolution reactions in WiS are expected to be different from that of carbon, which helps explain the slightly different discharge and recharge characteristics as shown in Figures 4A and S5. Our goal of introducing Ru was mainly to compensate the ORR activity when replacing the unstable carbon with the stable carbon-free TiSi₂ cathode (Figure S25). The targeted ORR catalytic effect in WiS was indeed prominent, although the OER catalytic effect was inferior to that in DME. For future optimizations, we envision that replacing Ru with a more effective OER catalyst could readily improve the recharge characteristics. Although additional research will be needed for fully understanding the behavior of Ru/TiSi₂ as a cathode for Li-O₂ battery operations, our previous research has already established that it functions as expected in catalyzing O₂ reduction and evolution reactions without exhibiting the parasitic chemical reactions that undermine carbon-based cathode materials. The results reported here thus prove that when a stable electrolyte and a stable cathode (both with minimum parasitic decomposition reactions) are used for Li-O₂ battery operations, long cycle lifetimes become attainable. The system studied here provides a platform for further optimization to better take advantage of this promising electrolyte system for Li-O₂ battery applications. For example, we envision that the WiS electrolyte can be readily used for constructing practical devices with stable anode materials (such as protected Li). To further demonstrate the value offered by the WiS electrolyte, we have fabricated proof-of-concept Li-O₂ batteries in which protected Li is used in conjunction with WiS. Both carbon (Figure 5A) and Ru/TiSi₂ (Figure 5B) cathodes were tested. The results shown in Figure 5 are encouraging. Nevertheless, the cyclability (ten cycles) remains relatively poor.
More engineering optimization, especially on the protected Li anode side, will enable us to take full advantage of the WiS electrolyte system.

**DISCUSSION**

The reversible formation and decomposition of Li₂O₂ in WiS electrolyte as reported here is unique. Although the formation of Li₂O₂ species in H₂O has been previously reported with a highly concentrated LiCl and LiOH mixture for aqueous Li-O₂ battery applications, LiOH was found to be used for part of the recharge process. Compared with other commonly used organic solvents, H₂O features a high acceptor number (ca. 60). It is known to solvate intermediates of Li-O₂ discharge and recharge such as superoxide species. Its positive effects toward Li-O₂ battery operations were not recognized until recently. For instance, McCloskey and co-workers found that H₂O (up to 4,000 ppm) is key to the formation of the characteristic toroidal structures and contributes to the high discharge capacity. Wang and colleagues reported that H₂O in electrolyte helps reduce discharge overpotentials through a proton-mediated mechanism. Zhou and co-workers reported similar reduction in the overpotentials during recharge by adding H₂O. The Zhou group further suggested that the presence of H₂O could improve the stability of organic electrolytes by interacting with the superoxide species. On the other hand, excess amount of free H₂O will induce the formation of LiOH, which is suggested to be detrimental for the cell operations. For the WiS electrolyte, H₂O replaces the organic solvent molecules that were popularly used in previous Li-O₂ research and enables the required functionalities of an electrolyte with superior stability for Li-O₂ battery operations. Notably, the characteristic toroidal structure of Li₂O₂ formed in WiS suggests that the solvation effect of H₂O exists and mediates the discharge process toward higher capacities. The good rate performance also lends strong support for the solvation effect by H₂O. The lack of LiOH detected in the product indicates that the proton in WiS exhibits little reactivity toward the electrochemically formed Li₂O₂ during discharge.

In conclusion, we have shown that WiS, as an electrolyte system for Li-O₂ battery operations, is stable against parasitic chemical reactions with reactive oxygen species. It provides the necessary functionalities to support aprotic Li-O₂ operations via reversible Li₂O₂ formation and decomposition. The lack of organic solvent molecules is a key advantage here. It eliminates the known reaction pathways that lead to by-product formation from organic electrolyte systems. Both qualitative...
and quantitative product analyses support that no measurable by-products form in the WiS system. With a carbon cathode, greatly improved cyclability of over 70 cycles can be obtained with WiS electrolyte in comparison with organic electrolytes. When the carbon cathode is replaced with a carbon-free material, up to 300 cycles of stable Li-O2 battery operations are obtained. This result sets a new benchmark in Li-O2 battery performance with quantitative product detection. It sets the stage for future optimizations to realize the full potential held by Li-O2 batteries as a stable, high-capacity electrochemical energy storage technology.

EXPERIMENTAL PROCEDURES

Electrochemical Measurements

All electrochemical tests were carried out with a VMP3 potentiostat (BioLogic) in either an electrochemical cell or a home-designed Swagelok-type cell. The electrochemical data were collected in an Ar-filled/O2-tolerant glovebox (MBRAUN, H2O < 0.1 ppm) at room temperature. CV measurements were carried out in an electrochemical cell. WiS electrolyte was bubbled with either O2 or N2 to maintain an O2- or N2-saturated solution, respectively. It has been shown that the solubility of O2 decreased from SiW (1 mol/1 kg, 1 m) to water-in-salt (21 mol/1 kg, 21 M) conditions, but the decreased O2 solubility was not found to be a limiting factor for the measurements in this study. The Pt wire and delithiated LFP film were immersed in the electrolyte as the counter and pseudo reference electrode, respectively. Glassy carbon (3 mm diameter) was applied as the working electrode. The CV measurements were performed at a scan rate of 25 mV/s. The home-designed Swagelok-type cell was equipped with three electrodes for galvanostatic measurements. Two delithiated LFP films were used as the pseudo anode (counter electrode, in excess) and the pseudo reference electrode. The total capacity of the delithiated LFP pseudo anode was at least three times higher than the tested capacities of the cathode for all measurements. The Li-O2 cell with protected Li anode was fabricated with Li-ion conducting glass-ceramics (LICGC, OHARA) as a protection layer. Vulcan carbon or Ru/TiSi2 was used as the cathode. The current density and capacity were normalized to the weight of Vulcan carbon or Ru or Ru plus TiSi2. Two pieces of glass microfiber (GF/F, Whatman) were introduced to separate each electrode. In a typical experiment, 200 μL of electrolyte was used. After the cells were assembled, ultrahigh purity oxygen (Airgas) was purged through the head space of the Swagelok-type cell at 20 sccm for 1 min. The cell was then isolated from the gas line after the pressure equilibrated to 760 torr. The galvanostatic cycling tests for understanding the behavior of the LFP counter and reference electrodes were conducted at a current density of either 20 or 50 μA/cm2. The capacity was set to 40 and 100 μAh/cm2, respectively (operating for 4 hr/cycle). The cycling tests to compare WiS, DME, and DMA electrolytes with a Vulcan carbon cathode and LFP pseudo anode were conducted with a current density of 50 mA/gcarbon at a cutoff capacity of 250 mAh/gcarbon (operating for 10 hr/cycle). The galvanostatic cycling test with WiS as the electrolyte, carbon as the cathode, and protected Li as the anode was conducted with a current density of 50 mA/gcarbon at a cutoff capacity of 500 mAh/gcarbon (operating for 20 hr/cycle). Ru/TiSi2 cathode was tested in the WiS electrolyte with the Swagelok-type cell with either an LFP pseudo anode or a protected Li anode for the cycling test at a cutoff capacity of 1,000 mAh/gRu or 500 mAh/gRu+TiSi2 (operating for 4 hr/cycle). The samples for spectroscopic and microscopic characterization with Vulcan carbon were operated at 50 mA/gcarbon to reach 500 or 2,500 mAh/gcarbon. The samples for spectroscopic and microscopic characterization with Ru/TiSi2 cathode were operated at 1,000 mAh/gRu. To simultaneously monitor the anode and cathode
potentials against the reference electrode, we studied the Swagelok-type cells by using the GCPL2 program (part of the Biologic software suite) to ensure voltage reliability. The equilibrium potential of the LFP electrode in DMA and DME electrolytes was measured against Li+/Li electrode to be 3.46 ± 0.01 V. In WiS, the LFP electrode potential was calibrated against a standard AgCl/Ag reference electrode (calibrated to be ca. 0.197 V versus normal hydrogen electrode) and converted to 3.46 ± 0.02 V versus Li+/Li (see Figure S4 for more discussions). More details about the materials can be found in the Supplemental Information.

**Material Characterization**

XRD measurements were conducted on a PANalytical X’Pert Pro diffractometer with Cu Kα radiation. XPS was carried out on a K-Alpha + XPS (Thermo Scientific) with an Al X-ray source (incident photon energy, 1,486.7 eV). The fitting of XPS data was performed by XPS Peak 4.1 software. Raman spectra were acquired with a micro-Raman system (XploRA, Horiba) with 532 nm laser excitation. FTIR was performed with a Bruker ALPHA FTIR spectrometer in a N2-filled glovebox. SEM was conducted with a JEOL 6340F microscope operated at a 10 kV accelerating voltage. EELS was used as a qualitative fingerprint to verify the presence of Li and the components in the toroid particles. The EELS spectrum was acquired on a Tecnai T20 G2 TEM (FEI, 200 kV) with a Gatan imaging filter. The energy resolution was ca. 2.1 eV as measured from the full width at half maximum of the zero loss peak. All EELS data were recorded with a pixel dwell time of 0.1 s, dispersion of 0.05 eV/channel, and a selected entrance aperture of 2 mm. Vulcan carbon cathode samples were discharged and/or fully recharged to 500 mAh/gcarbon for XRD, XPS, Raman spectroscopy, FTIR, SEM, and pressure monitoring measurements. The deeply discharged samples (2,500 mAh/gcarbon) were also prepared for XRD and SEM. Ru/TiSi2 cathode samples were operated at 1,000 mAh/gRu or 500 mAh/gRu+TiSi2 for XPS, SEM, and Raman spectroscopy. The electrode samples were collected in an O2-tolerant Ar-filled glovebox (MBRAUN, H2O < 0.1 ppm), washed in DME at least five times to remove residue salts, and then dried under a vacuum at room temperature for 6 hr before characterizations. For XPS measurements, an airtight Ar bag was used to transfer samples. Samples were then mounted onto the stage with short exposure to the ambient air (typically for ca. 5 min). For XRD and Raman characterization, an airtight sample holder was assembled in the O2-tolerant Ar-filled glovebox and transferred out for direct measurement through an observation window. FTIR was conducted in a N2-filled glovebox (MBRAUN, O2, H2O < 0.1 ppm), and the samples were transferred in an airtight Ar bag but with a short exposure to ambient air (typically for ca. 5 min). The SEM samples were mounted onto a stage with a short exposure in the ambient air (typically for ca. 5 min) before being transferred to the high-vacuum chamber. The TEM samples were prepared by first sonicating the discharged samples in DME for 2 min in an airtight vial and then drop casting onto the TEM grid in a N2-filled glovebox. The samples were exposed in ambient air for ca. 10 min. Gas chromatography mass spectrometry (GC-MS) measurements were performed with a Shimadzu QP2010 Ultra and a Carboxen 1010 PLOT column. The 36O2 calibration curve was constructed by manually injecting known amounts of air into the injection port at 298 K. For in situ gas evolution detection, a Swagelok-type cell with a Vulcan carbon cathode, an LFP anode, and the WiS electrolyte were connected to the GC-MS sampling loop (500 μL in volume) with He as the carrier gas (ultrahigh purity, 10 sccm flow rate). The total discharge and recharge capacity was limited to 200 mAh/gcarbon for data acquisition. The current density was consistent with previous test conditions. The cell was allowed to rest for 1 hr to achieve a flat baseline before applying potentials. After the recharge process was completed, the gaseous
products were further sampled for 1 hr to let the MS signals reach a stable baseline again. The MS signals during recharge processes were recorded for gas evolution and faradic efficiency calculations. For the titration experiments, Swagelok-type cells were discharged to the cutoff voltage of 2.5 V versus Li+/Li and then disassembled in an O2-tolerated Ar-filled glove box (H2O level < 0.1 ppm, MBRAUN) immediately. For each individual cell, the cathode and electrolyte were collected separately in glass vials for titration. The samples were soaked in 3.0 mL deionized H2O and 1.0 mL HCl (1 M) for 15 min. Before titration, 2 mL of 2% KI solution and 50 μL of Mo catalyst solution were added in sequence and then kept in the dark. The reaction mixture was then titrated with a calibrated Na2S2O3 solution (4.3 mM). Each condition was repeated at least four times. 1H NMR was performed on a 600 MHz spectrometer. The electrodes and all electrolytes from each cell were collected and soaked with same amount of D2O or CDCl3 to normalize the amount of by-products. For a more accurate normalization, a trace amount of C6H6 (benzene) was added as the internal standard for the first discharge. All 1H NMR chemical shifts were reported in ppm in relation to a residual HDO peak at 4.78 ppm (trimethylsilylpropanoic acid at 0 ppm). The loading of Ru for the carbon-free cathode was quantified by inductively coupled plasma optical emission spectrometry. The mass ratio of Ru and TiSi2 was found to be ca. 1:1, consistent with our previous results. Pressure monitoring tests were carried out by connecting the Swagelok-type cell to an airtight pressure gauge with a sensitivity of 0.1 torr (MKS, 902B Piezo). The current density was set at 100 mA/gcarbon to maximize the signal/noise ratio. The pressure for the first ten cycles was monitored in situ.

SUPPLEMENTAL INFORMATION
Supplemental Information includes Supplemental Experimental Procedures, 25 figures, and 1 table and can be found with this article online at https://doi.org/10.1016/j.chempr.2018.02.015.

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AUTHOR CONTRIBUTIONS
Q.D. and D.W. conceived the idea. Q.D. carried out most of the experiments. X.Y. prepared the TiSi2 cathode substrate and assisted with the XRD and GC-MS measurements. Y.Z. and H.S performed the TEM and EELS experiments. M.Q. assisted with the NMR and FTIR experiments. X.Z. prepared the carbon electrodes and contributed to the schematic design. Y.H. participated in designing the Swagelok-type cell. All authors contributed to the discussions. Q.D. and D.W. wrote the manuscript with input from all authors. D.W. supervised the research.

DECLARATION OF INTERESTS
The authors declare no competing interests.

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REFERENCES AND NOTES


