High Capacity Na–O2 Batteries: Key Parameters for Solution-Mediated Discharge

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ABSTRACT: The Na–O2 battery offers an interesting alternative to the Li–O2 battery, which is still the source of a number of unsolved scientific questions. In spite of both being alkali metal–O2 batteries, they display significant differences. For instance, Li–O2 batteries form Li2O2 as the discharge product at the cathode, whereas Na–O2 batteries usually form NaO2. A very important question that affects the performance of the Na–O2 cell concerns the key parameters governing the growth mechanism of the large NaO2 cubes formed upon reduction, which are a requirement of viable capacities and high performance. By comparing glyme-ethers of various chain lengths, we show that the choice of solvent has a tremendous effect on the NaO2 growth mechanism. Strong solvent–solute interactions in long-chain ethers shift the formation of NaO2 toward a surface process resulting in submicrometric crystallites and very low capacities (ca. 0.2 mAh/cm2). In contrast, short chains, which facilitate desolvation and solution-precipitation, promote the formation of large cubic crystals (ca. 10 µm), enabling high capacities (ca. 7.5 mAh/cm2). This work provides a new way to look at the role that solvents play in the metal–air system.

INTRODUCTION

Increasing energy storage demands, driven by the needs of electric vehicles and the field of renewable energy sources, motivate the search for lower-cost, higher-capacity, and sustainable rechargeable batteries. Metal–air batteries are of great interest because of their large theoretical capacity, which relies on the redox reaction of gas species rather than solid-state intercalation reactions, such as those that occur in Li-ion and Na-ion batteries.

Although the capacity is lower than the well-known Li–O2 battery, the Na–O2 battery has recently attracted considerable attention because of its apparent ease of cycling, high-energy efficiency, and chemical reversibility. This is in part due to the lack of side reactions when compared to Li–O2 batteries. It also benefits from the lower cost and abundance of sodium compared to lithium.

While Na–O2 batteries certainly show promise, a recent review of the reported discharge products and capacities of NaO2 cells clearly demonstrates a lack of understanding in the field. For example, the capacities and products can vary drastically and are strongly dependent on the electrolyte system as well as the type of carbon and the mass loading used. As a consequence, a number of key challenges remain, and these include maximizing discharge capacities, achieving high round trip efficiencies, and suppressing parasitic reactions. In this
work we investigate the discharge mechanism, which is critical to achieve a maximum capacity in the NaO2 battery. In contrast to the lithium system, where the peroxide product (Li2O2) is thermodynamically favored, in the sodium air battery, the formation energy of the superoxide and peroxide are comparable (E° NaO2 = 2.27 V vs. Na+/Na, E° Na2O2 = 2.33 V vs. Na+/Na).13 In practice, NaO2 is typically observed as the discharge product in dry systems. Recent density functional theory (DFT) calculations suggest that superoxide formation occurs because of a lower surface energy compared to peroxide.14 Additionally, this low surface energy favors the formation of high surface area, cube-like structures.15 It is well-known that most alkali oxides are essentially insoluble, suggesting that the large cubic NaO2 product cannot form via an electrochemical deposition pathway.15,16 Rather, discharge is believed to be dominated by a solution mechanism (also termed a solution precipitation route) in which soluble NaO2 species precipitate from solution, as proposed by several research groups.15,17–21 The alternative is termed the surface mechanism, which is defined by a surface confined growth. The existence of soluble NaO2 within the battery has been proven experimentally by Hartmann et al.12 As the discharge product is dissolved in the electrolyte solution, one would expect the nature of the solvent to have a profound effect on the discharge mechanism as observed in the Li−O2 battery.

For the Li−O2 system, the different parameters affecting the solvation properties, the donor number (DN) and acceptor number (AN) of the solvent, have been shown to play a critical role.22−24 High-DN solvents solvate cations extremely well, whereas on the other hand, the solvation of anions is greater for high-AN solvents. Hence, it has been shown that increasing the solvation of the Li+ ion with higher DN solvents will promote LiO2 solubility and disproportionation, in regions away from the electrode surface, increasing the discharge capacity.24 A similar effect can be obtained when varying the solvent acceptor number and by the addition of additives to the electrolyte, such as water.23,25 Recent reports have also shown that the solvation of cations can be altered by changing the DN of the salt anion.26,27

In the Na−O2 battery, glyme-ethers are the primary solvent of interest because of their compatibility with metallic sodium. As mentioned, discharge in these systems is expected to occur by a solution mechanism involving a soluble Na−O2 intermediate. In contradiction to this, the overall solubility of Na2O2 in glymes is expected to be rather low.15 Other researches have invoked inherent water content and more specifically water as a phase-transfer catalyst to explain the solubility.26 Even if all the aforementioned parameters indeed play a role, the lack of a detailed study of the intrinsic effect of glyme-ethers as Na−O2 solvents demands attention.

In this paper we aim to identify the critical physical parameters of glyme-ethers that control the solution-precipitation of NaO2. When comparing the electrochemical response of Na−O2 systems using the three glyme-ethers (ethylene glycol dimethyl ether, diethylene glycol dimethyl ether, and tetraethylene glycol dimethyl ether), we observe a significant influence of the ether-chain length on the discharge product formation mechanism. It is known that the solvent−solute interactions in the long-chain ethers are of a different nature, i.e., stronger, than in short-chain ethers because of chelation of Na+. We reveal that this affects the solvation−desolvation kinetics, altering the mechanism of NaO2 formation. Long-chain ethers result in a dominant surface mechanism due to a kinetic barrier during desolvation and growth, resulting in premature cell death through passivation of the electrode. In contrast, short-chain ethers are able to maintain a solution mechanism and consequently display high capacities. Our findings illustrate the importance of comparing the same solvent systems in various reports throughout literature.

### RESULTS AND DISCUSSION

To be able to compare the herein reported solvents, we summarized a variety of important parameters of the most commonly used glyme-ethers in Table 1. As already stated, the DN and AN are of particular interest with regard to the solvation of NaO2 and the resulting interaction with oxygen radicals, respectively. High dielectric permittivities favor fast electron transfer reactions and separation of ion pairs. Large conductivities in the batteries are essential to allow for high efficacy of charge transport during cycling. The dynamic viscosity of solvents has great influence on ion mobility, which can fundamentally affect the nucleation and crystal growth from solution. Finally, because the metal−air systems use oxygen as a reactant, the amount (HO2) and diffusion (DO2), the total O2 availability of oxygen, are extremely crucial to reach optimized capacities in this battery technology.

| solvent    | DN [kcal/mol] | AN [kcal/mol] | permittivity at 25 °C | conductivity 0.5 NaTFSi [mS/cm] | viscosity 25 °C [×10−3 cm2/s] | H2O2 [mmol] | DO2 [×10−3 cm2/s] |
|------------|---------------|---------------|-----------------------|-------------------------------|-----------------------------|-------------|-----------------|
| DME        | 19 ± 1        | 10.2±10       | 7.07±10               | 8.4                          | 4.2             | 10.1±10      | 6.0±12           |
| DGME       | 18 ± 1        | 9.9±10        | 7.63±10               | 5.4                          | 10.0±10         | 6.4±12       | 4.4±12           |
| TGME       | 12 ± 4        | 10.5±10       | 7.78±10               | 2.0                          | 32.9±12         | 4.3±12       | 2.6±12           |

Table 1. Summary of Potential Metal−Air Battery Electrolyte Solvents and Their Intrinsic Properties Collected from the Literature and Donor Number and Conductivity Values Determined Experimentally in Italic (see Experimental and Theoretical Methods)
per mole of gas for DGME and DME, as deduced from pressure measurements, suggesting the formation of NaO₂ during discharge (Figure 1b). The rapid discharge in TGME (low O₂ consumption) did not allow for an accurate analysis of the pressure change. The specific capacities for each solvent were highly reproducible (Figures S2–S4). The discharged electrodes were further investigated by scanning electron microscopy (SEM) and X-ray diffraction (XRD) analysis (Figure 2). For DME and DGME, highly crystalline NaO₂ was confirmed by XRD as the discharge product (green and blue lines, respectively). In both cases, a dense coverage of NaO₂ cubes on the electrode surface (facing the O₂ reservoir) was provided by M. Jansen, MPI-FKF, Stuttgart, Germany (red line).

formation of NaO₂ cubes, rotating ring disc electrode (RRDE) experiments were performed to measure the relative amount of soluble superoxide species (Figure 3). The amount of soluble species detected at the ring is found to increase considerably when increasing the chain length from DME, DGME, to TGME; this trend is contrary to the evolution of the DN. It is worth noting that decreasing the Na⁺ ion concentration shifts the equilibrium toward soluble NaO₂ species, as demonstrated by RRDE measurements (Figure S7).

The fact that no superoxide was detected by RRDE for DME can be related to the detection limit of the RRDE. Consequently, the solubility of superoxide was measured using KO₂ as an analogue for NaO₂, which is not commercially available. The solubility of KO₂ is expected to differ from that of NaO₂, and the values thus represent a lower limit. The KO₂ solubility was determined by means of ultraviolet–visible (UV–vis) absorption of TiOSO₄, a technique that is commonly used to determine the chemical yield of M₂O₄ discharge product in metal–air batteries. Based on these measurements, the approximate solubilities of KO₂ in TGME (3 × 10⁻⁴ mol/L), DGME (2 × 10⁻⁴ mol/L), DME (5 × 10⁻⁵ mol/L) were determined (Figure S8). The values are in good agreement with the trend deduced from RRDE as well as with the estimated values reported by Hartmann et al. These measurements also demonstrate that the values obtained for the short ether DME are in the range of low DN nonether solvents, for instance acetonitrile (ACN) (8 × 10⁻⁵ mol/L). Hence, this finding shows that regardless of the variance in DN between these ethers, the solubility of NaO₂ is the highest in TGME; therefore, the solubility cannot explain the results obtained in Figures 1 and 2. These large differences in performance call for a deeper understanding of the solvents’ influence on the formation of NaO₂ cubes during discharge.

It is known that glyme-ethers, in comparison to other solvents have the ability to chelate hard cations. Several groups have shown that long-chain glyme-ether can chelate small cations. This solvation effect is relatively unexplored in metal–air and could introduce unconventional behavior with regard to metal–air batteries. To illustrate the chelation of sodium by these three glyme-ethers, DFT geometry optimizations as well as classical molecular dynamics (MD) simulations were performed.
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Figure 3. Detection of soluble superoxide species in different solvents by RRDE. Increasing ring currents indicate higher solubility. RRDE experiments were performed using an Au/Au electrode in glyme-ethers: (a) DME, (b) DGME, and (c) TGME. Each solution contained 0.5 M NaTFSi as conductive salt. The anodic ring current is shown as a negative value for comparison.

Figure 4 shows both the DFT-optimized structures and representative snapshots of the MD simulations. To get an insight into the way the solvents chelate Na⁺ cations, we analyzed radial distribution functions (RDF) and coordination numbers of the oxygen atoms around the Na⁺. These magnitudes are obtained by averaging in space and time the atomic positions during the MD simulations. The RDF represents the probability of finding an atom at a given distance of the central atom, while the spherical integration of the RDF gives the average number of atoms that surround the central atom, usually called coordination number. The MD simulations show a clear first coordination peak reflecting the strong interaction between Na⁺ cations and the O atoms of the ethers (Figure S9). The positions of the peaks are close to the distances found in the DFT optimized geometries (Figure 4a–c), except for TGME, where the Na–O distance appears underestimated, possibly due to limitations of the force field used. The height and position of the peaks show that solvation is much more intense in TGME than in DGME and DME (Figure S9). The coordination number exhibits a clear plateau (first coordination sphere) at intermediate distances (3−4 Å), corresponding to 6, 6, and 5 oxygen atoms for DME, DGME, and TGME, respectively. This indicates that 3, 2, and 1 ether molecules strongly solvate the Na⁺ cation in each of these cases. This observation is confirmed by the representative snapshots obtained from the MD simulations in Figure 4, where one can see a top view of how DME (a), DGME (b), and TGME (c) molecules coordinate to Na⁺ cations, by interaction with the oxygen atoms from the ether chain. Atoms at distances closer than 4 Å have been highlighted to show how the ether molecules organize around the Na⁺ cation. The fact that oxygen atoms of the same ether molecule are responsible for the formation of the first coordination sphere in TGME Figure 4c appears to be related with the stronger solvation found for this system in comparison with the two other systems. In Figure 4d–f a more realistic solvation of Na⁺ by 3, 2, and 1 ether molecules is shown (using a total number of 64 solvent molecules). The resulting increase in solvation strength upon an increase of the size of the solvating molecule DME < DGME < TGME strongly influences the solubility of NaO₂, explaining the RRDE results in Figure 3. Therefore, in addition to the expected enthalpy contribution represented by the DN/AN common to all aprotic solvents, the introduction of chelation to the overall solvation influences the entropy of solvation. The fact that one TGME molecule is sufficient to solvate Na⁺ results in a lower entropy penalty during the solvation process, leading to a higher overall NaO₂ solvation energy.

These results raise the question of how the chelation of the Na⁺ influences the discharge in the battery. Within the context of the scientific understanding developed for the Li–O₂ system, these results may indicate that a greater discharge capacity would be obtained when using TGME for the Na–O₂ system, because the higher solubility should prevent premature electrode blockage. However, at this point it is important to recall that the chemical disproportionation to peroxide is not favored for the Na–O₂ system; therefore, stabilization of NaO₂ in solution (solubility) might not be the determining parameter for this system.

Indeed, our study implies that the small amount of soluble NaO₂ species (10⁻⁵ mmol) in ethers is sufficiently large to allow for a solution-mediated growth of NaO₂ during discharge. The high capacities obtained for DGME and DME...
unambiguously demonstrate that the present understanding is not sufficient to explain the NaO\textsubscript{2} formation mechanism. We herein propose, based on our experimental findings, that the limiting steps governing the discharge product formation in DME, DGME, and TGME are different. For Na–O\textsubscript{2} batteries, several groups have shown that the mechanism of NaO\textsubscript{2} growth follows a solution precipitation route, where O\textsubscript{2}\textsuperscript{−} is solvated after reduction on the electrode and precipitates upon saturation as large cubes on the electrode surface.\textsuperscript{15,20,21} Figure 5. Overview of oxygen reduction mechanism in glyme-ether solvents during discharge of a NaO\textsubscript{2} battery. When \( k_1 < k_2 \), large particles form in solution (as observed in DME). In comparison, when \( k_1 > k_2 \), surface films are formed because of saturation of the solution and confinement of NaO\textsubscript{2} onto the electrode surface (as observed in TGME).

Figure 5 shows a schematic for discharge via the solution mechanism containing the key steps in this process as previously reported. These include reduction of O\textsubscript{2} dissolution of NaO\textsubscript{2} in the liquid phase, and crystallization of NaO\textsubscript{2}, where solubility is deemed critical. Herein, we evolved this model and identified four key processes during the formation of NaO\textsubscript{2} that are associated with the \( k_\text{e-transfer} \), \( k_\text{solvation} \), \( k_\text{desolvation} \), and \( k_\text{nucleation/growth} \) rate constants, and these are shown in Figure 5. First, concerning the electron transfer (step 1 in Figure 5), we found a positive shift in the onset reduction potential of O\textsubscript{2} measured by cyclic voltammetry (CV) in the presence of Na\textsuperscript{+} when compared to free superoxide formed in TBA\textsuperscript{−}-containing solution (Figure S10). This shift is due to stabilization of the O\textsubscript{2} by Na\textsuperscript{+} and underlines the interaction of the superoxide with Na\textsuperscript{+} cations during reduction. The second step (step 2, Figure 5) describes the equilibrium existing between NaO\textsubscript{2} on the electrode surface and solvated NaO\textsubscript{2}. The herein performed RRDE and UV–vis measurements (Figure 3 and Figure S8) show solubilities in the range of \( 10^{-4} \)–\( 10^{-5} \) mol/L for glyme-ethers. However, the exact nature of the solvated NaO\textsubscript{2} is strongly dependent on the solvent. The final two steps describe the desolvation of species in solution before nucleation and growth of NaO\textsubscript{2} particles (steps 3 and 4 in Figure 5, respectively).

At this point it is worth recalling the fact that NaO\textsubscript{2} is the main product found for dry Na–O\textsubscript{2} systems, whereas Li\textsubscript{2}O\textsubscript{2} is formed for the lithium system. This is crucial because the superoxo and peroxo products have very different solubilities. This fact leads to profoundly different discharge mechanisms. In the lithium system, the stabilization (solvation) of the LiO\textsubscript{2} intermediate is key to delaying the disproportionation to Li\textsubscript{2}O\textsubscript{2} and the immediate blockage of the electrode by quasi insoluble and insulating Li\textsubscript{2}O\textsubscript{2}. The crystallization of large particles via solution precipitation can be achieved only by the use of high DN solvents, again making the dissolution the key process for efficient Li–O\textsubscript{2} batteries. In the Na–O\textsubscript{2} system, however, the NaO\textsubscript{2} is rather stable in solution (no disproportionation to Na\textsubscript{2}O\textsubscript{2}). The above-described results clearly demonstrate that even low-DN solvents sufficiently solvate the NaO\textsubscript{2}, which can then slowly saturate the solution and recrystallize as large cubes on the electrode surface. When the solvent is saturated with NaO\textsubscript{2}, to maintain an equilibrium of solute \( k_\text{solvation} \) has to be faster than the formation of NaO\textsubscript{2} (\( k_\text{e-transfer} \)). If the desolvation energy barrier is increased, no further product can be dissolved and the quasi-equilibrium between formation and solvation is shifted toward surface confinement of the NaO\textsubscript{2}. Therefore, we propose that a low desolvation energy barrier is vital for a successful solution precipitation of NaO\textsubscript{2} to achieve large capacities. We further postulate that in the case of TGME, the strong solvent–solute interaction is much increased compared to DME, leading to an increased activation barrier for desolvation (inset in Figure 5) resulting in hindered growth via solution precipitation.

In the following section we investigate the influence of the solvent on Na\textsuperscript{+} solvation. In a first step the effect of the anionic species toward the solvated/chelated Na\textsuperscript{+} cations in solution was explored. In general, the equilibrium describing the interaction between cation and anion can simply be written as \( M_x^+ + X_y \leftrightarrow (MX)_z \), where M represents the alkali metal cation and X a Lewis base; S indicates a solvated species. Strongly solvated cations have minor direct interaction with anionic species in solution, and the equilibrium lies on the left...
(see TGME solvation in Figure 5). On the other hand, for weakly solvated cations the equilibrium is shifted toward the right, where the formation of contact ion pairs is favored (see DME solvation in Figure 5). The formation of strong contact ion pairs was probed by $^{23}\text{Na}$ NMR. For DME, the chemical shift of Na$^+$ is greatly influenced (more than 2 ppm) by the nature of the anion (ClO$_4^-$, PF$_6^-$, TFSi$^-$, and OTf$^-$), indicating a strong interaction of Na$^+$ with the anion Lewis base (Figure 6). For TGME, no clear influence of the anion and hence no contact ion pair was observed, while DGME shows an intermediate behavior.

TGME. This is also supported by the RRDE data that showed larger amounts of soluble superoxide species in TGME when compared to DME (Figure 3). Although the RRDE does not directly identify contact ion pair formation, the relative solubility of a salt is related to this process, where a propensity to form ion pairs generally mirrors decreasing solubility.

To further evidence the different solvent–solute interaction strength, the lifetime of the Na$^+$–solvent complexes was analyzed. In a first step, the full width at half-maximum (fwhm) values of the $^{23}\text{Na}$-NMR peak in Figure 6 were compared. One can observe a significant (5-fold) broadening when changing from DME to TGME as solvent. This broadening can be explained partially by the higher viscosity and by the decreased ligand-exchange rate of TGME. Indeed, the ligand exchange rate is directly related to the stability of the Na$^+$ solvent complex. The ligand exchange rates of Li$^+$–TGME were found to be 100 times slower$^{34}$ than for DME, demonstrating the drastic differences in Na$^+$–solvent complex stabilities among these solvent systems. Moreover, the ratio of $D_{\text{sol}}/D_{\text{Na+}}$, herein further referred to as the self-diffusion coefficient ratio of Na$^+$ (SDCR), is an effective metric to determine the strength of the Na$^+$–solvent complex in solution. Therefore, the diffusion coefficients for Na$^+$ ($^{23}\text{Na}$) and solvent ($^1\text{H}$) were determined by pulsed field gradient stimulated-echo (PGSE) NMR measurements (Table S1). A ratio close to unity results from the linked diffusion of Na$^+$ with the solvent molecules, indicating a strong solvent–solute complex.

However, because PGSE gives an average of all, free, and coordinated solvent molecules for organic solvents with low concentrations of conductive salt, the solvent molecules are always in excess, and the SDCR is therefore always greater than 1. The increasing SDCR values found for DME (2.47) > DGME (1.97) > TGME (1.8) indicate a stronger solvent–solute complex formation with increasing ether chain-length, in good agreement with the aforementioned results. In summary, the strong solvation of Na$^+$ in long glyme-ethers prevents the formation of contact ion pairs with Lewis bases. These results demonstrate that for glyme-ether solvents, increasing the chain length not only decreases the mass transport of the solute throughout the solvent but also increases the free-energy barrier.
for desolvation, which will decrease the rate of ion desolvation and therefore hinder particle nucleation and growth. In light of these findings, the effect of solvent chain length on the Na−O2 battery performances shown in Figure 1 can be explained as follows. We consider a model where the dissolved NaO2 concentration in solution is in equilibrium with the solid NaO2 (this condition will be satisfied during the majority of discharge, but may not be at early times). As the electrolyte is saturated with NaO2, any electrochemically formed NaO2(sol) can dissolve only if an equivalent amount of NaO2(sol) desolvates and forms or grows a particle elsewhere.

If the rate of these two processes is equivalent, the majority of the electrode surface will remain clear, large amounts of charge will be passed through the electrode surface, and NaO2 can grow via the suggested solution route (high capacity and large particles).15,20,21 When NaO2 formed at the electrode surface can no longer dissolve, the product will be confined to the electrode surface and the discharge will then be dominated by a surface mechanism. Even though the conductivity of NaO2 is expected not to be negligible and higher than for Li2O2,35 others have shown that the formation of this insulating NaO2 layer will eventually lead to limited reduction of O2 and therefore to the end of the discharge with limited capacity, explaining the results in Figure 1.16 In practice, all of these processes are in a dynamic equilibrium. Regarding our results, we propose that for DME the rate-determining step is indeed the reduction of O2 because the lower desolvation barrier as explained as follows. We consider a model where the dissolved NaO2 concentration in solution is in equilibrium with the solid NaO2 (this condition will be satisfied during the majority of discharge, but may not be at early times). As the electrolyte is saturated with NaO2, any electrochemically formed NaO2(sol) can dissolve only if an equivalent amount of NaO2(sol) desolvates and forms or grows a particle elsewhere.

Two conclusions summarize our results. First, we confirm that the most relevant indicator to achieve high discharge capacities in these systems is a moderate solvent–solute interaction allowing for contact-ion pair formation, which appears to be crucial for the growth of NaO2 crystals. Several further studies to the present work are immediately apparent. In particular, an improved electrolyte formulation could maximize the discharge capacities by adjusting the delicate balance of solubility and solvation.
necked round-bottom flask. The disc potential was scanned at a speed of 20 mV/s. The ring potential was kept at 0 V vs. Ag+/AgCl. During RRDE measurements a rotation speed of 1000 rpm was applied to the working electrode.

**Cell Assembly and Electrochemical Measurements.**

Na–O₂ cells were built from a modified Swagelok setup. The Swagelok cell was connected to a pressure monitor to analyze pressure changes during cycling. The cell was vacuum-dried under elevated temperature and transferred into a glovebox (0.1 ppm of H₂O, 0.1 ppm of O₂). The anode was made from metallic sodium (Sigma-Aldrich) cut into a 0.5 cm² disc. Dried electrolyte solution (0.5 M NaOTf in DME, DGME, and TGME) was imbibed on two Whatman glass filter papers (QMA grade) (dried under vacuum at 260 °C, 8 h), about 0.3 mL. A piece of GDL (1.13 cm² surface area, 210 µm thick, with a weight of 10 mg) was used as cathode and held by an aluminum current collector containing holes for gas exchange. The assembled cells were transferred from the glovebox to a filling station, and after a first evacuating step, the cells were pressurized with dry, ultrapure O₂ to 1.3 bar. To guarantee stable temperature conditions, the cells were mounted inside a temperature-controlled incubator (25.0 ± 0.1 °C). The electrochemical measurements were performed under temperature-controlled conditions (25.0 °C) after resting for 4 h at the open-circuit voltage and using a Bio-Logic VMP3 potentiostat. Pressure analysis decay analysis and e⁻/O₂ ratios were calculated as described elsewhere.¹⁷

**Scanning Electron Microscopy.** Samples were washed with dried DME prior to SEM imaging. All samples were transferred by means of a hermetic transfer chamber to avoid exposure to ambient air. SEM images were acquired on a FEI Magellan 400 XHR microscope equipped with a FEG source. An Oxford Instruments Energy Dispersive X-ray (EDX) spectroscopy system mounted on a Zeiss Merlin SEM was used for chemical composition analysis. The micrographs were obtained with a 5 kV voltage, and the EDX analysis was performed with an accelerating voltage of 5 kV.

**X-ray Diffraction.** Samples were washed with dried DME prior to XRD analysis. A Bruker D8 Advance diffractometer with a Cu Kα radiation source (λ₁ = 1.5405 Å, λ₂ = 1.5443 Å) and a LynxeyeXE detector was used to collect the XRD patterns. The XRD patterns were recorded for 30 min in the 2θ range of 20–65°. A special airtight cell with a beryllium window was used to guarantee no ambient air contamination during XRD measurements.

**UV–Vis Measurements.** Solvents were saturated with KO₂ by vigorous stirring for 1 h inside a glovebox (0.1 ppm H₂O, 0.1 ppm O₂). The mixtures were then left to rest for 12 h to prevent the detection of undissolved particles. A small fraction of the clear, upper part of the solution was taken out of the glovebox and allowed to react with an aqueous 1 M H₂SO₄ containing 2% TiOSO₄. UV–vis measurements were subsequently carried out at room temperature using a Thermo Scientific Evolution 220 UV-spectrometer.

**Raman Spectroscopy.** Raman spectra were recorded using a custom-built confocal Raman microscope with a 50× 0.45 NA objective (Nikon). The Raman system was equipped with a 785 nm diode laser (Sacher Lasertechnik) and a spectrometer (Shamrock SR-303i, Andor Technology) which employed a 400 lines/mm grating, blazed at 850 nm and was equipped with a deep depletion, back-illuminated, and thermoelectrically cooled CCD camera (Newton, Andor Technology) for the detection of the Raman signal.

²³Na NMR Measurements. The ²³Na-containing solutions were placed in 4 or 8 mm NMR tubes in an argon glovebox, closed tightly with caps and Teflon film. The measurements were performed under N₂ atmosphere to avoid moisture and oxygen contamination. The spectra were acquired on a 4.7 T Avance III HD Bruker spectrometer (²³Na frequency of 52.9 MHz) at room temperature. The ²³Na spectra were obtained using a simple pulse. Sixty-four transients were accumulated for each sample, and a repetition time of 4 s was used for complete relaxation. All spectra were referenced to a 1 mol/L aqueous solution of NaCl at 0 ppm.

²³Na and ¹H NMR Diffusion Coefficients Determination. The self-diffusion coefficient measurements were performed using a 9.4 T Avance I Bruker spectrometer (¹H and ²³Na Larmor frequencies of 400.13 and 105.8 MHz, respectively) with Dif30 Bruker probe, delivering pulsed field gradients up to 1200 G/cm. The sealed samples (8 mm NMR tube) were centered in the 10 mm ¹H or ²³Na coil. The pulsed field gradient stimulated-echo (STE) was chosen for the samples having short relaxation times T₁. The STE combined with ramped bipolar pulse pair longitudinal eddy current delay (BPP-LED) sequence was applied in diffusometry measurement. The length of effective gradients ranges from 1.6 to 3.0 ms, and the diffusion times are in the range of 2–40 ms. Gradient steps were optimized to get proper signal attenuations, namely, from 10 to 300 G/cm for the samples relaxing relatively slowly and 10 to 1000 G/cm for the fast-relaxing samples (such as the salt in TGME with T₁ of 2.5 ms). All measurements were carried out at 298 K.

**Conductivity Measurements.** All conductivity measurements were carried out using a Metler Toledo SevenCompact S230 conductivity meter inside an argon-filled glovebox (0.1 ppm of H₂O, 0.1 ppm of O₂).

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b07659. Please find Oxford University Research Archive (ORA) deposit at DOI: 10.5287/bodleian:eyKvDJmM0.

Donor number evaluation of solvents, additional discharge plots to show reproducibility, cyclic voltammetry, and further analysis of discharge products (PDF)

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Notes

The authors declare no competing financial interest.

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