Nitronyl-nitroxide-based Redox Mediators For Li-O$_2$ Batteries

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ABSTRACT

Electrochemical processes in Li-O$_2$ batteries benefit from the action of soluble electrocatalysts (redox mediators) that can facilitate charge or discharge reactions and minimize blockage of the cathode with the insoluble discharge product Li$_2$O$_2$. In this work, 2-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl 3-oxide (PTIO) analogues (RPTIOs) as new redox mediators for Li-O$_2$ batteries have been investigated. Cyclic voltammetry, SEM, XRD studies and galvanostatic cycling of the Li-O$_2$ batteries showed that the RPTIOs could effectively catalyze the charge process while having a low impact on the discharge reaction. A direct connection was observed between the character of the substituent on the 2-position of the imidazoline ring, the oxidation redox potential of the RPTIO, and the value of the charge voltage of the battery with this RM, paving a path for further optimization.

Introduction

Li-O$_2$ batteries can source the reactive cathode material, oxygen, directly from air. This, combined with the benefits of Li metal as an anode material, gives Li-O$_2$ batteries very high theoretical gravimetric specific energies. In Li-O$_2$ batteries, soluble electrocatalysts for the charge process (charging redox mediators, RMs) can help effectively decompose solid insulating discharge product, Li$_2$O$_2$, which clogs the cathode surface leading to high charge voltages and short cycle life.[1-5] An effective charging RM can provide significant improvement to the oxygen evolution reaction (OER).

However, low discharge capacity, poor rate performance and high discharge overpotentials remain serious drawbacks preventing the commercial use of Li-O$_2$ batteries. RMs that can facilitate the discharge reaction (discharging RMs) by assisting the formation of Li$_2$O$_2$ either by interacting with Li ions or with oxygen, are important to combat these issues. Systems where both discharging and charging RMs are added are known as dual RM systems.[6-9]

Discharging RMs reported to date include 2,5-di-*tert*-butyl-1,4-benzoquinone,[7,9-10] other quinone derivatives,[11-13] iron phthalocyanine,[14] and ethyl viologens[8,15-16]. Among the reported charging RMs there are nitroxide radicals,[3,5,17] tetrathiafulvalene, *N*-methylphenothiazine, *tris*[4-(diethylamino)-phenyl]amine,[1] *N,N,N',N'*-tetramethyl-*p*-phenylenediamine, 5,10-dimethylphenazine, ferrocene,[2] cobalt(II) *bis*(terpyridine),[18] metal porphyrins, metal phthalocyanines,[1,4] LiI,[2] CsI,[19] InI$_3$,[20] LiBr, and LiNO$_3$[1]. 2-Phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl 3-oxide (PTIO) is a phenyl-substituted nitronyl nitroxide (Fig. 1) that combines charging and discharging redox mediation functions in one molecule; there are two redox processes occurring at 2.1 and 3.7 V vs Li/Li$^+$.[21] PTIO also has high solubility and fast diffusion in common battery electrolytes.[21-22]
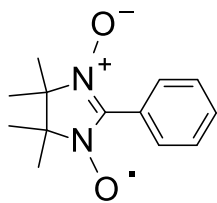
Figure 1. The structure of PTIO.

The electrocatalytic action of PTIO is similar to that of nitroxide radicals, which have received extensive attention as RMs for Li-O$_2$ batteries (Scheme 1).[3,5,9,23-24] The reduction of a nitroxide radical into a hydroxylamine anion (n-doping) is a quasi-reversible process with a very large anodic-to-cathodic peak separation shortening at higher pH values.[25] This process has sluggish kinetics due to further protonation of the hydroxylamine anion (facile at lower pH) to yield hydroxylamine and hydroxylammonium cation and a slow electron transfer back to the hydroxylamine anion form (Scheme 2).[25-26] Thus, nitroxide radicals are commonly used only as charging RMs.
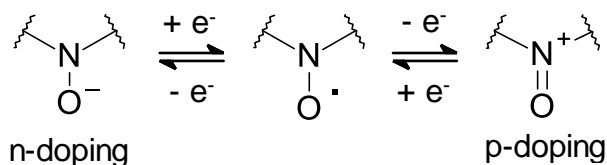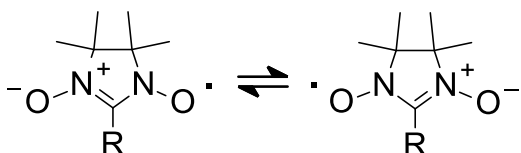

Scheme 1. Redox processes in nitroxide radicals.
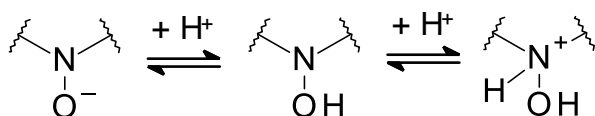
Scheme 2. Protonation of hydroxylamine anion.

In nitronyl nitroxides (NNs), an unpaired electron is delocalized between five atoms with the positive spin density spread almost evenly between the two nitrogen and two oxygen atoms. The system may be represented by the resonance structures shown in Scheme 3.[27-29]

Scheme 3. Resonance structures of NN radicals.

Due to the effective distribution of the electron density, the n-doped state of NN radicals have been proposed to be more stable than that of nitroxides.[30-31] It is therefore feasible that these molecules can act as dual RMs. A recent study demonstrated that the addition of PTIO to a Li-O$_2$ battery as a RM not only reduced the charge overpotential but also increased the discharge capacity because PTIO is capable of improving the solubility of oxygen.[21] Here, we report the findings of our studies into PTIO analogues as RMs for Li-O$_2$ batteries.

PTIO and its analogues benefit from straightforward synthetic methods that allow variation of substituents that can modify the redox potentials of the compounds.[26,32-33] Thus, the potential of the RMs can be gradually adjusted until the desired battery performance is achieved. In addition, PTIO and its analogues possess a radical-scavenging action due to the presence of the nitroxide group, which might provide them with increased stability and protect other battery components from reactive oxygen species.[34-36] In the current study, we have chosen PTIO as a model compound and three analogues with different substituents on the 4-position of the benzene ring. We have investigated the effect of altering the substituents on the redox potential of the compounds and the performance of Li-O$_2$ batteries incorporating these RMs.

Results and Discussion

For PTIO analogues (RPTIOs), we have chosen R = MeO and NMe$_2$ due to their strong electron-donating effect and thus a lower oxidation potential. A strong electron-withdrawing group NO$_2$ was included for comparison and with the possibility of enhancing stability of the n-doped state that might improve the discharge capacity.[37] The synthesis of RPTIOs was achieved using the Ullman method modified by other researchers (Scheme 4).[38-40] Crystals of the obtained RPTIOs are shown in Figure 2. The crystals of NMe$_2$PTIO are greenish-blue, NO$_2$PTIO – dark green, while MeOPTIO and PTIO are blue colour, typical for NNs with an aromatic substituent.[41] All of the prepared RPTIOs are soluble in ether-based electrolyte solvents DEGDME and TEGDME, which are preferred due to their stability in a Li-O$_2$ battery environment.

PTIO: R = H; NMe$_2$PTIO: R = NMe$_2$; MeOPTIO: R = MeO; NO$_2$PTIO: R = NO$_2$
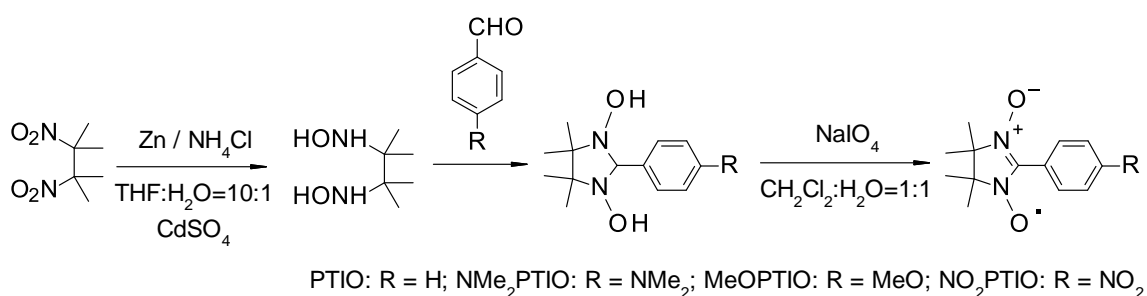
Scheme 4. Synthesis of RPTIO compounds.

Figure 2. Photographs of the crushed crystals of RPTIO compounds: (a) NMe$_2$PTIO, (b) MeOPTIO, (c) PTIO, (d) NO$_2$PTIO.

To effectively decompose Li$_2$O$_2$, the redox potential for the oxidation of RPTIOs should be higher than 2.96 V, while to catalyze the formation of Li$_2$O$_2$, the redox potential for the

reduction should be lower than 2.96 V. To maximize energy efficiency, both processes should be as close to 2.96 V as possible. The redox characteristics of RPTIOs were measured using cyclic voltammetry (CV) performed in a three-electrode setup with glassy carbon, platinum wire and non-aqueous Ag/Ag^+ as a working, counter and a reference electrode, respectively. Cyclic voltammograms of RPTIOs obtained under an argon atmosphere (Figure 3) revealed two redox processes: an oxidation into the N-oxoammonium salt (RM^+) and a reduction into the hydroxylamine anion (RM^-).
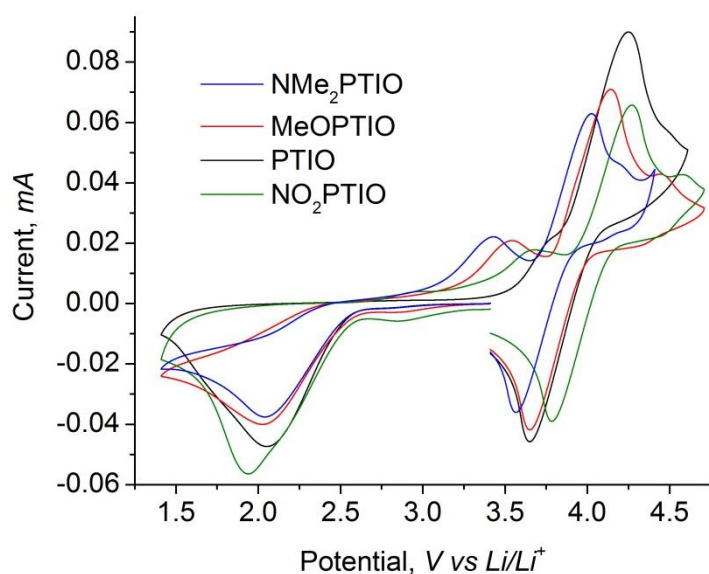

Figure 3. Cyclic voltammograms of RPTIOs (10 mM), LiTFSI (0.1 M) in TEGDME under an argon atmosphere.

Formal redox potentials for the oxidation process of RPTIOs ($\mathbf{E^{o\prime}_{ox}}$) were calculated by averaging the potentials of the cathodic and anodic peaks (Table 1). As expected, the values of $\mathbf{E^{o\prime}_{ox}}$ were the lowest for the compounds with electron-donating substituents NMe_2 and MeO.

Table 1. Redox potentials for the oxidation of RPTIOs.

Redox mediator	$E^{o'}_{ox}$, V $vs.$ Li/Li^+
NMe_2PTIO	3.79
MeOPTIO	3.91
PTIO	3.95
NO_2PTIO	4.03

The long-term electrochemical stability of PTIO under an oxygen atmosphere (Figure 4) was examined using TBATFSI (instead of LiTFSI) to avoid clogging of the glassy carbon electrode with Li_2O_2, which leads to a gradual shift in the potentials. The increase in the intensity of the anodic peak related to the oxidation of PTIO and its shift to higher potential values indicates a pronounced effect of this compound on the OER. There were no significant changes in the peaks during the subsequent 50 cycles, which demonstrates high electrochemical stability of PTIO in oxygen. A highly reversible peak at ~2.3 V vs. Li/Li^+ is also evident and indicates the stability of the redox couple $PTIO^-/PTIO$.
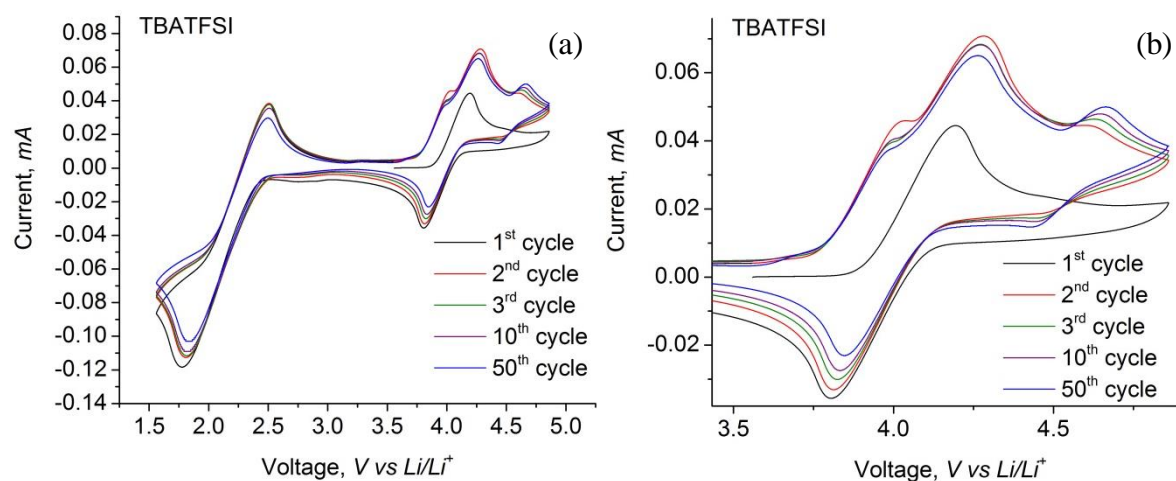

Figure 4. Cyclic voltammograms of PTIO (10 mM) in TBATFSI/TEGDME under an oxygen atmosphere: (a) full scan range, (b) enlarged region at higher positive potentials.

Regarding the reduction process, cyclic voltammograms obtained using LiTFSI under an argon atmosphere (Figure 3) showed cathodic peaks at ~2.0 V vs. Li/Li$^+$, but did not contain any anodic peaks at ~2.4 V vs. Li/Li$^+$, which have been reported by others and assigned to re-oxidation of RM$^-$.[21-22] Instead, we observed low-intensity anodic peaks at 3.4–3.8 V vs. Li/Li$^+$. We attribute these differences to the solvent (TEGDME vs DMSO or acetonitrile). A more acidic environment (pKa(DMSO)>pKa(MeCN)>>>pKa(TEGDME)) would shift the equilibrium shown in Scheme 2 towards the formation of hydroxylamine,[45] and the CV in Figure 3 is likely a result of a coupled chemical reaction, while the reduction process in TEGDME remains reversible or quasi-reversible.[25,46] The separation of the anodic and cathodic peaks for the reduction of RPTIOs is less than that of nitroxides,[25] indicating higher stability of the n-doped state. The modest improvement in the discharge overvoltage is attributed to the interaction of the reduced forms of the RPTIOs (LiRPTIO) with O$_2$ forming a complex (LiRPTIOO$_2$) which then releases Li$_2$O$_2$ stepwise, as has been previously reported in studies of PTIO.[47]

However, the low reduction potentials of the RPTIOs reported here may not significantly improve the performance of the ORR and the reduction potentials of discharging RMs reported to date are greater than 2.4 V vs. Li/Li$^+$.[7-16] CV experiments showed that there was only a slight increase in the intensity of the ORR peak upon the addition of RPTIOs in an oxygen atmosphere (Figure S1). Generally, the voltage in Li-O$_2$ batteries does not reach such low values unless the battery is close to failure (the onset of the reduction of RPTIOs was observed at ≈2.3 V vs. Li/Li$^+$, Figure S2). Thus, here we focus further on the action of RPTIOs as charging RMs.

It is important to confirm that the RPTIOs do not contribute to the capacity of a battery by shuttling from the cathode to the anode, but rather catalyze the decomposition of Li$_2$O$_2$. For this purpose, SEM, XRD and battery experiments were conducted in an argon atmosphere.

Battery tests in argon were performed in Swagelok cells with a sealed O_2 inlet using Li metal, carbon black (CB) and glass fibre as anode, cathode and separator, respectively. The electrolyte was composed of 10 mM RPTIO dissolved in 0.5 M LiTFSI/DEGDME (Figure 5a). The obtained capacity was negligible enough to affirm that the addition of the RPTIO does not significantly affect the overall capacity of the Li-O_2 batteries.
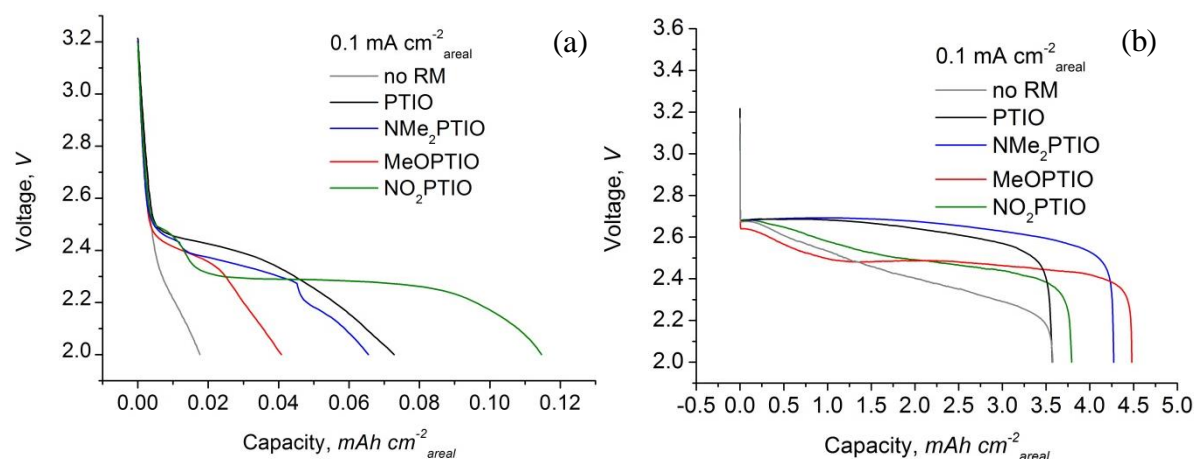

Figure 5. Full discharge curves of the batteries with RPTIOs (10 mM) in LiTFSI/DEGDME and pure LiTFSI/DEGDME electrolyte in argon (a) and oxygen (b).

SEM images of the cathodes with and without RMs showed the morphology of the battery discharge product and the action of the RMs towards it (Figures 6 and S3). With the addition of PTIO, thin plates of the discharge product were formed (Figure 6b), which fully decomposed upon charging (Figure 6d). Without PTIO, the formation of larger particles was recorded (Figure 6c). The same effect was observed for the other RPTIOs.
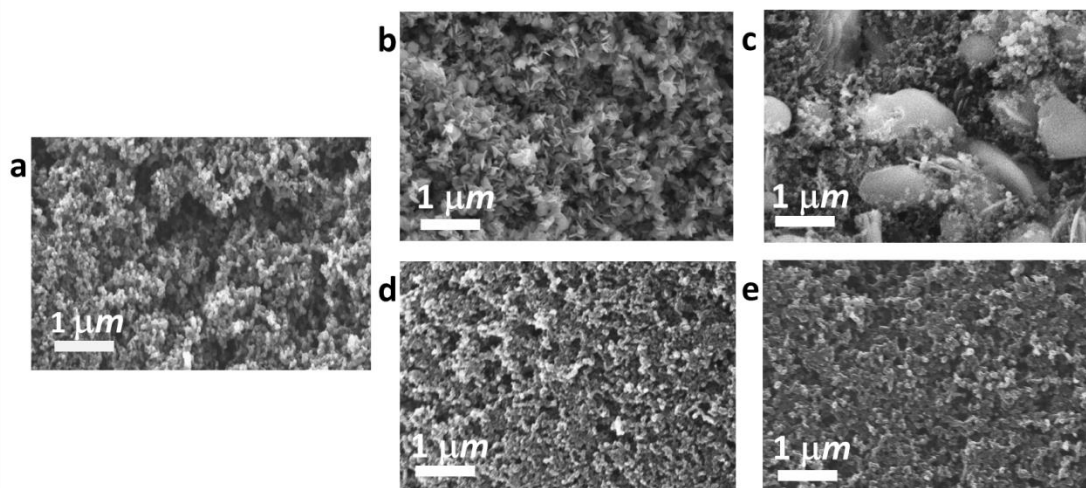
Figure 6. SEM images of CB cathodes: (a) pristine, (b) discharged containing PTIO, (c) discharged without PTIO, (d) charged containing PTIO, (e) charged without PTIO.

XRD studies showed that the particles observed in the SEM images belonged to the discharge product Li_2O_2 (Figures 7 and S4). XRD patterns of the discharged cathodes with and without PTIO contained all of the characteristic signals assigned to Li_2O_2, and no other signals were apparent. These results suggest that the overall reaction in the batteries with RPTIOs is the same as in Li-O_2 batteries cycled without RMs.
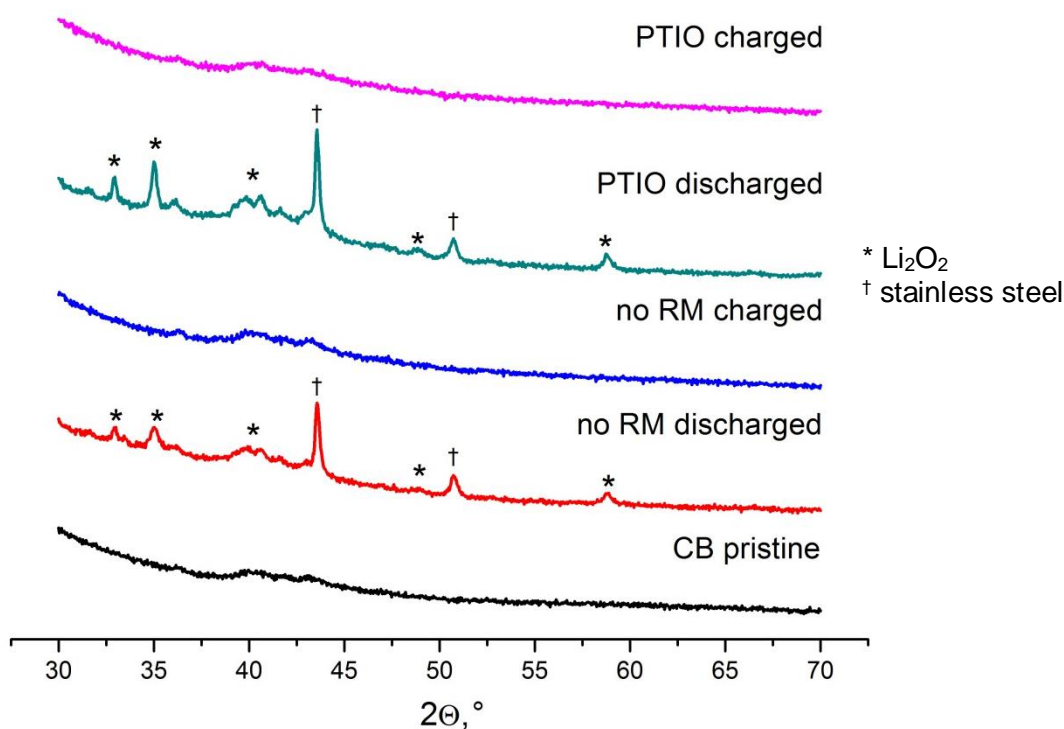
Figure 7. XRD patterns of pristine, discharged and charged CB cathodes with and without PTIO. Note: discharged cathodes remained attached to the stainless steel current collectors, peaks assigned to stainless steel are indicated in the diffraction patterns by †.

To test the effect of RPTIOs on the ORR, Li-O$_2$ batteries with CB cathodes and 10 mM RPTIOs in LiTFSI/DEGDME electrolyte were discharged until 2 V (Figure 5b). The discharge curves of all RPTIOs, except for PTIO, demonstrated a slight increase in the discharge capacity compared to the battery with a pure LiTFSI/DEGDME electrolyte, up to 0.9 mAh cm^{-2} for MeOPTIO, while the batteries with PTIO and NMe$_2$PTIO showed lower discharge overpotentials. The discharge performance was not improved significantly, as was predicted from our CV results. However, unlike some TEMPO-containing RMs,[5,48] the RPTIOs did not reduce the discharge capacity. The discharge capacities for batteries containing each of the RPTIOs were much greater when discharged in an oxygen atmosphere compared to argon (Figure 5a) indicating that the compounds facilitate the reactions in the Li-O$_2$ battery, rather than contributing to the capacity by redox shuttling.
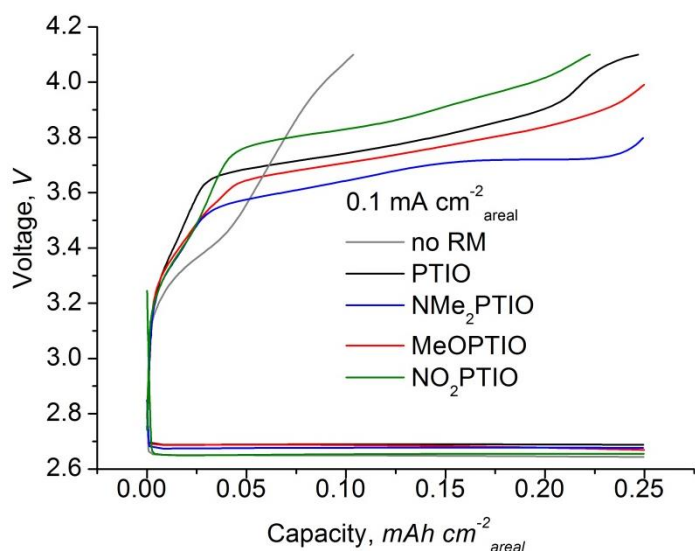
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Figure 8. Galvanostatic discharge/charge curves of RPTIOs (10 mM) in LiTFSI/DEGDME (1st cycle).

The action of RPTIOs on the OER was investigated by discharging and then charging to 0.25 mAh cm^{-2} the Li-O$_2$ batteries with the same composition in the voltage range of 2–4.1 V (Figure 8). The batteries with all RPTIOs exhibited a pronounced effect on the OER, decreasing the charge overpotential by up to 0.3 V for NMe$_2$PTIO in the studied voltage window and with a more than double charge capacity. Importantly, the battery charge potentials followed the same order as the oxidation potentials for the RPTIOs (E(NMe$_2$PTIO)<E(MeOPTIO)<E(PTIO)<E(NO$_2$PTIO)), consistent with our hypothesis that changes in the structures of RPTIOs will have a direct and predictable effect on the charge overpotential.

The long-term effect of the RMs on battery performance was investigated by cycling the Li-O$_2$ batteries with and without RPTIOs for 30 cycles in the voltage range of 2–4.1 V at a fixed capacity of 0.25 mAh cm^{-2} (Figure 9). The batteries containing RPTIOs maintained lower charge voltages than the battery without added RM for at least 15 cycles, which supports our hypothesis that they facilitate the OER during repetitive cycling. The long-term performance

of the battery with MeOPTIO was better than that with NMe$_2$PTIO, with the charge potential lower than 3.9 V vs. Li/Li$^+$ by the 15th cycle and greater charge capacity for the former. The discharge capacity of the battery with NO$_2$PTIO dropped after the 25th cycle and the battery ceased cycling earlier than that without RM, possibly due to the high oxidation redox potential of this RM.

The deterioration of performance of the batteries containing the RPTIOs may arise from an accumulation of by-products from side reactions associated with carbon-based cathodes, Li metal anode and ether-based electrolyte. Issues associated with the instability and reactivity of these materials are known,[49] but they are currently the most favorable for high-performance Li-O$_2$ batteries.[9,50-51] The use of these popular materials also facilitates comparison of the effects of the redox mediator performance with other reported materials.
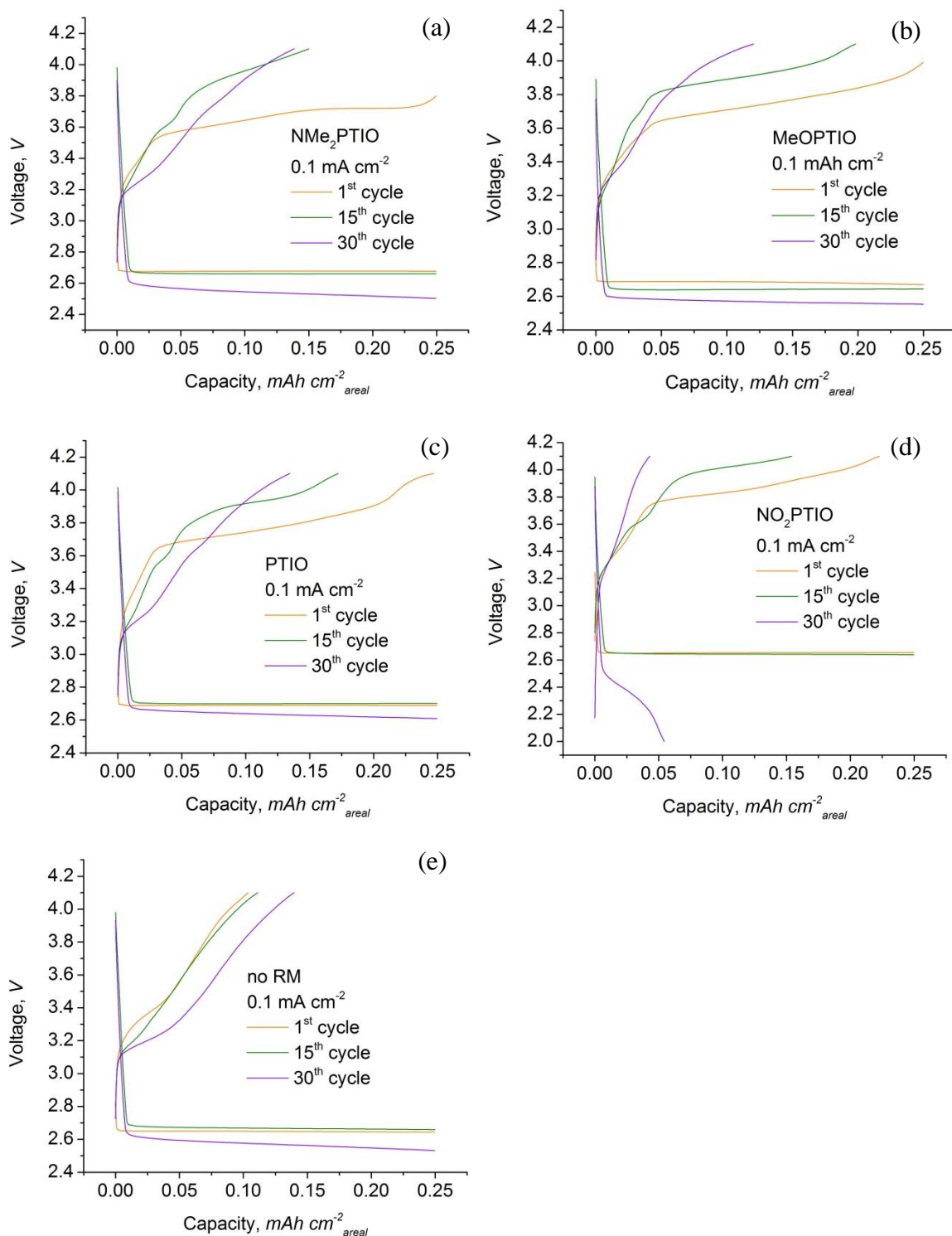
Figure 9. Galvanostatic cycling profiles of batteries (RPTIO (10 mM) in LiTFSI/DEGDME): (a) NMe$_2$PTIO, (b) MeOPTIO, (c) PTIO, (d) NO$_2$PTIO, and (e) pure LiTFSI/DEGDME electrolyte.

MeOPTIO provided the longest cycle life and cycled slightly longer than batteries without RMs at fixed capacities of 0.25 mAh cm^{-2} and 0.5 mAh cm^{-2} (Figure S5). The catalytic action

of MeOPTIO leads to the formation of very thin plates of Li_2O_2 that were observed in SEM images (Figure S3). These particles are easier to be decomposed during discharge than larger particles formed in the battery with a pure LiTFSI/DEGDME electrolyte, leading to lower charge overpotentials and longer cycle life.

Conclusion

In conclusion, three new RMs for Li-O$_2$ batteries were proposed and synthesized. The stability of the n-doped state of the RPTIOs was greater than that of nitroxides with the return peak for the reduction observed in CV experiments at lower voltages than the oxidation process, suggesting that they can operate as charging and discharging RMs combined in one molecule, with more improvement expected for the charge performance. The addition of RPTIOs to Li-O$_2$ batteries led to a lower discharge overpotential with a slight increase of the discharge capacity, unlike some other nitroxide-group-based RMs. More importantly, RPTIOs provided a significant decrease of the charge overpotential (up to 0.3 V in the studied voltage window), and the order of the obtained charge voltages was the same as the redox potentials for the oxidation calculated from the CV curves, which proves a pronounced catalytic effect of RPTIOs on the OER. This study demonstrated a clear dependence of the charge potential on the character of the substituent on the position 2 of imidazoline moiety in nitronyl-nitroxide-based RMs. The advantage of this type of RMs is that the synthetic method allows for an easy adjustment of the structures and correction of the redox potentials to the optimum values. A variation of the structures, e.g., replacing a benzene ring with a pyrazole, might further improve the stability of the n-doped state and provide a more significant increase of the discharge capacity.

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Notes

The authors declare no competing financial interests.

Supporting Information Available: synthetic procedures, characterization data, cyclic voltammetry data, scanning electron micrographs, X-ray diffraction data, galvanostatic cycling profiles.

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