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A stable sulfone based electrolyte for high performance rechargeable Li–O$_2$ batteries†

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A tetramethylene sulfone based electrolyte was used in rechargeable Li–O$_2$ batteries for the first time. Without a catalyst, superior battery performances were successfully obtained, and desired lithium peroxide (Li$_2$O$_2$) dominates the discharge product.

Rechargeable lithium–O$_2$ batteries are the subject of significant interest because of their extremely high energy density.[1] A typical rechargeable non-aqueous Li–O$_2$ cell is composed of a Li metal anode, a non-aqueous Li$^+$ conducting electrolyte, and a porous cathode. During discharge, oxygen is first reduced to superoxide (O$_2^−$) and supposed to react with Li$^+$ to form unstable intermediate lithium superoxide (LiO$_2$), followed by disproportion into the principal reversible discharge product, lithium peroxide (Li$_2$O$_2$) (overall reaction: $2Li^+ + O_2 + 2e^− \leftrightarrow Li_2O_2$). Until now, although much progress has been made, Li–O$_2$ batteries are still in their infancy and great improvements are urgently needed, with the top of the list being the cathode and especially the electrolyte.[2]

An ideal electrolyte for non-aqueous Li–O$_2$ batteries should possess many important physicochemical properties, including low volatility, high oxygen solubility, and in particular, to ensure repeated and highly reversible formation and decomposition of Li$_2$O$_2$ on cycling. However, none of the reported electrolytes can completely meet these requirements.[3a] For example, early investigations of non-aqueous Li–O$_2$ cells focused on the use of organic carbonate based electrolytes due to their high boiling point and ion conductivity. Unfortunately, Li–O$_2$ batteries with carbonate based electrolytes suffer from insufficient capacity, high charge potential, low energy efficiency, and irreversible decomposition at the cathode on discharge to form unwanted products such as lithium carbonate (Li$_2$CO$_3$) and other organic lithium salts with little or none of the desired product (Li$_2$O$_2$).[3b–e] Later research turned to studying ethers such as dimethoxy ethane (DME), 1,3-dioxolane, and tetraethylene glycol dimethyl ether (TEGDME) as electrolytes.

Although Li$_2$O$_2$ was shown to be dominant product, especially with a TEGDME based electrolyte, electrolyte decomposition on cycling still could be not absolutely excluded.[4] In addition, ether electrolytes are often plagued by high volatility (DME) and/or high viscosity (TEGDME), which might limit the cycle life and/or rate performance of Li–O$_2$ batteries. Up to now, although the detailed mechanism of electrolyte decomposition during the processes that occur on discharge and subsequent charge is still not absolutely clear, it is beyond doubt that the very active intermediates (O$_2^−$, LiO$_2$, *etc.*) should be blamed most for the poor reversibility and cycle life of Li–O$_2$ batteries. Therefore, development of novel electrolytes by investigating their behaviour in an O$_2$/O$_2^−$ environment and further studying the electrochemical products and reversibility in Li–O$_2$ batteries is urgently important.

To this end, we have recently studied the electrochemical performance a of dimethyl sulfoxide (DMSO) based electrolyte in Li–O$_2$ batteries. Interestingly, with this novel electrolyte and a common carbon cathode, high capacity and good reversibility were obtained.[5a] Very recently, Bruce *et al.* further improved the performance of Li–O$_2$ batteries with DMSO by using porous Au as the cathode.[5b] Although DMSO has been shown to be a powerful solvent for Li–O$_2$ batteries, it is still unsatisfactory when considering that the formation of Li$_2$O$_2$ is still accompanied by unwanted by-products when carbon is employed as the cathode material.[5a] This led us to further consider why DMSO can stabilize O$_2^−$ but not enough for Li$_2$O$_2$, and whether there are other solvents that inherit the advantages of DMSO and also support more robust Li$_2$O$_2$ formation.

Tetramethylene sulfone (TMS), as a universal dipolar solvent, is a kind of sulfone which has the oxidation state of sulfoxide. Besides high solubility, low toxicity, superior safety as well as sufficient ion dynamics,[6] TMS also has superior properties to DMSO, including much lower volatility and higher resistance to electrochemical oxidation (Table S1, ESI†).[7] Therefore, TMS possesses many desirable properties but its electrochemical behaviour in a Li$^+$ containing environment and its performance in Li–O$_2$ batteries remains unexplored.

Herein, we employed TMS as a novel electrolyte solvent and evaluated its performance in Li–O$_2$ batteries. Interestingly, superior performances including high capacity, good reversibility and rate performance were achieved, and the performance could be improved by using an optimized graphene

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† Electronic supplementary information (ESI) available: Experimental details and supplementary figures. See DOI: 10.1039/c2cc36815c
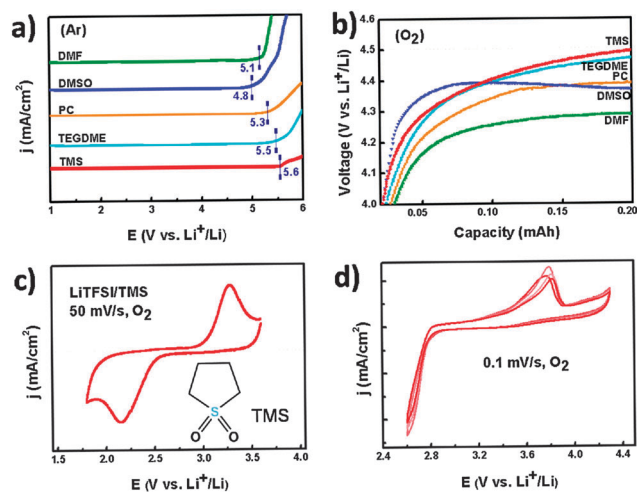
Fig. 1 (a) Electrochemical windows of solvents commonly used in Li–O_2 batteries. (b) Decomposition voltage of solvents in a Li–O_2 battery under an O_2 atmosphere. (c) CV curve of 1 M LiTFSI/TMS electrolyte saturated with O_2. (d) CV curves of a Li–O_2 battery with a TMS based electrolyte.

Fig. 2 Li–O_2 battery performance at room temperature under 1 atm O_2 atmosphere. (a) First discharge/charge curve at a current density of 0.1 mA cm^{-2}, (b) rate capability, and (c) gravimetric energy and power density. (d) Discharge/charge curve of a Li–air battery under a current density of 0.2 mA cm^{-2}. (e) Cycle stability of Li–O_2 batteries with a KB carbon cathode and (f) with an optimized cathode.

oxide derived carbon cathode. Furthermore, Li_2O_2 was confirmed to be the dominant discharge product.

The basic electrochemical properties of common electrolytes used in Li–O_2 batteries were firstly investigated. As clearly shown in Fig. 1a, under an Ar atmosphere, the oxidation potentials were found to be 5.3, 5.5, 5.1, 4.8, and 5.6 V versus Li$^+$/Li for PC, TEGDME, DMF, DMSO, and TMS, respectively, indicating that their electrochemical stability increases following the order of DMSO < DMF < PC < TEGDME < TMS. This demonstrates that TMS possesses the highest resistance toward electrooxidation. It is well known that an electrolyte for a Li–O_2 battery should endure high overpotential during charge and thus superior antioxidant ability is a prerequisite to obtain a stable Li–O_2 battery. Therefore, based on the above results we can reasonably expect that a Li–O_2 battery with TMS could have the best stability under an oxygen atmosphere. To confirm this point, the decomposition voltages of the solvents were examined in a Li–O_2 battery during charge without the previous discharge process. As shown in Fig. 1b, the stability decreases with a sequence similar to that of the electrochemical window (TMS > TEGDME > PC > DMSO > DMF). TMS shows the best stability (no decomposition until 4.5 V), illustrating the favourability of TMS as a stable solvent for Li–O_2 batteries.

The reversibility of electrochemical reactions in the TMS based electrolyte saturated with O_2 was then investigated. Only one pair of well-defined reduction/oxidation peaks could be found (Fig. 1c), which can be attributed to the reversible formation/decomposition of Li_2O_2. This result is consistent with the CV curves of Li–O_2 cells with a TMS based electrolyte (Fig. 1d).

Fig. 2a shows the first discharge and charge curves of Li–O_2 batteries with a KB carbon based cathode. It was found that the discharge voltage plateau is 2.7 V and the specific capacity is 7735 and 6305 mAh g^{-1} for the discharge and charge processes at a current density of 0.1 mA cm^{-2} respectively, corresponding to a high round-trip efficiency of 81.5%.
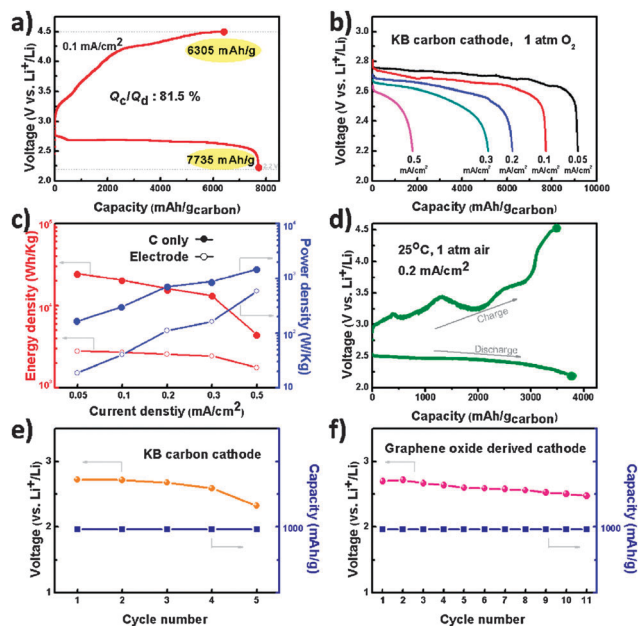
The rate capacity demonstrated in Fig. 2b indicates that an even higher capacity of 9100 mAh g^{-1} is obtained at a lower current density of 0.05 mA cm^{-2}. Although the discharge capacity decreases with increasing current density, the Li–O_2 battery with TMS still shows a high capacity of 1700 mAh g^{-1} at a high current density of 0.5 mA cm^{-2}. Fig. 2c shows the energy and power density of a Li–O_2 battery with a TMS based electrolyte and a KB carbon cathode. Interestingly, it was found that the energy density reaches up to 24 679 W h kg^{-1} by carbon weight and 2790 W h kg^{-1} by whole weight of the electrode (C + PVDF + Li_2O_2). The electrochemical performances obtained are much higher than those of the most advanced Li ion battery,[8a] and are quite impressive for a Li–O_2 battery with a carbon based cathode (without catalysts).[3b,5b]

The electrochemical performance of the TMS based electrolyte in a Li–air battery was also investigated (Fig. 2d), and although the O_2 partial pressure decreases significantly in air, a high capacity of 3700 mAh g^{-1} was still obtained. It should be noted that compared to a Li–O_2 battery, the charge profile of the Li–air battery is quite complicated, which might be due to complex reactions caused by CO_2 and H_2O in the air.

The cycle performance was evaluated by controlling discharge depth to 1000 mAh g^{-1}. As shown in Fig. 2e and S2 (ESI†), a Li–O_2 battery with a TMS based electrolyte can keep 5 cycles on a conventional KB carbon cathode, which is similar to those observed for TEGDME and DMSO based electrolytes using the same cell technology. It should be noted that after substituting the KB carbon cathode with an advanced graphene oxide derived cathode,[8b] cycle performance improved significantly (Fig. 2f and S3, ESI†), which might indicate that the poor quality of the O_2 electrode,
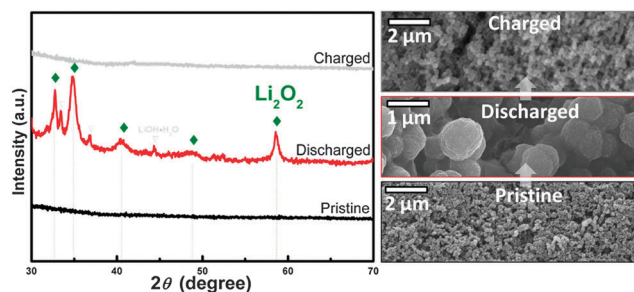
Fig. 3 XRD profiles and SEM images of pristine, discharged, and recharged O_2 electrode of a Li–O_2 battery with a TMS based electrolyte.

and not the solvent itself, should be mainly responsible for the limited cycle life of the Li–O_2 battery. These facts further support the feasibility of TMS as a solvent for Li–O_2 batteries, and we believe that the performance can be further improved by employing suitable combinations of electrolyte, cathode, and cell technology.[5b,8c]

The morphology of the O_2 electrode before and after discharge was then investigated using scanning electron microscopy (SEM). As shown in Fig. 3, after a deep discharge, the porous O_2 electrode is fully covered by a large number of spheres with a wide diameter dispersion (100 nm ∼ 1 μm). The powder X-ray diffraction (XRD) profile illustrates that the dominant product is well crystallized Li_2O_2. Meanwhile, a negligible amount of lithium hydroxide hydrate could also be detected as a by-product. After recharge, all of the crystallization peaks in the XRD profile disappear, indicating that the discharge products decompose thoroughly, which is consistent with the SEM image. Both SEM and XRD analysis indicate the good reversibility of Li–O_2 batteries with a TMS based electrolyte.

Now it is well considered that the formation and dominance of Li_2O_2 in the discharge product is critical to the operation of a Li–O_2 battery. Interestingly, the dominance of Li_2O_2 can easily be found in Li–O_2 batteries with a TMS based electrolyte (Fig. S4a and S4b, ESI†). On the other hand, besides Li_2O_2, a large amount of nanosheet-like LiOH is observed in Li–O_2 batteries with DMSO (Fig. S4c and S4d, ESI†), implying that there are fewer possible side reactions in a Li–O_2 battery with TMS compared to one with DMSO. The underlying mechanism might be related to the kinetics of superoxide and/or Li_2O_2-induced decomposition of solvent, PVDF, or C in the Li–O_2 battery, which can be greatly affected or controlled by the solvent (Fig. S5, ESI†).

Here, we firstly propose and demonstrate a novel TMS based electrolyte with attractive physicochemical properties for rechargeable Li–O_2 batteries. Interestingly, superior performances including high capacity, good round-trip efficiency and cycle life especially when combined with an optimized O_2 electrode were successfully obtained. The dominant discharge product in this novel electrolyte was confirmed to be the desired Li_2O_2. The promising results obtained are believed to open new and exciting possibilities to promote the development of rechargeable Li–O_2 batteries.

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