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A High-Capacity Li-Ion/ Li-Oxygen Hybrid Cathode

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A hybrid Li-ion/Li-oxygen cathode is demonstrated. With a stable ionic liquid electrolyte, the capacity of a conventional LiCoO₂ cathode is greatly enhanced with Li-oxygen mechanism. Further more, the Li-ion mode operation helps to improve the cyclability of the Li-oxygen mode. The Li-oxygen capacity can be a backup power source for occasional usage.

Lithium-ion battery (LIB) is nowadays the most successful commercial electrochemical device.¹ However, its energy density is still not high enough to meet the needs of intelligent portable electronic devices and electric vehicles.² Because the Li-ion intercalation mechanism requires certain crystal structure, the bottleneck of LIB cathodic capacity is very difficult to break through. More and more researchers are looking for next-generation high-capacity rechargeable batteries with other charge-discharge mechanisms, such as lithium-oxygen battery (LOB).^{3,4} The LOB is based on the electrochemical reaction $2\text{Li}^+ + \text{O}_2 + 2\text{e}^- \leftrightarrow \text{Li}_2\text{O}_2$ (2.96 V vs. Li^+/Li). It has the highest theoretical energy density of 3460 Wh kg^{-1} based on the molecular weight of Li_2O_2 .⁵ However, some major challenges, especially the poor cyclability, impede its practical application.⁶ Tremendous efforts have been devoted to solving the cycling problem,⁷⁻¹⁰ but it is almost impossible to make the LOB with cyclability as good as the LIB.

In this communication, we design a novel strategy to take advantage of both LIB and LOB in one battery, i.e., a hybrid mode of LIB and LOB. LiCoO_2 (LCO) cathode with optimized electrolyte is charged/discharged in oxygen. In the potential range from 3.0 to 4.2 V, LCO acts as normal LIB cathode with excellent cyclability. If the discharge goes deeper, an additional capacity of more than 200 mAh g^{-1} will appear at about 2.6 V vs. Li^+/Li due to the LOB

discharge mode. Like other LOBs, the cyclability of the lithium-oxygen part is still limited, but it may serve as an effective supplementary power supply for occasional emergency usage.

We firstly measured the cyclic voltammetry (CV) curves of the LCO electrode in different atmospheres (Fig. 1a). The LCO electrode was made of 85 wt% LCO, 10 wt% super P and 5 wt% polyvinylidene fluoride binder (PVDF). The electrolyte was 0.5 mol L^{-1} lithium bis(trifluoromethane)sulphonamide (LiTFSI) in anhydrous tetra(ethylene) glycol dimethyl ether (TEGDME) solution. In Ar, the CV curve (black line) only exhibits the redox peaks corresponding to the Li-ion intercalation and extraction.¹¹ But in O_2 (red line), the oxygen reduction current can be also observed at below 2.8 V. What's more, in the voltage range higher than 3.1 V, we can see an additional oxidation peak in the 2nd cycle, which is resulted from

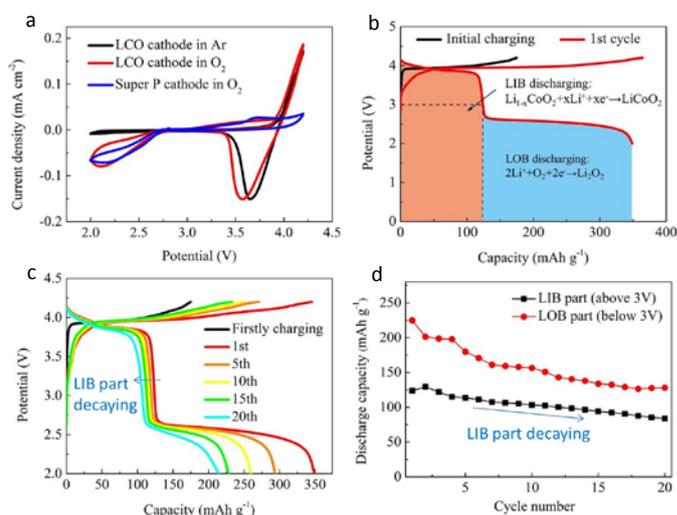


Fig. 1 (a) CV curves of the LCO and Super P cathode in different atmosphere with TEGDME electrolyte. Scanning rate = 1.0 mV s^{-1} . (b,c) Galvanostatic charge/discharge curves of the LCO cathode in TEGDME electrolyte. Current density = 0.1 mA cm^{-2} . The red and blue colored areas indicate the out-put energy of different discharge modes. (d) Evolution of the discharge capacity corresponding to different discharge part. The cells were cycling in the range of 2.0 – 4.2V.

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the oxidation of Li_2O_2 . This oxidation peak did not appear in the 1st cycle, which is because there was no Li_2O_2 on the electrode since the 1st scan was from 3.0 V to higher voltage. We also tested the CV curve of super P in oxygen atmosphere (blue line). The curve only shows the redox peaks attributed to the lithium-oxygen reactions. The CV curve of LCO in O_2 can be viewed as a combination of the CVs of LCO in Ar and super P in O_2 , indicating that both LIB and LOB electrochemical reactions can happen on the LCO cathode in oxygen.

We tested the discharge/charge performance of the hybrid LIB-LOB system in O_2 on the coin cell with lithium metal foil as anode and 0.5 mol L^{-1} LiTFSI in TEGDME as electrolyte. The cell was initially charged to 4.2 V and then cycled in the voltage range of 2.0–4.2 V. The specific capacities were calculated based on the mass of the whole cathode, including LCO, super P and PVDF. As shown in Fig. 1b, two discharge plateaus are clearly observed, which are assigned to the LIB and LOB electrochemical reactions, respectively. The LOB part contributes 220 mAh g^{-1} to the capacity of the LCO cathode. This number is not very high because the density of our cathode is 3 g cm^{-3} , and the loading is 4 mg cm^{-2} , much higher than those ultra-light cathode materials used in other LOBs. But from the LIB side of view, adding an extra capacity of over 200 mAh/g is very desirable. It should be noticed that the following charging voltage increases not as obviously as it does in the initial charge process (Fig. 1c), which is because the Li_2O_2 decomposition started at lower voltage ($< 4 \text{ V}$).¹² Due to the high charging overpotential of LOB, the majority of the Li_2O_2 can only decompose at above 4.0 V, close to the lithium ion extraction voltage. This is the reason why the charging curve only shows one plateau. Overall, the electrochemical performance of LCO electrode in O_2 atmosphere shows the features of both LIB and LOB cathodes. As expected, it is a hybrid cathode.

However, the LOB mechanism may bring some unfavourable side-effects to the LIB part electrochemical performance. If we divide the discharge process into two sections: LIB part (above 3.0 V) and LOB part (below 3.0 V), we can see a decreasing trend in capacity of the LIB part over cycling (Fig. 1d). The discharge of the LIB part is based on Li-ion intercalation, which should be highly reversible. We ascribe this capacity decay to the accumulation of the by-products during LOB discharge and charge. As reported by some literatures,^{13, 14} TEGDME may decompose during lithium-oxygen cycling. Its decomposition products, such as Li_2CO_3 , may deposit on the LCO surface and block the pathway of Li-ion intercalation. This consumption can be further confirmed by monitoring the surface composition during cycling.

Fig. 2 shows the morphology and surface composition evolution of the LCO cathode during cycling. The pristine cathode consists of LCO particles and super P particles, which can be easily identified in the SEM image (Fig. 2a). The existence of Li (Fig. 2e), Co (Fig. 2f) and C (Fig. 2g) is certified by the X-ray photoelectron spectroscopy (XPS). After initial charging to 4.2 V, the morphology does not change so much (Fig. 2b). But the valence of Co partially changes from +3 to +4 according to the XPS of Co 2p. Furthermore, the Li 1s peak disappears after charging, indicative of the extraction of Li^+ from LiCoO_2 .¹⁵ After the 1st discharge to 2.0 V, the discharging products of the lithium-oxygen reaction, such as Li_2O_2 , accumulate on the surface of LCO and super P,¹⁶ which can be confirmed by the SEM image in Fig. 2c. Meanwhile the Co 2p peak can no longer be

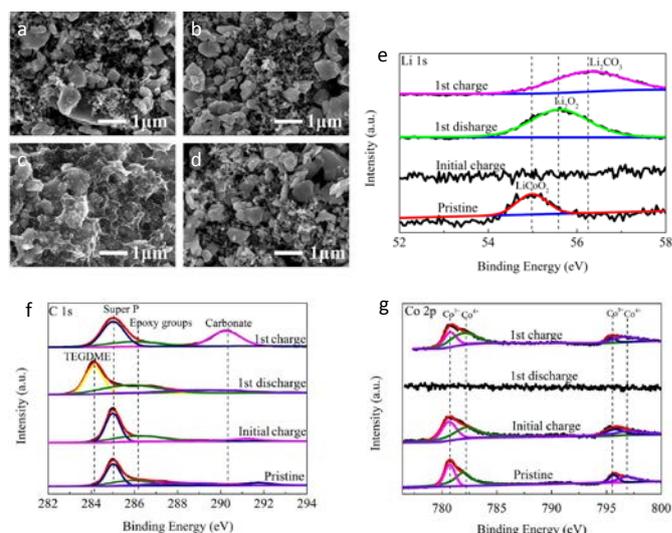


Fig. 2 SEM image of (a) pristine cathode, (b) initial charged cathode, (c) discharged cathode and (d) first charged cathode. XPS spectra of (e) Li 1s, (f) C 1s and (g) Co 2p.

observed, demonstrating that all LCO particles are covered by the discharging products. Interestingly, the Li 1s peak shows up again with the position shifting to higher binding energy, which is the obvious signal of Li_2O_2 .¹⁷ The shift of C 1s peak to lower energy is mainly due to the carbon yielded from the TEGDME residue.¹⁸ When the cell is charged back to 4.2 V, the SEM image (Fig. 2d) shows that most of the coated discharge products are decomposed. The Co 2p peak after the 2nd charge was similar to which collected after 1st charge, showing that the electrochemical reaction is somewhat reversible. But the C 1s and Li 1s spectra indicated a carbonate-type component in the 2nd charged product, which should be the Li_2CO_3 formed from the TEGDME decomposition during cycling as expected from previous report.¹³

In order to reduce the electrolyte decomposition, an ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) (EMITFSI), was tested to replace TEGDME. Unlike TEGDME in which the ether groups are vulnerable under the attack of superoxide radicals, the EMITFSI electrolyte has no any ether groups. It has been reported as a more stable electrolyte than TEGDME.¹⁹ The XPS (Fig. 3a) shows no Li_2CO_3 accumulation on the surface after the first LOB discharge/charge cycle. The discharge/charge curves are displayed in Fig. 3b. As compared with Fig. 1c, we can see that the improvement in cyclability of the LIB part is quite obvious by using EMITFSI. The discharge capacity in the voltage range of above 3.0 V keeps almost unchanged during the initial 20 cycles. The electrolyte decomposition is indeed alleviated by using EMITFSI. However, the fade in capacity of lithium-oxygen part is still very fast. We ascribe this to the incomplete oxidation of Li_2O_2 . In Fig. 3c, the charge capacity in each cycle is always lower than the discharge capacity. As a result, the residual Li_2O_2 in each cycle would accumulate. Unlike the lithium carbonate problem in TEGDME electrolyte, the incomplete decomposition of Li_2O_2 is mainly because of the poor solid-solid contact. The Li_2O_2 particles that are closely touched with the LCO surface can still be oxidized. So the accumulation of Li_2O_2 does not block the Li-ion intercalation pathway, instead it only hinders the oxygen diffusion and the Li_2O_2 formation in the next cycle.

Fortunately, this problem can be solved by changing the operation mode of the battery. Since the LIB discharge and charge potential plateaus at 3.8–4.2 V are higher than the decomposition potential of Li_2O_2 (or even Li_2CO_3),²⁰ running the battery in LIB mode can actually help to decompose the residual LOB discharge products. Therefore, if the battery is just occasionally deep-discharged to 2.0 V, we can still renew the cathode by running a few cycles in solo LIB mode. This idea is proven to be effective in Fig. 3d, e & f. Two shallow discharges with LIB mode were carried out between the deep discharges with “LIB+LOB” mode. As seen in Fig. 3f, in each LIB mode cycle, the charge capacity is always higher than the discharge capacity, indicating that there are some extra oxidation current other than the lithium ion-extraction current, which is likely due to the oxidation of the residual LIB discharge products. As a result, the cycle life of the hybrid battery is prolonged. The “LIB+LOB” capacity is still higher than 220 mAh g^{-1} after 10 times deep discharge and 18 times shallow discharge.

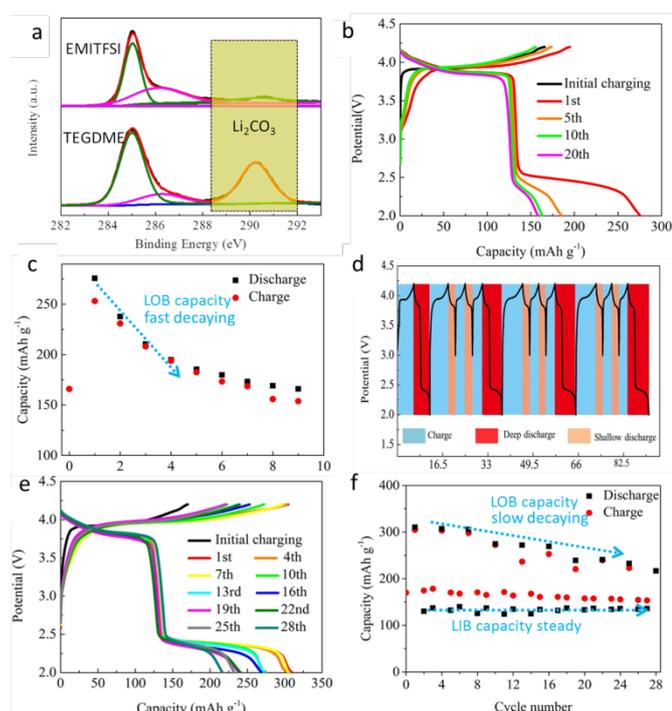


Fig. 3 (a) C 1s XPS of the LCO cathodes with different electrolytes after the first LOB discharge/charge cycle; (b,c) Charge /discharge curves of the LCO cathode with EMITFSI electrolyte cycled in the range of 2.0–4.2 V; (d-f) The “cathode renewing” mode operation, also with EMITFSI electrolyte: (d) Potential vs. time curve, (e) Charge and discharge curves of the deep discharge cycles, (f) Discharge capacity variation.

Considering the LOB mechanism, operating the hybrid battery with LIB mode at 3.8–4.2 V has some similarities with the LOB charging process at constant potential. It will only renew the cathodes with electrolytes which are stable at high potential in oxygen atmosphere.²¹ Operating the TEGDME cathode with LIB mode for a long time may cause serious electrolyte decomposition and Li_2CO_3 accumulation, and hence be harmful to the cathode.

Almost everyone has the experience that the battery has no power when an important phone is calling. Such situation is more serious if an electric vehicle is out of power and there are still a few

miles to reach the charging station. The LCO-Li battery demonstrated in this paper may give the users some chances to solve these occasional troubles by flowing some air to the battery. It should be pointed out that there are some other challenges on the full cell level, such as the anode protection, the air-filtering and the gas diffusion channel design. For example, a corrugated aluminum foil can be used as the cathode current collector with oxygen channels.²² Our results only show that the cathode chemistry is workable.

Conclusions

In summary, our study demonstrates the possibility to enlarge the capacity of conventional LIB cathodes with collaboration of LOB. The hybrid cathode can also be used as normal LIB cathode with good cyclability. To do so, using an electrolyte with high stability, e.g., ionic liquid, is very desirable. Running the battery with LIB mode may also help to promote the cycle life of the LOB mode by slowly oxidizing the LOB discharge product residues. Although there are still challenges to make a practical LIB/LOB hybrid full cell, this strategy gives us a potential range-extending technique for electric vehicles or emergency power source for mobile electronic devices.

Acknowledgements

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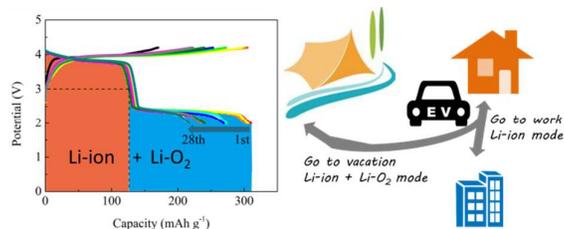
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Table of Contents Entry

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The capacity of a conventional LiCoO₂ cathode is greatly enhanced with Li-oxygen mechanism.