Short communication

An O_2 cathode for rechargeable lithium batteries: The effect of a catalyst

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Abstract

The energy density of current rechargeable lithium batteries is limited by the capacity of the $LiCoO_2$ positive electrode ($140 \, \text{mA h g}^{-1}$). The best intercalation electrode is only likely to increase this by a factor of 2 (1Li/Tm). Replacing the intercalation cathode with an O_2 electrode could raise the capacity 5–10-fold. Here, we explore the influence of the catalyst could have on the performance of a non-aqueous O_2 electrode on a Li/O_2 cell. Of the catalysts studied the highest initial capacity was observed with Fe_2O_3 ($2700 \, \text{mA h g}^{-1}$), the highest capacity retention with Fe_3O_4, CuO and $CoFe_2O_4$ (6.67% per cycle). Co_3O_4 gives the best compromise between initial capacity ($2000 \, \text{mA h g}^{-1}$) and capacity retention (6.5% per cycle), as well as the lowest charging voltage 4 V. All capacities expressed per gram of carbon and at a rate of $70 \, \text{mA g}^{-1}$.
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1. Introduction

A significant increase in the energy density of rechargeable lithium batteries is required to meet the future demands of consumer electronics, implantable medical devices and clean energy storage. The positive electrode represents a major obstacle to progress. $LiCoO_2$ is restricted to a reversible capacity of around $140 \, \text{mA h g}^{-1}$, corresponding to approximately 0.5Li/Co. Most of the research effort on cathode materials is devoted to the discovery and optimization of new lithium intercalation electrodes to replace $LiCoO_2$. However, such efforts are likely to lead only to a 2-fold increase in the energy density of the cathode, i.e. to 1Li/Tm. Therefore, it is essential to explore alternative strategies that can offer a route to a step change in charge storage significantly greater than can be delivered by intercalation electrodes.

One promising approach is the use of nanocomposite cathodes, which can store energy in a two-phase reaction analogous to conversion reactions such as $2Li + CoO \leftrightarrow Li_2O + Co$ used as anodes [1,2]. Fluorides or oxyfluorides may be used to increase the potential to a level suitable for cathodes, e.g. $BiOF + 3Li \leftrightarrow Bi + Li_2O + LiF$ [3,4]. An alternative approach involves replacing the intercalation electrode with a porous electrode and allowing lithium to react directly with O_2 from the air [5–10]. There is no need to carry the reactants around in the cell, and the supply of O_2 from air is in effect infinite. Freed from the constraints imposed by intercalation cathodes, higher capacities are possible approaching $1170–1800 \, \text{mA h g}^{-1}$, based on the formation of Li_2O_2 or Li_2O (practical capacities will of course be somewhat less due to the presence of carbon in the electrode).

Although electrochemical reduction of O_2 has been studied intensively in aqueous media, and aqueous based Zn/air and Al/air primary batteries have been known for some years [11–14], the possibility of a non-aqueous based Li/O_2 cell has received much less attention. Work is taking place on primary Li/O_2 non-aqueous cells because of their potentially very high energy densities [6–9]. Very few studies have explored the possibility of rechargeability [5]. Recently, we demonstrated by powder X-ray diffraction and *in situ* differential electrochemical mass-spectrometry that the Li_2O_2, which forms on discharging the Li/O_2 cell, is decomposed on charging. We also demonstrated sustainability of cycling with capacities of $600 \, \text{mA h g}^{-1}$ being delivered after 50 cycles [10].

Although the non-aqueous oxygen electrode in a lithium cell offers the exciting possibility of substantially higher capacities, much remains to be done in order to understand the processes and to optimize performance. Many factors can influence the performance of the non-aqueous O_2 electrode. In this paper, we explore the role of a catalyst. This is a preliminary study aimed at screening a number of materials in order to establish which

give poor, which moderate and which promising performance, as a basis for further investigation.

2. Experimental

2.1. Preparation of cathode and electrochemical measurements

The electrochemical cells used to investigate cycling were based on a Swagelok[TM] design and composed of a Li metal anode, an electrolyte (1 M LiPF$_6$ in propylene carbonate (Merck)) impregnated into a glass fibre separator and a porous cathode. The cathode was formed by casting a mixture of Super S carbon (MMM), catalyst and Kynar 2801 (a co-polymer based on PVDF) (mol ratios: 95:2.5:2.5) onto an Al grid. The cathode construction followed well-established procedures for porous electrodes [15]. The cell was gas-tight except for the Al grid window that exposed the porous cathode to the O$_2$ atmosphere. Experiments were carried out in 1 atm of O$_2$. To investigate specifically the electrochemical decomposition of Li$_2$O$_2$ on charging, electrodes were prepared by mixing 100 nm Li$_2$O$_2$ particles (ballmilled powder from Aldrich, 90%), Super S carbon, electrolytic manganese dioxide (EMD) and PTFE (Aldrich) (mol ratios: 16:80:2:2). The electrodes were again incorporated into cells with Li foil and 1 M LiPF$_6$ in propylene carbonate as the electrolyte. Electrochemical measurements were performed at room temperature using a Bio-Logic Mac Pile II.

2.2. Sample characterization

Powder X-ray diffraction (XRD) was carried out using a STOE STADI/P diffractometer operating in transmission mode with a primary beam monochromator and position sensitive detector. Fe Kα_1 radiation ($\lambda = 1.936$ Å) was employed. Examination of charged electrodes involved first disassembling the cell in the glove box, rinsing the cathode twice with dimethyl carbonate, removing the solvent under vacuum, and then introducing the electrode into an air-tight X-ray holder.

3. Results and discussion

The electrochemical reduction of O$_2$ in an aqueous electrolyte may be described by the classic four-electron process. $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$. This is of course in reality a multi-step process, which takes place on the electrode surface. Recent results have indicated that O$_2$ is reduced to the super oxide O_2^- and then be further reduced to the peroxide O_2^{2-} species [16]. In aqueous media, the processes are dominated by reactions between these species and H$^+$/H$_2$O, with for example the O_2^{2-} species combining with H$^+$ to form H$_2$O$_2$. In the non-aqueous environment within the lithium cell, evidence to date indicates that the principal product of O$_2$ reduction is Li$_2$O$_2$. It is known that catalysts can play an important role in facilitating the electrochemistry of O$_2$ in aqueous and non-aqueous media, therefore, it is interesting to explore the extent to which they can facilitate the oxygen electrode reaction in a lithium cell.

The $2Li + O_2 \leftrightarrow Li_2O_2$ reaction can take place even in the absence of a catalyst, as demonstrated in Fig. 1a, where a Li/O$_2$ cell in which the O$_2$ porous electrode consists of only carbon and Kynar as binder, has been discharged then charged. Discharging occurs at a potential of around 2.6 V with subsequent charging occurring at around 4.8 V.

Taking an identical cell and charging it, without prior discharge, under the same conditions gives rise to a higher voltage plateau, 5.1 V, corresponding to electrolyte oxidation and indicating that the 4.8 V plateau is associated with Li$_2$O$_2$ decomposition. This was confirmed by powder X-ray diffraction data collected in a cell constructed in the discharged state, i.e. containing Li$_2$O$_2$, before and after charging, which clearly indicated the disappearance of Li$_2$O$_2$ on passing a sufficient charge to decompose all the lithium peroxide (Fig. 2). Although it is possible to discharge then charge the Li/O$_2$ cell in the absence of a catalyst, the use of a catalyst significantly facilitates the process, as demonstrated in Fig. 3a where mol 2.5% of electrolytic manganese dioxide (EMD), has been incorporated into the porous electrode. This has little effect on the discharge potential but shifts the charging potential to a significantly lower voltage, 4.3 compared with 4.8 V. The retention of capacity on cycling is also
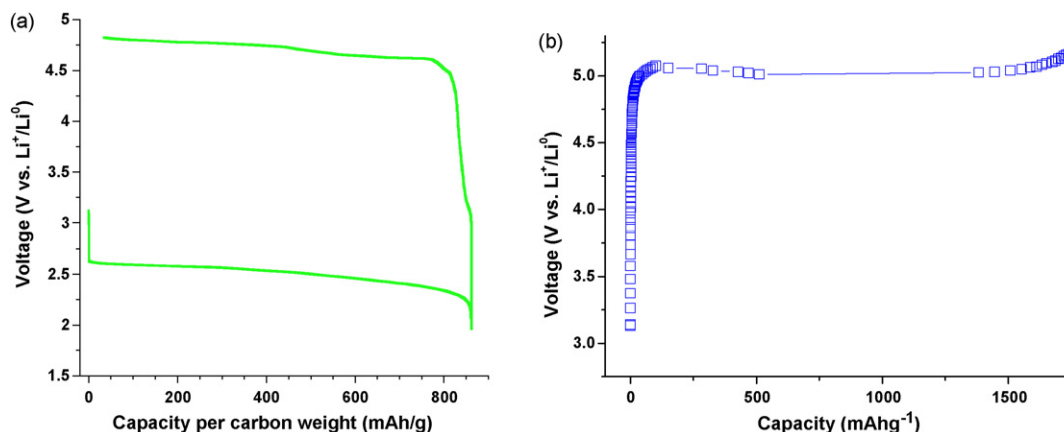

Fig. 1. (a) Variation of voltage on discharge then charge for the porous electrode, Super S:Kynar, mol ratio 97:3, at a rate of 70 mA g^{-1}. Capacities are expressed per gram of carbon in the electrode. (b) Variation of voltage on charging cell with the same porous cathode at a rate of 50 mA g^{-1}.
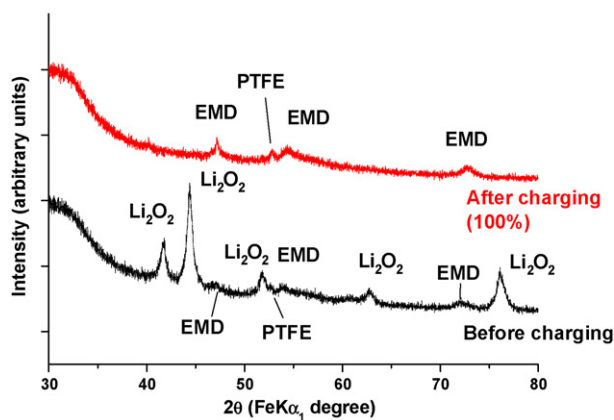
Fig. 2. Powder X-ray diffraction data for a Li_2O_2:Super S:EMD:PTFE electrode before charging and after passage of sufficient charge to decompose all the Li_2O_2.

significantly better with a catalyst as demonstrated in Fig. 3b, where we compare the discharge capacity versus cycle number with and without the EMD catalyst.

These results serve to illustrate the significant role of the catalyst on the electrochemistry of the O_2 electrode in a Li/O_2 cell. Although in general, the catalyst in oxygen reduction is responsible for assisting the cleavage of the di-oxygen bond, the fact that EMD enhances the discharge and charge capacities of an electrode reaction involving the formation of Li_2O_2 (i.e. no di-

oxygen bond cleavage) means that, at least for the non-aqueous case, the catalyst assists with the reduction of O_2 to O_2^{2-} and its subsequent oxidation. We anticipate that the oxygen on the surface of the oxide catalyst may participate in the electrode reaction. However, the mechanism is as yet unclear. Further work is underway to investigate the role of the catalyst in aiding the electrochemical reaction.

As a result, we have explored a number of other catalysts. Many materials have been investigated as electrocatalysts for O_2 electrochemistry in aqueous media over the last 200 years [11,17–21]. We could not of course hope to examine all of these. Instead, we have explored the best oxygen electrocatalyst for aqueous media, Pt, a fuel-cell cathode, $La_{0.8}Sr_{0.2}MnO_3$, the simple binary oxides of Fe, Co and Ni and Cu, as well as a ternary oxide combining two of the most promising binary oxides, i.e. $CoFe_2O_4$. In all cases, the electrode construction was identical, including the ratios of carbon:catalyst:Kynar (mol ratios: 95:2.5:2.5).

The influence of different catalysts on the gross electrochemical performance of the porous O_2 electrode is shown in Table 1; where we report the discharge voltage and discharge capacities for cycles 1, 5 and 10 (capacities are expressed per gram of carbon in the electrode). In all cases, except the Fe_2O_3—carbon loaded, catalyst particle sizes were in the range 1–5 μm. It is clear that the discharge voltage is affected very little by changing the catalyst whereas the discharge capacity and its retention on cycling changes dramatically depending on the catalyst used.
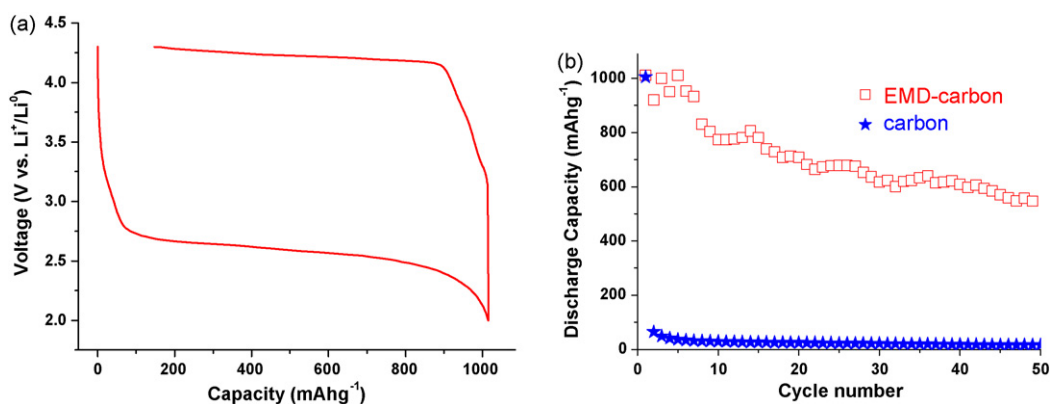

Fig. 3. (a) Variation of voltage on discharge then charge corresponding to the 3rd cycle for the porous electrode, Super S:EMD:Kynar, at a rate of 70 mA g^{-1}. (b) Variation of discharge capacity with cycle number for an O_2 cathode with (□) and without EMD (★) as catalyst at a rate of 70 mA h g^{-1}.

Table 1
Discharge voltage and discharge capacities of cycles 1, 5, and 10

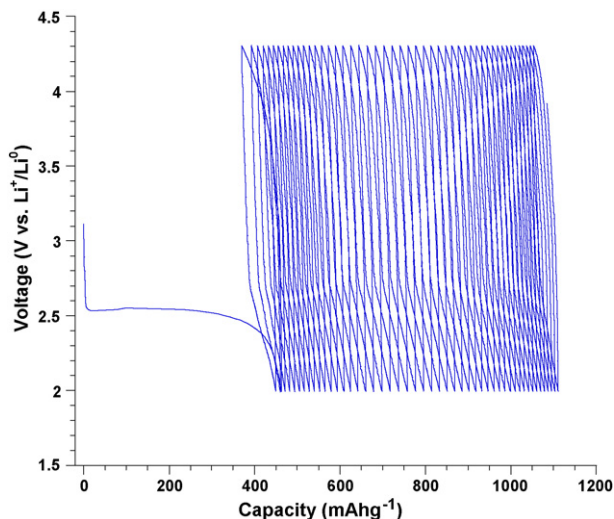| Catalyst	Discharge voltage (V)	Capacity of cycle 1 (mA h g^{-1})	Capacity of cycle 5 (mA h g^{-1})	Capacity of cycle 10 (mA h g^{-1})	Capacity retention per cycle (%)
Pt	2.55	470	60	60	1.28
$La_{0.8}Sr_{0.2}MnO_3$	2.6	750	75	40	0.53
Fe_2O_3	2.6	2700	500	75	0.28
Fe_2O_3-carbon loaded	2.6	2500	280	75	0.3
NiO	2.6	1600	900	600	3.75
Fe_3O_4	2.6	1200	1200	800	6.67
Co_3O_4	2.6	2000	1900	1300	6.5
CuO	2.6	900	900	600	6.67
$CoFe_2O_4$	2.6	1200	900	800	6.67

Fig. 4. Variation of voltage on discharge then charge for the porous electrode, Super S:Pt:Kynar, at a rate of 70 mA g^{-1}.

Considering first platinum, it exhibits one of the lowest discharge capacities and this capacity drops rapidly on cycling. The variation of voltage on discharge and charge for the O$_2$ electrode with Pt is shown in Fig. 4. It is clear that the reduction of capacity occurs mainly on charging, i.e. the charge/discharge efficiency is less than 100%, this is true for all the catalysts used, although to different extents. Considering the performance of the fuel-cell cathode La$_{0.8}$Sr$_{0.2}$MnO$_3$, Table 1, although its first discharge capacity is higher than Pt, capacity fading is again significant. In summary, neither of the two classic oxygen electrodes exhibit good performance, with low discharge capacities on the first cycle and rapid capacity fading.

Fe$_2$O$_3$ exhibits the highest first discharge capacity but this decreases rapidly on cycling, Table 1. It is well known that the activity of catalysts can be improved by "loading" the catalyst on carbon, involving precipitating the catalyst on the carbon support so that it is intimately mixed and dispersed [22]. In order to investigate whether such loading is beneficial in the Li/O$_2$ cell we have prepared Fe$_2$O$_3$-loaded carbon by impregnating a aqueous solution of Fe(NO$_3$)$_3$ onto carbon, then drying the mixture at 70 °C, followed by calcination for 1 h at 400 °C in flowing Ar. It is evident from Table 1 that such activation brings little benefit to either the initial discharge capacity or its retention on cycling. We can conclude overall that Fe$_2$O$_3$ does not exhibit promising performance and therefore we do not consider its behaviour in more detail. The other well-known form of iron oxide is the inverse spinel Fe$_3$O$_4$. Table 1 reports the basic electrochemical properties of the O$_2$ electrode containing this catalyst. Although the first discharge capacity of Fe$_3$O$_4$ is lower than that of Fe$_2$O$_3$, the capacity retention on cycling is far superior for the spinel.

Given the good capacity retention of Fe$_3$O$_4$ we present the variation of voltage on discharge and charge for this catalyst, Fig. 5. There is a clear step in the charge potential, which we do not understand at this stage The discharge and charge potentials move to values approximately 100–200 mV higher on cycling, the discharge voltages are again around 2.6 V with the charging voltages being around 4.25 V.
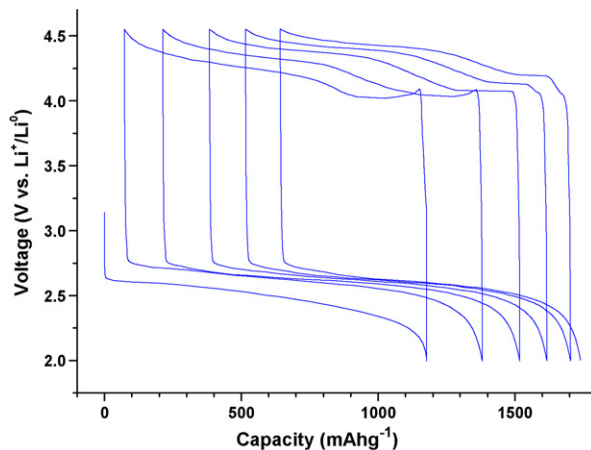

Fig. 5. Variation of voltage on discharge then charge for the porous electrode, Super S:Fe$_3$O$_4$:Kynar, as catalyst at a rate of 70 mA g^{-1}.

Considering catalysts based on other transition metal oxides, we examined Co$_3$O$_4$. Table 1 indicates that this catalyst gives the best combination between a high first discharge capacity, around 2000 mA h g^{-1} and capacity retention on cycling. Given the promising performance of the cobalt oxide material, its electrochemistry is presented in more detail in Fig. 6. As observed for Fe$_3$O$_4$, both the discharge and charge potentials increase by 100–200 mV on cycling. Whereas the average discharge potential is the same as other catalysts, the Co$_3$O$_4$ material gives the lowest charge potential with a value of around 4 V. The variation of charging potential with different catalysts and with none, ranging from 4 to 4.8 V contrasts with the invariance of the discharge voltage suggesting that the mechanism of the charging process depends on the nature of the catalyst.

The performance of NiO is shown in Table 1. Although the initial discharge capacity is relatively high, 1600 mA h g^{-1} this decreases substantially on cycling, indicating that this is not an attractive catalyst. In contrast, CuO, although it gives a lower initial capacity, shows good capacity retention on cycling. The variation of voltage on discharge and charge for CuO is shown in Fig. 7a. In this case, the charging voltage is around 4.3 V.
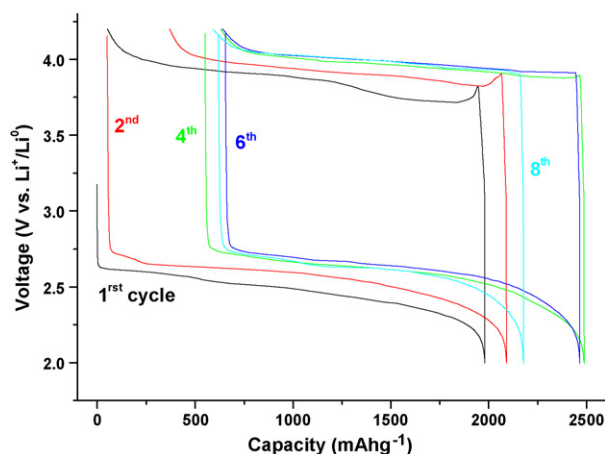

Fig. 6. Variation of voltage on discharge then charge for the porous electrode, Super S:Co$_3$O$_4$:Kynar, at a rate of 70 mA g^{-1}.
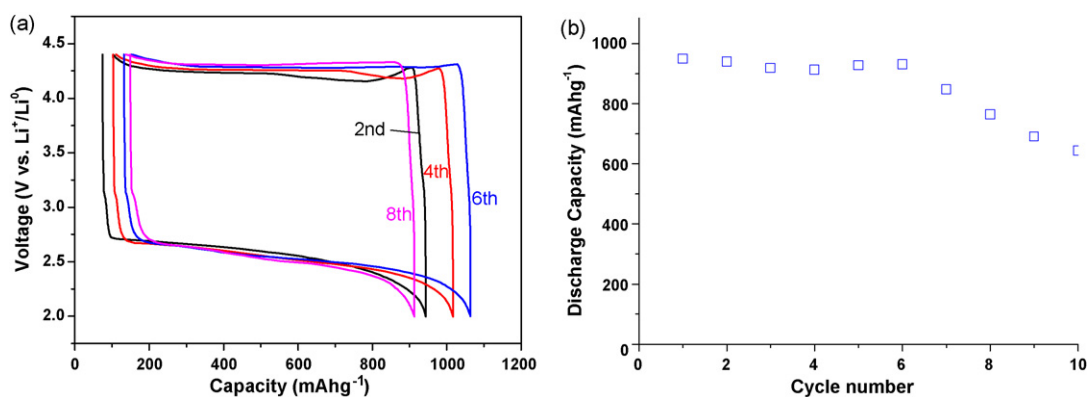
Fig. 7. (a) Variation of voltage on discharge then charge for the porous electrode, Super S:CuO:Kynar, at a rate of $70\,mA\,g^{-1}$. (b) Variation of discharge capacity with cycle number for the same cell.
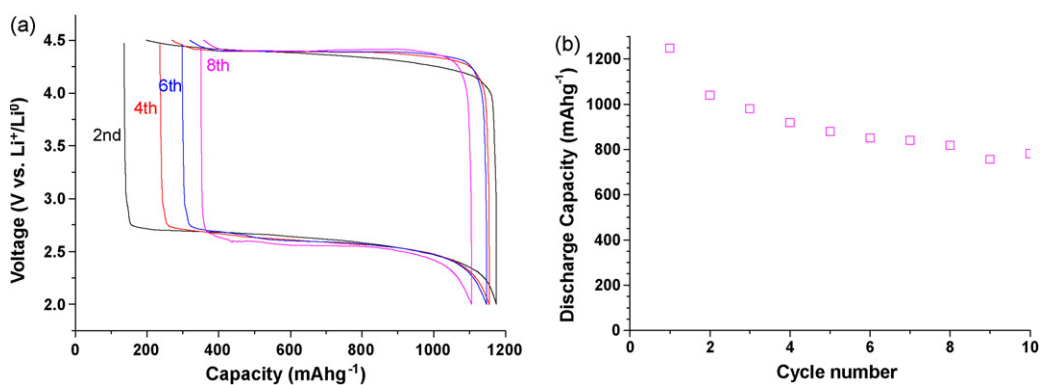

Fig. 8. (a) Variation of voltage on discharge then charge for the porous electrode, Super S: CoFe$_2$O$_4$:Kynar, at a rate of $70\,mA\,g^{-1}$. (b) Variation of discharge capacity with cycle number for the same cell.

Many ternary transition metal oxides could be investigated. We have chosen to examine one that combines the two transition metal ions from two of the most promising binary catalysts, namely Fe$_3$O$_4$ and Co$_3$O$_4$, and with the same spinel structure, CoFe$_2$O$_4$. The performance is summarized in Table 1 and shown in more detail in Fig. 8. This catalyst exhibits good capacity retention, with a capacity of $1200\,mA\,h\,g^{-1}$ on the first cycle dropping to only $800\,mA\,h\,g^{-1}$ after 10 cycles. The discharge and charge voltages are 2.6 and 4.3 V, respectively (Fig. 8a).

4. Conclusions

The paper reports a preliminary screening of some of the many catalysts that could be explored for their role in facilitating the electrochemical properties of the O$_2$ electrode in a non-aqueous Li/O$_2$ cell. The screening process has indicated that two of the conventional oxygen electrocatalysts, platinum and the mixed metal perovskite Li$_{0.8}$Sr$_{0.2}$MnO$_3$, do not perform well, something that is also true for Fe$_2$O$_3$ and NiO. Activating the catalyst by mixing it intimately with carbon does not appear to enhance performance. Of the catalysts studied, Fe$_3$O$_4$, CuO and CoFe$_2$O$_4$ give the best capacity retention. Co$_3$O$_4$ gives the best compromise between the discharge capacity and the retention on cycling. More detailed investigations are required in order to confirm these preliminary findings, to investigate the more promising catalysts in more detail, especially the electrode reaction mechanism and the role of the catalyst.

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