Volume 1 | Number 1 | Jan 2013 | Pages 1–100

ChemComm

Chemical Communications
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Organic radicals for the enhancement of oxygen reduction reaction in Li-O₂ batteries

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We examine for first time the ability of inert carbon free-radicals as soluble redox mediators to catalyze and enhance the oxygen reduction reaction in a TEGDME-based electrolyte. We demonstrate that the tris(2,4,6-trichlorophenyl)methyl (TTM) radical is capable of chemically favoring the oxygen reduction reaction improving significantly the Li-O₂ battery performance.

Aprotic Li-O₂ batteries are electrochemical storage devices that have been drawing high interest and large investments in the past few years, due to the high specific energy, safety and potential low cost compared to the conventional Li-ion batteries.[1-4] This is particularly relevant for automotive applications,[5] which are currently limited by the battery autonomy. However, the huge interest in Li–O₂ batteries has been frustrated by their poor reversibility[6] and cyclability.[7] In effect, different from Li-ion batteries, in this case the electrochemical process implies a continuously evolving interface. The cathode discharge reaction, often referred to as oxygen reduction reaction (ORR) is an electro-deposition, where an insulating Li₂O₂ precipitate (i.e. via disproportionation or via reduction from LiO₂) forms on the cathode.[8] This often promotes a fast passivation of the electrode and therefore a very short discharge.[9] To solve this problem, the introduction of solution-phase catalysts has been proposed recently to displace the formation of Li₂O₂ from the cathode to the solution. In particular, soluble redox shuttles such as ethyl viologen (EtV)[10-12] or organic-electrolyte-dissolved iron phthalocyanine[13] and quinone derivatives[14] have shown promising behaviors. Nevertheless, the use of solution-phase mediators to avoid the formation of the solid Li₂O₂ via the aprotic ORR, still remains a not very exploited issue. Among the requirements for these catalysts, one can mention a redox potential below the thermodynamic ORR potential (generally considered equal to 2.96 V vs. Li⁺/Li),[1, 14, 15] but close to that value, since it determines the reaction onset voltage. Also, a solubility of at least 1 mM, fast diffusivity and chemical stability are important features.[14]

Derivatives of polychlorotrisphenylmethyl (PTM) radicals, are molecules of low citotoxicity[16] known as inert carbon free radicals for their stability to oxygen and many other aggressive reagents. They are reported to show redox behavior in aprotic solvents and are characterized by an extremely high persistence and stability.[17-19] This stability is attributed to the steric shielding effect of the six chlorine atoms in the ortho position. PTM radicals are also interesting because they are electro-active species from which it is possible to generate the corresponding carbanionic and carbocationic species being remarkable the low reduction potential at which the carbanion is formed.[20-24] In addition, their easy modulation and control of the electronic structure by chemical substitution in the meta and para positions of the phenyl rings make this family of molecules excellent building blocks to develop new systems giving place to promising multifunctional molecular materials for a range of applications particularly related to signal transduction, such as optoelectronics, spintronics, sensors, among others[25-31] On the other hand, potential of radical polymers as cathode-active material for batteries has been recently demonstrated,[32-36] however there is no example of the possible use of open-shell small molecules, with singly occupied molecular orbitals, to enhance the ORR in Li-O₂ batteries.

In this work we propose, for first time the utilization of tris(2,4,6-trichlorophenyl)methyl (TTM) radical to accelerate the reactions required for improving the energy efficiency in non-aqueous Li-O₂ batteries, and therefore, to increase the discharge capacity of these batteries.

Based on previous studies, the TTM radical appears as a potential good reversible redox mediator for ORR in a Li–O₂ battery since it presents a reduction potential of about 2.6 V

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vs. Li/Li$^+$ together with a large persistence and stability in solution. In order to test the redox behavior of this radical, cyclic voltammograms (CVs) were firstly performed in a standard three-electrode cell under argon flux using a TEGDME-based aprotic electrolyte. TTM radical showed a clear reversible redox couple with the cathodic peak at approximately -0.8 V vs. Ag/AgCl, corresponding to the formation of TTM-anion, and the anodic peak at around -0.6 V vs. Ag/AgCl corresponding to the formation of TTM-radical (see Figure S2). CVs are well consistent with those published previously by Hattori et al.[37] Before assembling the battery, TTM chemical stability with metallic lithium was also tested and no decomposition was observed (see Figure S3).

Figure 1 depicts CVs of a common Super P electrode in O$_2$-saturated electrolyte containing TEGDME and LiOTf (1M) with and without TTM-radical (1 mM), performed in a Teflon homemade Li-O$_2$ cell. Compared with the electrolyte without radicals, with the presence of TTM radical the onset potential shifts significantly to a positive value allowing much larger cathodic and anodic currents, which is indicative of an excellent ORR electrocatalytic activity of this radical. TTM radical shows a reversible redox couple centered at around 2.6 V vs. Li$^+$/Li for reduction and 2.8 V vs. Li/Li$^+$ for oxidation, respectively, and well consistent with values measured against the Ag$^+$/Ag couple in the 3 electrode cell.[37, 38] The cathodic potential is close to those observed for other non-radical redox couples that have been mentioned as effective catalysts for ORR. [10, 11, 13, 14]
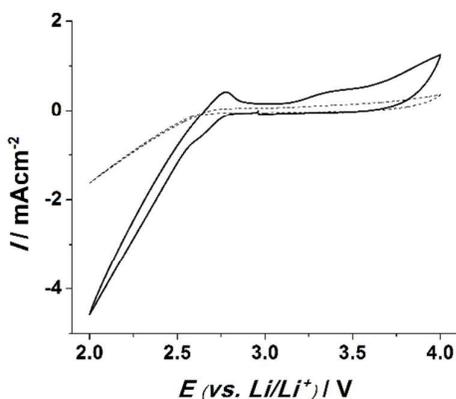

Figure 1. CVs of Super P electrode in O$_2$-saturated electrolyte containing TEGDME-LiOTf (1 M): (dashed) without and (solid) with saturated solution of TTM-radical at 20 mV s^{-1}.

In order to test the stability of the TTM-anion in the battery environment, bulk electrolysis of TTM-radical was carried out in the same electrolyte in presence and in absence of oxygen. In solvents such as filtered on basic alumina dichloromethane, acetonitrile or THF, the TTM anion is easily observed after an electrochemical reduction, but in the presence of oxygen, significant amounts of TTM radical is also obtained. In our case, after a current of 100 µA was applied for 1800 s to a solution of TTM radical (1 mM) in TEDGME-LiOTf (1M) under oxygen, an absorption spectrum was acquired (see Figure 2).

The absorption spectrum of the solution does not show any absorption peak of the TTM anion, expected around 500 nm, while a small decrease of the radical absorption peak at 373 nm was observed. We attribute this effect to the presence of oxygen in the solution, which is able to rapidly re-oxidize the TTM anion to radical without significant degradation to other side products. In order to verify this hypothesis the same experiment was performed in argon atmosphere. However, in this case instead of the expected anion absorption peak we observed an intense decrease of the radical band. This can be explained if we admit that the TEDGME-LiOTf medium, generally considered aprotic for Li-O$_2$ batteries, actually has some acidic character. In effect, in an acid medium, the TTM anion can be easily protonated to form the corresponding protonated close shell TTM-αH molecule.[39] The TTM-αH molecule does not present any absorption peak in the region 300-800 nm but presents a very weak absorption peak at 288 nm that can be recognized also in the absorption spectrum of the solution after the bulk electrolysis in absence of oxygen (see insert of Figure 2). TTM-αH is not electroactive, and cannot be re-oxidized to TTM radical causing a dramatic loss of efficiency as redox mediator. Nevertheless, the protonation results much slower than the electron transfer to dioxygen molecules, at least when these are present at a concentration close to saturation as in our case.

According to this behavior, comparing a cyclic voltammetry of TTM performed in the battery under argon with another one under oxygen, a significant difference in the cathodic currents can be observed, due to the ORR in the latter case, which covers reduction of the TTM radical (see Figure S4). Remarkably, in both cases a peak corresponding to the oxidation of the TTM anion at 2.8 V vs. Li/Li$^+$ is clearly observed, meaning that the slower diffusion in the small volume of electrolyte does not provide enough protons or oxygen molecules that react quantitatively with the anion localized at the electrode surface within the time scale of the CV scan. The smaller height of this anodic peak in presence of oxygen proves that part of the TTM anion is oxidized chemically by oxygen, confirming that the TTM radical acts as ORR catalyst. The TTM anion concentration is then lower than in absence of oxygen, causing a decrease of anodic current.

As it is possible to observe in Figure 2, the kinetics of reaction between the anion and the oxygen to give the radical is so fast that it is not possible to isolate the anion in the solution of the electrolysis cell. Only by in-situ UV-Vis measurements using a setup described elsewhere[40] we have been able to detect some spectroscopic evidence of anion formation during discharge in this cell (see Figure S5). The TTM anion formed in solution during discharge facilitates the formation of Li$_2$O$_2$ at a certain distance from the electrode surface delaying the passivation of the electrode by Li$_2$O$_2$ deposition and thereby increasing the battery capacity. Notice that the oxygen present in the electrolyte solution inside the battery keeps TTM as radical, avoiding the reaction to give the inactive TTM-αH form. The possible reaction paths of the TTM radical discussed in this work can be summarized as illustrated in Scheme 1. In

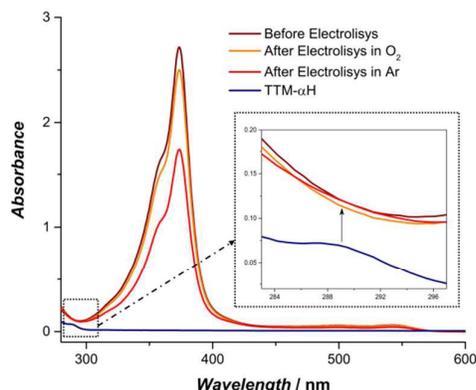our conditions reaction of the anion with oxygen clearly prevails over protonation.

Figure 2. UV-Vis absorption spectrum of a TTM saturated solution in TEDGME-LiOTf (1M) before and after bulk electrolysis. The insert provides a detail around 300 nm, where a characteristic TTM-αH peak is evident (marked with vertical arrow).

Figures 3a-b show the galvanostatic discharge and charge of a carbon Super P-based electrode in a Li-O$_2$ cell with and without TTM radical at two different current densities (i.e. 0.5 mA cm^{-2} and 0.1 mA cm^{-2}). It can be seen that the addition of TTM radical to the electrolyte provided a lower overpotential for the ORR at both current densities. Similar results were observed using EtV as soluble redox couple.[10, 11] In our case the discharge voltages are higher, but the effect is still observed, thanks to the higher reduction potential of TTM compared to EtV^{2+} (about 2.6 V instead of 2.4 V vs. Li [10]). From Figures 3a-b, another notable aspect is the fact that the specific discharge capacity increases significantly when TTM radical is added. The effect is still important at the remarkable current of 0.5 mA cm^{-2}, where limitation in the oxygen supply should start occurring. We did not notice a significant TTM activity during oxidation within our 4.0 V vs. Li voltage cutoff. Re-charges have similar shapes independent of the discharge capacity obtained, only a low percent of the total charge is recovered.

Scheme 1. Chemical and electrochemical reactions of TTM in presence of O$_2$.
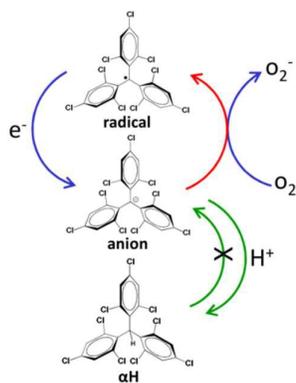
In summary, this study shows for the first time, the utilization of an inert carbon free-radical as a catalyst for non-aqueous Li–O$_2$ batteries. We have proved that the TTM radical is a useful redox mediator to the oxygen reduction reaction in aprotic media, increasing substantially the battery capacity and the potential of discharge, when it is used in a Li–O$_2$ cell. A reaction mechanism was proposed based on the fast reaction between TTM anion and oxygen. This reactivity prevents the possible formation of TTM-αH even in the slightly protic TEDGME-LiOTf medium that is commonly found in Li-O$_2$ batteries, leading to a long lifetime of this mediator in operating conditions.

Further improvements of this system may be achieved by using a more strictly aprotic medium or modifying the PTM structure in order to tune its redox voltage, solubility and diffusivity. This finding opens new ways to enhance the capacity and kinetics of Li-O$_2$ batteries by using variants of this family of open-shell molecules with synthetically tunable properties. The *para* and *meta* positons of the chlorinated phenyls can be substituted with different functional groups. In fact, several molecules of this family have already been prepared with a wide range of properties that may result useful in a Li-O$_2$ battery. Moreover, their potentially low environmental impact make of them an interesting choice for large scale applications.
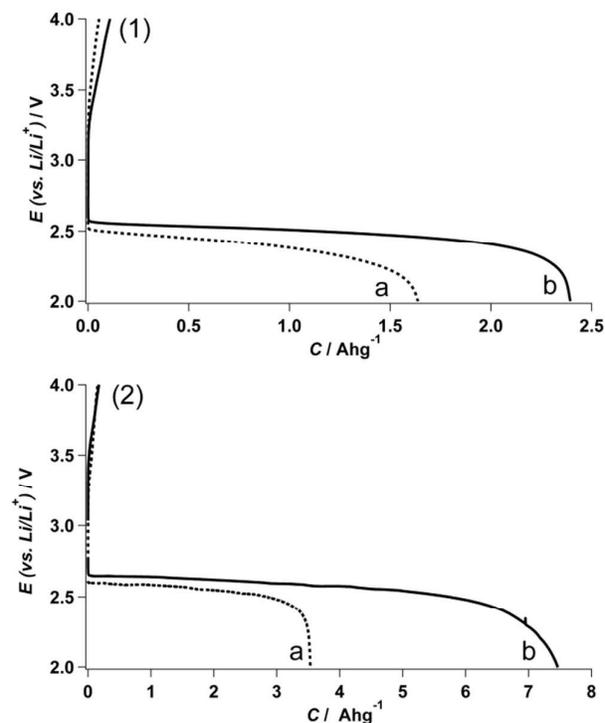

Figure 3. Galvanostatic discharge and charge of a super P electrode in oxygen-saturated TEGDME containing 1M of LiOTf (a) and 1 M LiOTf with saturated solution of TTM-radical (b) at 0.5 mA cm^{-2} (1) and 0.1 mA cm^{-2} (2).

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