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Novel DMSO-based electrolyte for high performance rechargeable Li–O$_2$ batteries†

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A dimethyl sulfoxide (DMSO) based electrolyte is first proposed for rechargeable lithium–O$_2$ (Li–O$_2$) batteries. Superior battery performances, including high discharge capacity and low charge potential, are successfully obtained.

Non-aqueous lithium–oxygen/air batteries have great potential for electric vehicles and renewable energy storage due to their extremely high energy density (11140 kW kg^{-1}), which is 5–10 times that of conventional lithium-ion batteries.[1,2] Prototype Li–O$_2$ batteries typically consist of a metal Li anode, a porous O$_2$ diffusion cathode and an organic electrolyte. During discharge, oxygen is first reduced to superoxide (O$_2^-$) and is supposed to react with Li$^+$ to form the unstable intermediate lithium superoxide (LiO$_2$) followed by disproportion into principal reversible discharge product lithium peroxide (Li$_2$O$_2$) (overall reaction: 2Li$^+$ + O$_2$ + 2e$^-$ ↔ Li$_2$O$_2$).[3] Up to now, although much progress has been achieved, Li–O$_2$ batteries are still in their infancy and great improvements are urgently needed, with the top of the list being cathodes and electrolytes. In particular, P. G. Bruce and other researchers have demonstrated that decomposition of the electrolyte caused by very active intermediates (O$_2^-$, LiO$_2$ and so on) should carry most of the blame for the terrible reversibility and cycle life of Li–O$_2$ batteries.[4] Therefore, development of a novel electrolyte by investigating its behaviours under O$_2$/O$_2^-$ environments and further studying the electrochemical products and reversibility in Li–O$_2$ batteries are highly important.

An ideal electrolyte for non-aqueous Li–O$_2$ batteries should hold low volatility, high oxygen solubility, and especially, be inert to superoxide radicals. However, none of the reported electrolytes can completely meet these requirements.[5] For example, carbonates such as propylenecarbonate (PC), ethylene carbonate, and dimethyl carbonate, are commonly used as solvent for Li–O$_2$ batteries in the early stages due to their high boiling point (B.P.) and considerable ion conductivity. However, Li–O$_2$ batteries with carbonate based electrolyte always suffer from insufficient capacity ($\sim$3000 mAh g^{-1}), high charge potential ($\geq$ 4.4 V) as well as low energy efficiency ($<$60%).[4a] And even more worse is that they are seriously subjected to nucleophilic attack at the carbonyl carbon and hydrogen abstraction at O-alkyl carbon that inevitably produces unwanted lithium carbonate (Li$_2$CO$_3$) and a variety of other organic lithium salts, which leads to the poor reversibility of the battery.[4a,6] Comparing to carbonates, esters, such as dimethoxyethane (DME), 1,3-dioxolane, and tetraethylene glycol dimethyl ether (TEGDME), have received more attention due to their high oxygen solubility and especially increased stability against O$_2^-$ (Li$_2$O$_2$ can be found in discharge products). Batteries with ester based electrolytes also show satisfactory capacity ($\sim$7000 mAh g^{-1}) and high coulombic efficiency (up to 95%). However, they are still not completely unreactive to O$_2^-$ due to the existence of electronegative –O– groups, resulting in minor formate, acetate, and polyester by-products.[7] In addition, ester based electrolytes are often plagued by the high volatility (DME) or high viscosity (TEGDME), which is a disadvantage to cycle life and rate performance of Li–O$_2$ batteries. Acetonitrile, another often mentioned stable solvent, although holds good physicochemical properties, still reacts with lithium metal and thus cannot be used in Li–O$_2$ batteries. DMSO, as a universal solvent, possesses favourable advantageous, including low volatility (B.P. 189 °C) and viscosity (1.948 cP), good oxygen diffusion ability, high conductivity (2.11 mS cm^{-1}) containing Li$^+$ salts, and especially, remarkable stability against superoxides.[8] Thereafter, it is highly desirable but still unexplored to investigate the electrochemical behaviours of DMSO in Li$^+$ containing environments and further evaluate its performance in Li–O$_2$ batteries.

Herein, we first employ DMSO as an electrolyte solvent and evaluate its performance in Li–O$_2$ batteries. Interestingly, with this novel electrolyte and common KB carbon based cathode, a high capacity of 9400 mAh g^{-1} and reversibility can be achieved. Furthermore, when we employ a special porous graphene oxide-derived carbon cathode, an improved capacity (10 600 mAh g^{-1}), cycle performance, and significantly reduced charge potential ($\sim$3.7 V) are observed, indicating the feasibly of DMSO as solvent in Li–O$_2$ batteries, which is further confirmed by the existence of Li$_2$O$_2$ in the discharged electrode.

Basic electrochemical properties of DMSO with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) as a lithium salt were firstly investigated. As shown in Fig. S1, ESI,† a wide

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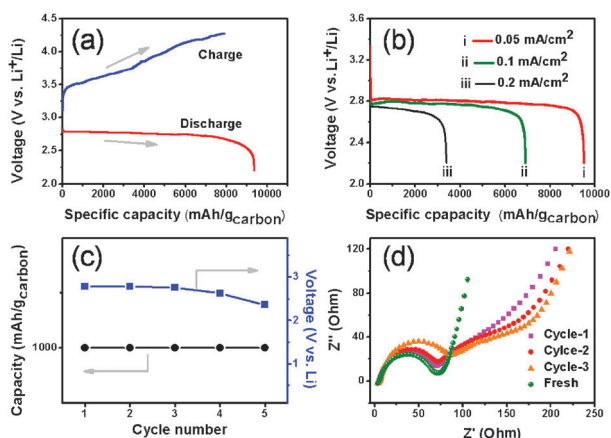
Fig. 1 (a) Discharge and charge curves of Li–O$_2$ batteries under 0.05 mA cm^{-2} and 1 atm O$_2$ pressure; (b) discharge capacity under different current densities; (c) cycle voltage *versus* cycle number by controlling discharge depth at 0.1 mA cm^{-2}; (d) electrochemical impedance spectra of the batteries according to (c) after each cycle.

electrochemical window from 2.0 to 4.5 V *versus* Li$^+$/Li (Fig. S1a†) can be obtained, which is electrochemically stable enough as an electrolyte for Li–O$_2$ batteries. Furthermore, cyclic voltammogram under an O$_2$ atmosphere (Fig. S1b†) indicates that the reaction (O$_2$/O$_2^-$) in a DMSO based electrolyte is quite active and reversible. Combining with its other favourable advantages mentioned above (parameters in detail are shown in Fig. S2–3, ESI†), DMSO can be considered as a promising solvent candidate for Li–O$_2$ batteries.

The performance of LiTFSI/DMSO as solvent in Li–O$_2$ batteries is shown in Fig. 1. The first discharge and charge curves of Li–O$_2$ batteries with a KB carbon based cathode are displayed in Fig. 1a, a high discharge voltage plateau (2.80 V) is observed, which is very close to the theoretical value (2.90–3.10 V) of formation of Li$_2$O$_2$, it is also much higher than that with PC (2.65 V) and TEGDME (2.70 V) based electrolytes (Fig. 2a). Furthermore, a high discharge capacity of about 9400 mAh g^{-1} is successfully obtained, which is extremely unprecedented when considering no catalyst is used in the oxygen cathode. It is speculated that the strong ability of DMSO to dissolve oxygen and Li$^+$ salts could promote the reaction in the triple phase boundary. Moreover, the molecular size of DMSO is relatively small and thus may benefit the penetration of the electrolyte into the micropores and improve the efficiency of the pores in the cathode.

The rate capability is shown in Fig. 1b. Although capacities decrease with increasing current density, the Li–O$_2$ batteries with DMSO show much higher capacity than that of TEGDME and
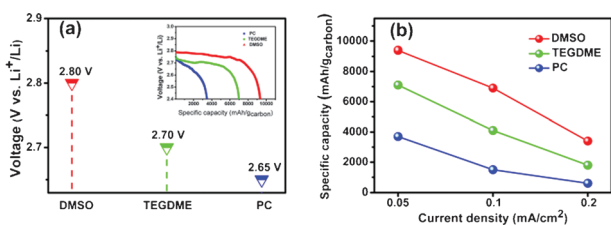
PC under all investigated current densities (Fig. 2b), which might be attributed to the high ion conductivity as well as good oxygen dynamic properties of the DMSO based electrolyte. Furthermore, by controlling discharge depth (1000 mAh g^{-1}), we then investigated the reversibility of the electrochemical reaction in Li–O$_2$ batteries with a DMSO based electrolyte. As shown in Fig. 1c, there is no serious discharge voltage decrease during the first 3 cycles, indicating an acceptable charge–discharge reversibility and stability, which is further confirmed by the electrochemical impedance spectrum (Fig. 1d) wherein resistance of the battery after charge recovery is very good and is comparable to that of the fresh battery (70 Ω). It is considered that the low volatility and stability of DMSO contributes the most to the good discharge–charge behaviour.

In order to further validate the reversible electrochemical process, XRD is utilized to analyze the composition of the discharge products. The diffraction peaks (2θ = 32.9°, 35.0°, 40.6°, 58.7°) shown in Fig. S7, ESI† clearly reveals that Li$_2$O$_2$ forms during discharge. Meanwhile, lithium hydroxide (LiOH) is also detected as a reasonable by-product. Fortunately, it is also an active material that can be recharged for Li–O$_2$ batteries. Therefore, these batteries still show high reversibility although accompanied with side reactions. The XRD profile of the recharged cathode was analyzed and shows that all the discharge products can be fully decomposed, which further confirms the reversibility. Moreover, the above obtained electrochemical impedance spectrum and cycle results are also vigorous proof that support the findings (Fig. 1c and d). SEM images of the O$_2$ electrode after discharge and charge are also investigated. Fig. 3a exhibits densely arranged products on the porous carbon electrode, suggesting the thoroughness of discharge in the DMSO based electrolyte, which is in accordance with a high discharge capacity. The inlet indicates that spherical crystalline discharge products with diameters in the range of 400–600 nm dominate, which exhibits similar morphology to toroids of earlier reported Li$_2$O$_2$.[3e] Meanwhile, some flakes are simultaneously found which may be attributed to LiOH lamellar structure. The O$_2$ electrode after charging is shown in Fig. 3b. The porous carbon framework is recovered after recharge, implying a complete decomposition of the discharge products, which further confirms the good reversibility of Li–O$_2$ batteries with a DMSO based electrolyte.

Inspired by the interesting properties and encouraging results obtained above, we then tried to further exploit the potential of DMSO as a solvent for high performance Li–O$_2$ batteries. In fact, commercial KB carbon electrodes restrict electrolyte performance as it lacks open and continuous 3D channels for gas and liquid mass. Therefore, we employed a
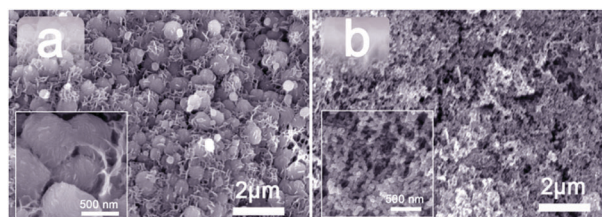

Fig. 2 Performance of Li–O$_2$ batteries with different electrolytes using KB carbon cathodes: (a) discharge voltage plateau; (b) rate capacity.

Fig. 3 SEM images with different magnification of O$_2$ electrode after discharge (a) and charge (b) under 0.05 mA cm^{-2} current density.
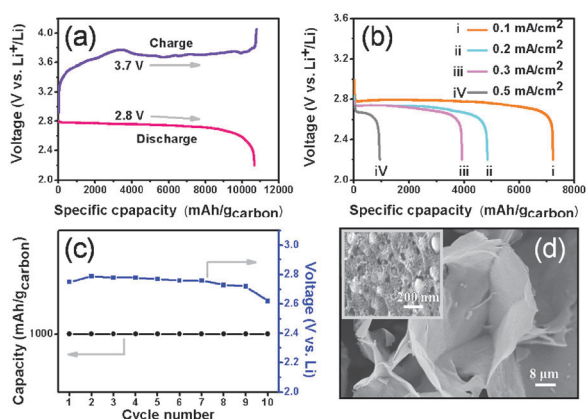
Fig. 4 (a) Discharge and charge curves under 0.05 mA cm^{-2} and 2 atm O$_2$ pressure; (b) rate capacities under different current densities; (c) cycle performance by controlling discharge depth under 0.1 mA cm^{-2}; (d) structure of novel graphene oxide-derived carbon cathode.

novel hierarchically porous graphene oxide-derived carbon cathode to explore the maximum performance of Li–O$_2$ batteries with a DMSO based electrolyte. The novel graphene oxide-derived carbon electrode shown in Fig. 4d is prepared by an *in situ* sol–gel method as described in the ESI.†[9] As shown in Fig. 4a, a higher discharge capacity of 10 600 mAh g^{-1} is obtained and more importantly, voltage polarization during recharge is suppressed remarkably with a voltage plateau of only 3.7 V. Furthermore, Li–O$_2$ batteries exhibit a high capacity of 7200 and 3900 mAh g^{-1} at 0.1 and 0.3 mA cm^{-2} respectively, indicating a good rate capability. Improved cycle performance is also achieved by combining with an optimized cathode. By restricting discharge depth to 1000 mAh g^{-1} at 0.1 mA cm^{-2}, the Li–O$_2$ batteries show a stable cycle performance for 10 cycles as shown in Fig. 4c. All of these results further confirm the feasibility and efficiency of DMSO for high performance Li–O$_2$ batteries.

In summary, we first propose and then demonstrate a novel DMSO based electrolyte for rechargeable Li–O$_2$ batteries. Interestingly, superior performances including good rate performance, especially high discharge capacity and low charge potential with an optimized cathode are successfully obtained. Furthermore, the formation of Li$_2$O$_2$ and its reversibility is confirmed. The obtained promising results are believed to open new and exciting possibilities to promote the development of rechargeable Li–O$_2$ batteries.

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