Preparation of Delithiated Li$_x$CoO$_2$ as Cathode Material for High Power Densities Primary Lithium Batteries

Ling-Ling Xie[1], Chao Li[1], Xiao-Yu Cao[1,*], Da-Wei Song[2], Jie-Jie Zhang[1], Hai-Lian Wu[1], Peng Ge[1], Ling-Bo Qu[1]

[1]School of Chemistry and Chemical Engineering, Henan University of Technology, Zhengzhou 450001, People's Republic of China
[2]School of Materials Science and Engineering, Tianjin University of Technology, Tianjin 300381, People's Republic of China
[*]E-mail: caoxy@haut.edu.cn

The dethiliated Li$_x$CoO$_2$ powder as cathode material for primary lithium batteries was prepared through a chemical delithiation reaction of LiCoO$_2$ powder with sulfuric acid solution. By using atomic absorption spectroscopy and potentiometric titration, the chemical formula for the dethiliated Li$_x$CoO$_2$ is determined to be Li$_{0.33}$CoO$_2$. XRD measurement reveals the lattice parameters of a = 2.8107 Å, c = 14.4252 Å, and V = 98.69 Å^3 based the hexagonal layered structure with $R\bar{3}m$ space group for the dethiliated Li$_x$CoO$_2$ powder. The intensities of diffraction peaks of the dethiliated Li$_x$CoO$_2$ powder are lower than those of LiCoO$_2$ powder, and the c-axis is expanded upon the Li$^+$ extraction from LiCoO$_2$. SEM analysis discloses the smaller particles with more evenly distributed dimension for the dethiliated Li$_x$CoO$_2$ powder. The galvanostatic discharge test shows that the Li/Li$_x$CoO$_2$ cells using LiClO$_4$ as electrolyte solution display excellent rate capability at different cutoff discharge voltages, where the capacities of 112.02 and 889.14 mAh g^{-1} can be acquired at the high current rates of 180 mA g^{-1} with the cutoff discharge voltage of 2.0 and 0.5 V, respectively. Moreover, the Li/Li$_x$CoO$_2$ cells also exhibit good storage performance and accepted low temperature performance, indicating that the dethiliated Li$_x$CoO$_2$ can be used a potential cathode material for high power densities primary lithium batteries.

1. INTRODUCTION

Primary lithium batteries (PLBs) employing metal lithium as anodes play a very important role because of their various applications such as camera, electrical lock, electronic counter, smart meter, remote monitoring system, emergency power source, memory back-up, military field and implantable

medical devices [1–7]. As qualified PLBs, they must demonstrate the following characteristics such as high energy densities, high power densities, high reliability, excellent safety, and long life. For a concrete application, the requirements for PLBs are not the same. For instance, in the important military application such as torpedo propulsion, the most important requirement for electrochemical batteries is high power densities. Because torpedo is used as the important weapon to attack ships in the sea combat, the time for detecting, identifying and locating target ships accounts for ninety-nine of the whole process, and only one percent of the time is used to attack. It is very obvious that development of high-performance batteries, especially high power densities batteries for torpedo propulsion, is very crucial.

At the present, there are two main power supplies for torpedo and small submersibles, namely, Al/AgO and Li/SOCl$_2$ batteries. In Al/AgO system, the cathode, anode and electrolyte solution are the mixture of AgO and Ag$_2$O, Al alloy and an aqueous solution of KOH or NaOH, respectively [8–10]. The Al/AgO battery is capable of delivering high power output from a small volume. However, the main disadvantage of Al/AgO system is that the viscosity of the electrolyte solution gradually increases with the decrease of concentration of KOH or NaOH solution and the increase of concentration of KAlO$_2$ or NaAlO$_2$, which engenders low ion conductivity for electrolyte solution. Thus, Al/AgO battery cannot always maintain a high discharge current during the torpedo propulsion. Up to now, there seems to be no a very good solution for this problem in Al/AgO battery. Li/SOCl$_2$ battery displays high energy density but poor high rate discharge performance [11], which restricts their high power output applications. Besides, the undissolved discharge products such as S and LiCl [12] during the discharge can deposit on the surface of porous carbon electrode, which will prevent the further reduction reaction of SOCl$_2$ [13,14].

Lithium ion batteries (LIBs) have undoubtedly achieved great success to assist in the development of portable electronic devices in terms of their high discharge voltage and excellent cycling life, and also demonstrate a potential application in military field. However, practical cathode materials for LIBs such as LiCoO$_2$, LiMn$_2$O$_4$, LiNi$_x$Co$_{1-x}$O$_2$ LiNi$_x$Mn$_y$Co$_{1-x-y}$O$_2$, and LiFeO$_4$ are all in the discharged state and cannot be directly discharged. In order to be directly discharged, LIBs must undergo the formation procedure prior to use, which is very troublesome in the military applications. Firstly, LIBs may not be immediately used and need to be temporarily charged once they are used. Secondly, approximative lithium intercalation potentials of graphite and metal lithium may lead to the growth of lithium dendrite on graphite surface during the process of LIBs′ formation [15], which consequently incites soft short circuit, hard short circuit or explosion. It is obvious that the high power densities and high reliability are indispensable for electrochemical batteries powering torpedo propulsion. Therefore, preparation of delithiated Li$_x$MO (M: transition metal elements) electrode materials with the charged state as a positive electrodes for PLBs which do not require formation procedure and can be directly discharged in military applications is a novel idea.

Based on this idea, we introduce a facile chemical delithiation method for preparing the delithiated Li$_x$CoO$_2$ powder as cathode for PLBs. Although there have some reports pertaining to the dethiliated Li$_x$CoO$_2$ [16–21], the research emphases are mostly placed on the structural evolutions and mechanism exploration during the intercalation/deintercalation of Li$^+$ in/from LiCoO$_2$. To the best of our knowledge, as of today, there is no report with respect to employing the dethiliated Li$_x$CoO$_2$ as

cathode for PLBs. At the present study, the structure, morphology, and electrochemical performances of the as-prepared Li_xCoO_2 powder, including the rate capability, storage performance and low temperature performance were extensively investigated.

2. EXPERIMENTAL

Commercial $LiCoO_2$ (LCO) powder from China was used as the pristine material for the preparation of the dethiliated Li_xCoO_2 (DLCO) powder. Similar to the previous preparation method described in literatures [18,19], chemical delithiation of LCO powder was carried out by stirring a suspension of 2.5 g of LCO powder in 35 ml redistilled water, and then 4 ml concentrated sulfuric acid (H_2SO_4) was slowly added in the mixture dropwise under magnetic stirring. After being stirred at room temperature for 24 h, the product was filtered and washed several times with redistilled water followed by absolute ethanol, and thereafter dried at 70 °C in a vacuum drying chamber for 12 h to obtain the final DLCO powder. The ideal reaction scheme was described as below:

$$2\,LiCoO_2\,(s) + 2(1\text{-}x)\,H^+\,(aq.) = 2\,Li_xCoO_2\,(s) + 2(1\text{-}x)\,Li^+\,(aq.) + (1\text{-}x)H_2\,(g)$$

Lithium contents of LCO and DLCO powders were tested by using Atomic absorption spectrometer (AAS, Thermo Scientific ICE 3300, USA), and cobalt contents of LCO and DLCO powders were determined by means of potentiometric titration (Mettler-ToledoT50 potentiometric titration, Switzerland). Surface areas teat was performed on a surface area analyzer (V-Sorb 4800P, Beijing Gold APP, China). The powders were degassed at 150 °C for 3 h in vacuum prior to measuremrnts. The specific surface areas were calculated using Brunauer-Emmett-Teller (BET) method. X-ray diffraction (XRD) analysis was carried out on Rigaku D/MAX-2500 diffractometer (Rigaku, Japan) with Cu Kα radiation (λ = 1.54056 Å). The morphological feature of the LCO and DLCO powders was observed on the SEM-JSM-6510LV (JEOL, Japan). The cathode films were composed of DLCO powder, acetylene black and polytetrafluoethylene emulsion binder (60 wt. %, Xinxiang Yilida Batteries Materials Co., Ltd, China) at a weight ratio of 80:10:10. The stainless-steel meshes were used as the current collectors. The CR2016 type coin cells were assembled with pure lithium foil as an anode and Asahi Hipore membrane as the separator. 1 mol dm^{-3} $LiClO_4$ (lithium perchlorate, LPC) and 1 mol dm^{-3} $LiPF_6$ (lithium hexafluorophosphate, LHFP) dissolved in ethylene carbonate (EC) and dimethyl carbonate (DMC) solution (v/v of 1:1, provided by Zhangjiagang Guotai-Huarong New Chemical Materials Co., Ltd, China) were used as the electrolyte solutions, respectively. For the sake of convenience, both the electrolyte solutions were referred to as LPC and LHFP, respectively. All the CR2016 type coin cells were assembled in a high purified argon-filled dry box (JMS-3, Nanjing Jiumen Automation technology Co., Ltd, China). Galvanostatic discharge tests were performed on a multi-channel CT-3008W-5V5mA-S$_4$ battery system (Shenzhen Neware Electronics Co., Ltd, China) with different current densities at the cut-off voltages of 2 V and 0.5 V at 25 °C. The discharge measurements at other temperatures of 15, 10, 5 and 0 °C were performed in a temperature cooling liquid circulating pump (DLSB-5/20, Zhengzhou Greatwall Scientific Industrial and Trade Co., Ltd, China). The CR2016 type coin cells wrapped by plastic pockets were immersed in cooling liquid composed of glycerol and water with volume ratio of 70:30. In order to examine the influence of

storage time on the electrochemical performance of the Li/DLCO cells, the fresh assembled Li/DLCO cells were stored at room temperature in air for different times.

3. RESULTS AND DISCUSSION

According to AAS and potentiometric titration testing results for lithium and cobalt contents, the chemical formulae for LCO and DLCO are $LiCoO_2$ and $Li_{0.33}CoO_2$. The XRD patterns of LCO and DLCO powders are presented in Fig. 1.
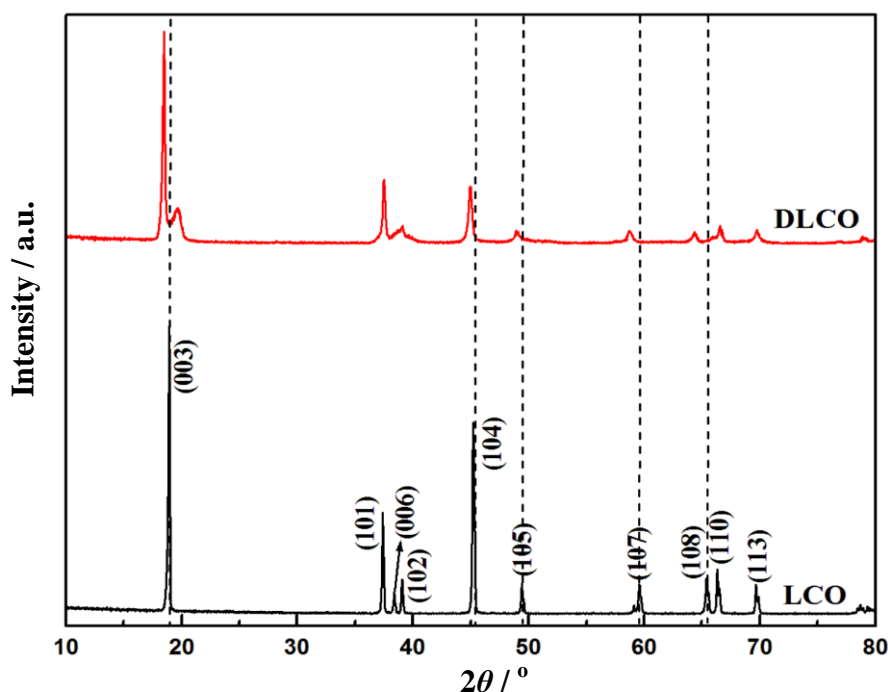

Figure 1. XRD patterns of LCO and DLCO powders.

Table 1. The lattice parameters of LCO and DLCO samples

Samples	a (Å)	c (Å)	c/a	V (Å^3)
LCO	2.8142	14.0497	4.992	96.36
DLCO	2.8107	14.4252	5.132	98.69

As seen in Fig.1, all the characteristic diffraction peaks of LCO powder have been labeled with miller indices and correspond to a well-defined hexagonal layered structure with $R\bar{3}m$ space group. Compared with LCO powder, DLCO powder displays weaker and broader Bragg diffraction peaks. In addition, the position of Bragg diffraction peaks of DLCO powder corresponding to (003), (104), (105), (107), and (108) csrystal planes slightly shift to lower angles, which is consistent with the previous report of Tian [20]. The lattice parameters of LCO and DLCO powders are calculated by means of least-squares method in terms of hexagonal structure with $R\bar{3}m$ space group and listed in Table 1. It is found that lattice constant a (2.8107 Å) of DLCO is smaller than that (2.8142 Å) of LCO,

whereas lattice constant c (14.4252 Å) of DLCO is larger than that (14.0497 Å) of LCO. Meanwhile, value of c/a (5.132) and cell volume (98.69 Å^3) for DLCO are higher in comparison with LCO. The evolution tendency of lattice constant a and c/a upon delithiation of LCO is in accordance with literatures [17, 19, 20]. This may be duo to the fact that shielding effect of O^{2-} on Li$^+$ is weakened in DLCO compared to LCO, which leads to the increase in the repulsion between the oxygen layers and the c-axis expansion [21]. On the whole, DLCO powder still maintains the good layered crystal structure that lays the foundation for Li$^+$ intercalation.
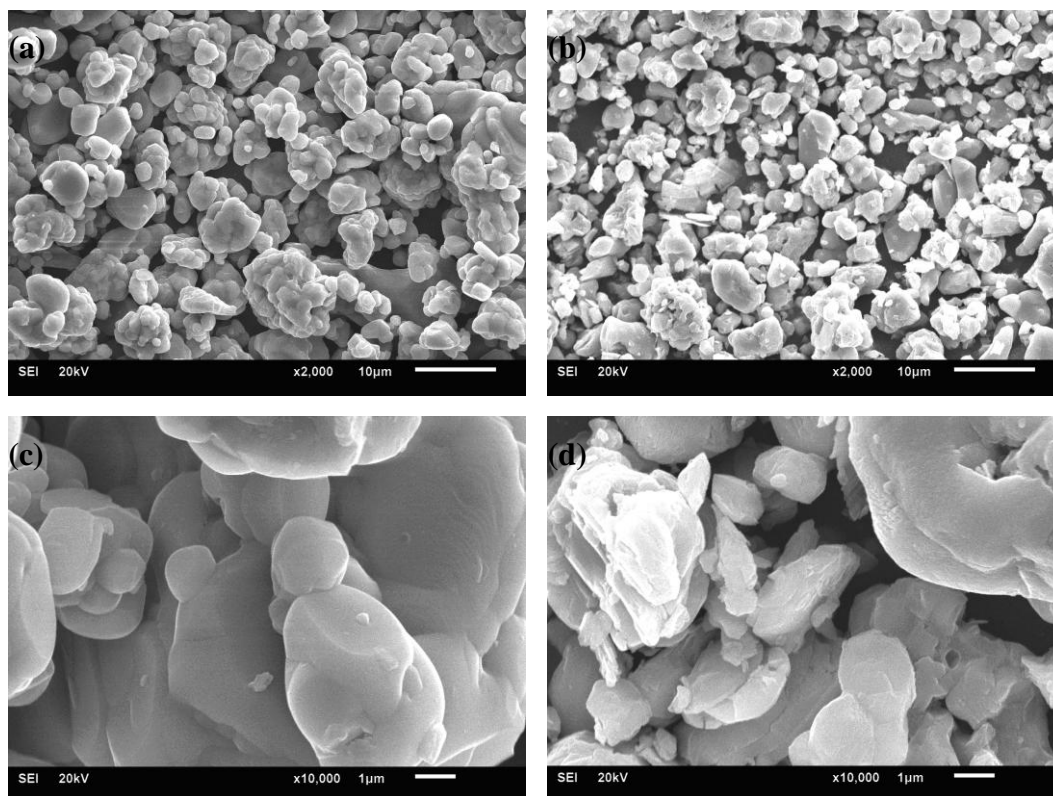

Figure 2. Different magnified SEM images of LCO (a and c, ×2000) and DLCO (b and d, ×10000) powders.

Fig. 2 presents a set of the different magnified SEM micrographs of LCO and DLCO powders. It is easily found that LCO powder exhibits well-developed and smooth particles, indicating a high crystallinity. With respect to DLCO powder, the particle sizes become somewhat smaller and large particles are split into smaller particles, hinting that more homogenized particles can be obtained by this chemical lithiation method. BET test results show that the specific areas of LCO and DLCO powders are 0.0883 and 0.101 g cm^{-2}, respectively, which is well agreeable to the SEM analysis.

Fig. 3 represents the galvanostatic discharge curves of the Li/DLCO cells, obtained at various current rates in different electrolyte solutions. As illustrated in Fig. 3a, the discharge profile of the Li/DLCO cell using LPC as electrolyte solution exhibits the smooth plateau at around 2.9 V with a discharge capacity of 132.65 mAh g^{-1} at the current rate of 30 mA g^{-1}. With increasing of the current rates, the discharge plateaus of the Li/DLCO cells show a slight drop. However, the decline of

discharge plateaus of the Li/DLCO cells is not obvious at the high current rates, indicating an excellent rate capability for the Li/DLCO cells.
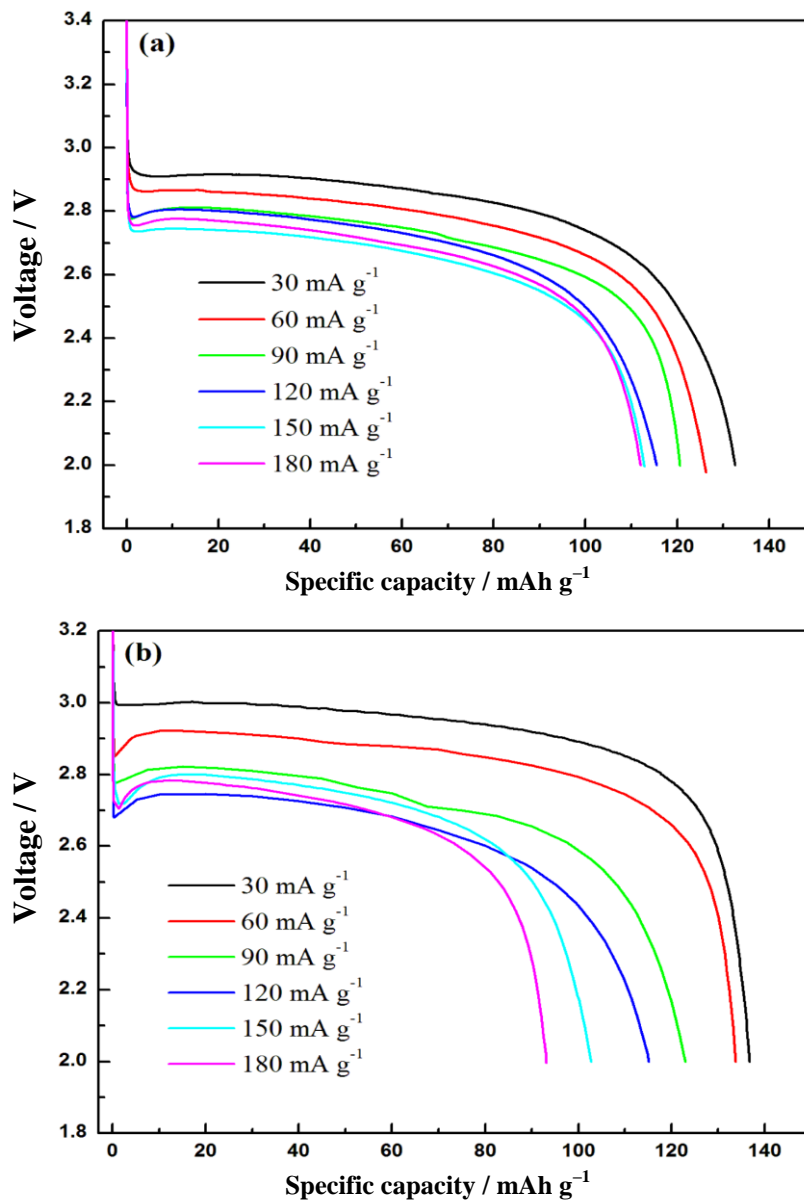

Figure 3. The discharge curves of the Li/DLCO cells using different electrolyte solutions at different current rates with a cutoff voltage of 2.0 V. (a) LPC, (b) LHFP.

The Li/DLCO cells display the discharge capacities of 126.27, 120.69, 115.56, 112.85, and 112.02 mAh g^{-1} at the current rates of 60, 90, 120, 150, and 180 mA g^{-1}, respectively. In the case of the Li/DLCO cells using LHFP as electrolyte solution, the Li/DLCO cell manifests the smooth plateau at around 3.0 V with a discharge capacity of 136.79 mAh g^{-1} at the current rate of 30 mA g^{-1}, which is slightly higher than that of the Li/DLCO cell using LPC as electrolyte solution. However, with intensifying of electrode polarization, discharge plateaus of the Li/DLCO cells begin to decline dramatically, and accordingly the lengths of discharge plateaus are shortened. The Li/DLCO cells

using LHFP as electrolyte solution yield the discharge capacities of 133.83, 123.03, 115.18, 102.71, and 93.15 mAh g^{-1} at the current rates of 60, 90, 120, 150, and 180 mA g^{-1}, respectively. In addition, the Li/DLCO cells using LHFP as electrolyte solution demonstrate obvious voltage hysteresis in the beginning of discharge, especially at high current rates. As far as this reason is concerned, it needs the further investigation. In overall terms, the rate capability of the Li/DLCO cells using LPC as electrolyte solution is slightly better than that of the Li/DLCO cells using LHFP as electrolyte solution. According to the report of Akimoto [19], the Li–O and the O–O′ distances in LiO_6 octahedron for DLCO are longer than those in LiO_6 octahedron for LCO, which brings about an apparent elongation of the LiO_6 octahedron in the *c*-axis direction for DLCO and accordingly contributes to a positive effect on Li^+ diffusion. This is perhaps one of the reasons for the Li/DLCO cells to be demonstrated excellent rate capability.
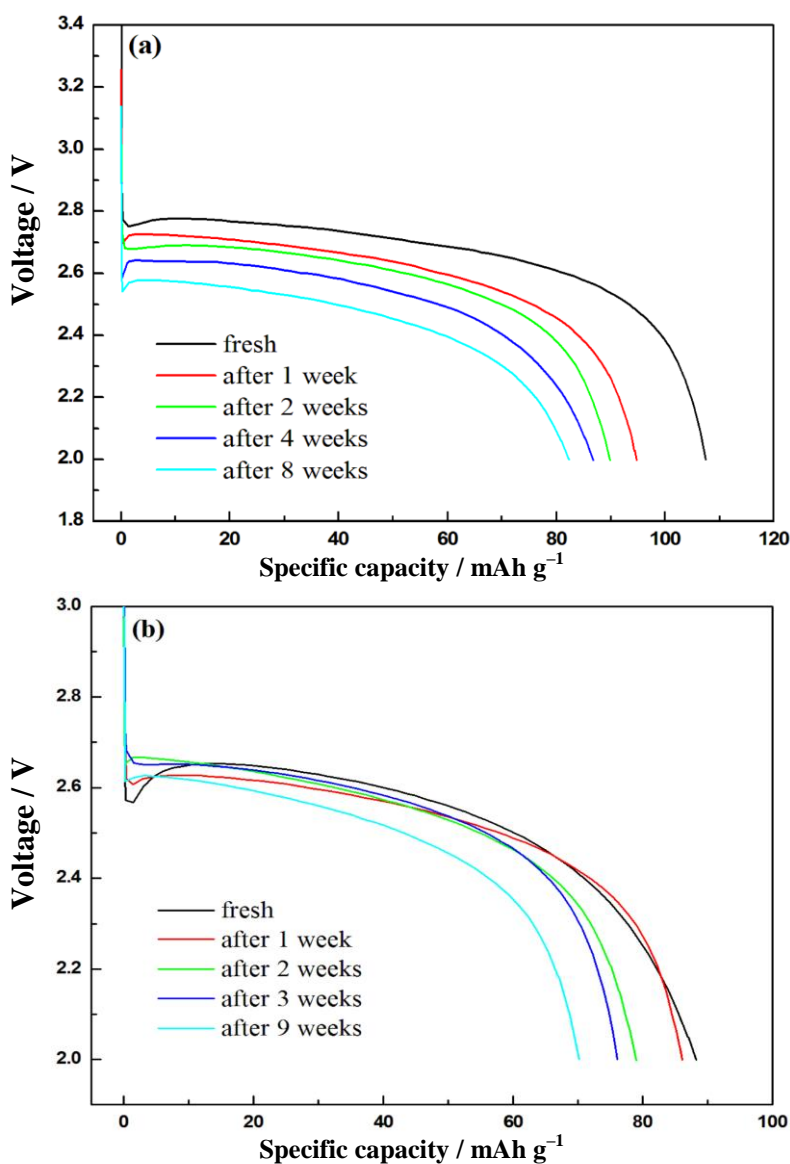

Figure 4. The discharge curves of the Li/DLCO cells using different electrolyte solution at current rate of 180 mA g^{-1} for different storage times. (a) LPC, (b) LHFP.

The capacity changes of the Li/DLCO cells at the current rate of 180 mA g^{-1} during storage in air are shown in Fig. 4. In the case of the fresh Li/DLCO cells using LPC and LHFP electrolyte solutions, the discharge capacities are 112.02 and 93.15 mAh g^{-1}, respectively. After 1 week of storage, their discharge capacities drop to 94.8 and 86.08 mAh g^{-1}, respectively. As seen from Fig. 4, the discharge voltage platforms of stored Li/DLCO cells are lower in comparison with those of the fresh Li/DLCO cells. With prolonging of the storage time, the discharge capacities of the Li/DLCO cells all decrease. The discharge capacity of the 8-week Li/DLCO cell using LPC as electrolyte solution is 82.36 mAh g^{-1} while the 9-week Li/DLCO cell using LHEP as electrolyte solution only delivers the discharge capacity of 70.21 mAh g^{-1}. The storage time testing indicates that capacity decay of the Li/DLCO cells takes place regardless of employing LPC or LHEP as electrolyte solution, which may be attributed to the thermal instability of DLCO [22, 23]. The previous reports show that the reaction of DLCO with electrolyte and the liberation of O_2 gas from DLCO lattice occur at above 160 ^{o}C [22, 23]. However, according to description of Yamaki [22], as the Li content decreases, the exothermic heat increases and the exothermic peak shifts toward the lower temperature. Perhaps, the reaction of DLCO with electrolyte and decomposition of DLCO is easy in this Li composition ($Li_{0.33}CoO_2$), which largely stems from the poor interfacial compatibility between the DLCO electrode and the electrolyte solution. Therefore, the Li/DLCO cells are preferred to fabricate the dry-charged type and injected into the electrolyte solution only when they are used.
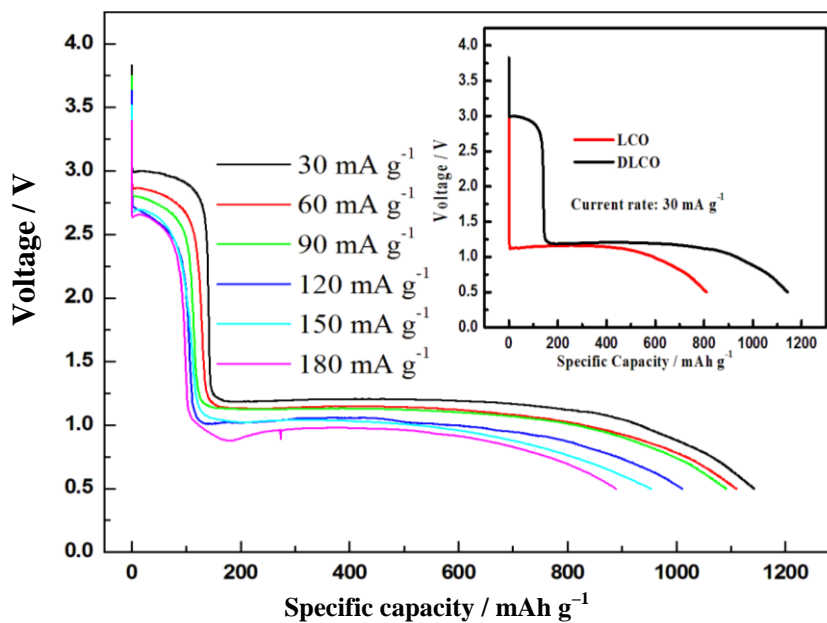

Figure 5. The discharge curves of the Li/DLCO cells using LPC as electrolyte solution at different current rates with a cutoff voltage of 0.5 V.

Fig. 5 shows the discharge curves of the Li/DLCO cells using LPC as electrolyte solution at different current rates with a cutoff voltage of 0.5 V. As shown in Fig. 5, the Li/DLCO cell demonstrates a long discharge plateau at around 1.2 V apart from plateau at around 2.9 V at the current rate of 30 mA g^{-1}, which should be ascribed to the reduction of Co^{3+}. With the increase in the current

rate, the discharge plateaus slightly begin to decline and accordingly length of plateaus is shortened. The Li/DLCO cells deliver the discharge capacities of 1142.59, 1109.86, 1091.18, 1010.65, 953.59 and 889.14 mAh g^{-1} at the current rates of 30, 60, 90, 120, 150, and 180 mA g^{-1}, respectively, indicating an excellent rate capability. The inset in Fig.5 is a view of the discharge curves of the Li/LCO and Li/DLCO cells at the current rate of 30 mA g^{-1} with a cutoff voltage of 0.5 V. It is clearly seen that the Li/LCO cell also displays a long discharge plateau at around 1.2 V while discharge capacity of Li/LCO cell (810.41 mAh g^{-1}) is lower than that of Li/DLCO cell (1142.59 mAh g^{-1}). The difference in their discharge capacities mainly originates from the absence of discharge plateau at around 2.9 V for Li/LCO cell. In fact, the discharge capacity of Li/LCO cell is only about 0.311 mAh g^{-1} at the current rate of 30 mA g^{-1} if the cutoff voltage is set at 2.0 V, which confirms that Li$^+$ can not be intercalated in LCO with full lithium state at the higher voltage above 3.0 V. That is, LCO with full lithium state can not be discharged and only first be charged and then discharged.
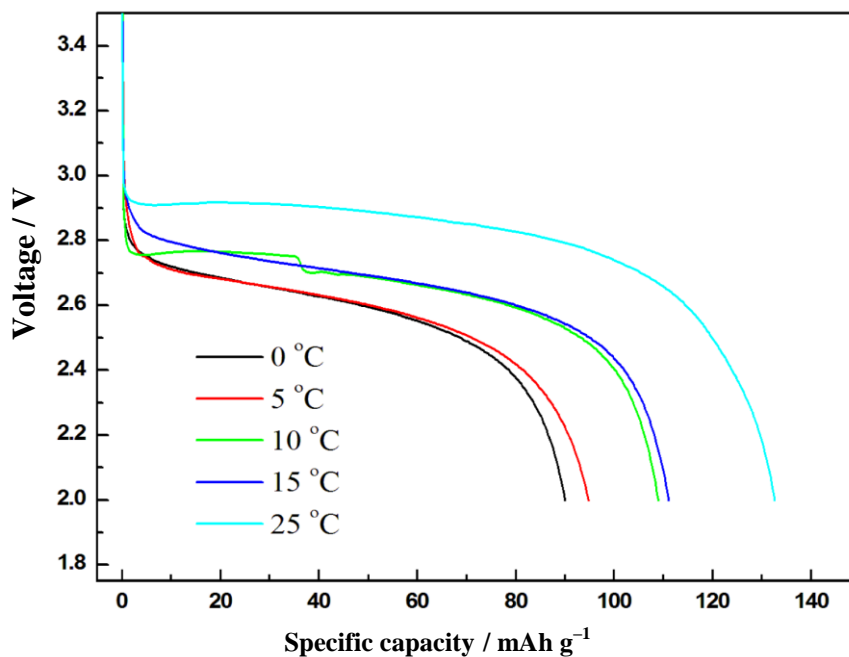

Figure 6. The discharge curves of the Li/DLCO cells using LPC as electrolyte solution at current rate of 30 mA g^{-1} at different temperatures.

It should be pointed out that PLBs should work effectively at low temperatures, especially for the practical application in winter or high latitudinal areas. Fig. 6 illustrates the temperature dependence of the Li/DLCO cells′ capacities under a current rate of 30 mA g^{-1} at 25, 15, 10, 5 and 0 °C, respectively. It can be seen that all the capacities of Li/DLCO cells drop with the temperature decreasing. The discharge capacities of 132.65, 111.13, 108.99, 94.83 and 90.06 mAh g^{-1} can be achieved at 25, 15, 10, 5 and 0 °C, respectively. It is well acknowledged that the kinetics of Li$^+$ transport from the electrolyte solution to the bulk electrode will be restricted at low temperature. Considering this fact, low temperature performance of the Li/DLCO cells in this work is also accepted.

In sum, all of the above results show that as-prepared DLCO powder is a very promising high power densities cathode material for PLBs, especially for the important military applications.

Certainly, the shelf life and low temperature performance of the Li/DLCO cells still need to be further improved. However, in any case, it is a useful attempt to employ DLCO as cathode in PLBs. So far, the work of improving the electrochemical performances of DLCO is under way.

4. CONCLUSIONS

The DLCO powder has been successfully prepared by the chemical delithiation method in this work. The structure, morphology and electrochemical performances of the DLCO powder were systematically investigated. The XRD results reveal that the *c*-axis of DLCO powder is expanded significantly compared to the LCO powder but DLCO powder still preserves good layered structure. The rate capability and storage performance of the Li/DLCO cells using LPC as electrolyte solution are better than those of the Li/DLCO cells using LPC as electrolyte solution, and the low temperature performance of the Li/DLCO cells is also accepted. When the cutoff discharge voltage is lowered to 0.5 V, the capacities of the Li/DLCO exceed 800 mAh g^{-1} even if operated in high current rate of 180 mA g^{-1}. The excellent rate capability of the Li/DLCO cells can be attributed to the good layered crystal structure, expanded lattice constants, smaller particles with more uniform dimension. Thus, the proposed DLCO powder as cathode material not only demonstrates a potential application in military field but also provides a novel idea in extending to the preparation of other dethiliated cathode materials such as $Li_xMn_2O_4$, $Li_xNi_{0.8}Co_{0.2}O_2$, $Li_xNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ and Li_xFePO_4 for PLBs.

References

1. J. Chen, F. Cheng, *Acc. Chem. Res*. 42 (2008) 713.
2. R. Yazami, A. Hamwi, K. Guérin, Y. Ozawa, M. Dubois, J. Giraudet, F. Masin, *Electrochem. Commun*. 9 (2007) 1850.
3. M. Duboisa, K. Guérin, W. Zhang, Y. Ahmad, A. Hamwi, Z. Fawal, H. Kharbache, F. Masin, *Electrochim. Acta* 59 (2012) 485.
4. O. Crowther, L.S. Du, D.M. Moureau, I. Bicaku, M. Salomon, J.W. Lawson, L.R. Lucente, K. Mock, J.P. Fellner, L. G. Scanlon, *J. Power Sources* 217 (2012) 92.
5. J. Giraudet, C. Delabarre, K. Guérin, M. Dubois, F. Masin, A. Hamwi, *J. Power Sources* 158 (2006) 1365.
6. Q. Zhang, S. D'Astorg, P. Xiao, X. Zhang, L. Lu, *J. Power Sources* 195 (2010) 2914.
7. X.Y. Cao, L.L. Xie, H. Zhan, Y.H. Zhou, *Inorg. Mater*. 44 (2008) 886.
8. Q. Li, N.J. Bjerrum, *J. Power Sources* 110 (2002) 1.
9. K.J. Gregg, M.J. Niksa, *Proceedings of the Symposium on Autonomous Underwater Vehicle Technology*, 1992, p. 181.
10. E.G. Dow, *The 17th Annual Battery Conference on Applications and Advances*, 1996, p. 61.

11. S. Wang, J. Zeng, H. Zhang, H. Zhao, W. Liu, *Int. J. Electrochem. Sci*. 7 (2012) 11264.
12. A. N. Dey, *J. Electrochem. Soc*. 123 (1976) 1262.
13. A. N. Dey, P. Bro, J. Electrochem. Soc. 125 (1978) 1574.
14. Y. L. Zhang, C. S. Cha, *Electrochim. Acta* 37 (1992) 1207.
15. T.F. Yi, L.J. Jiang, J. Shu, C.B. Yue, R.S. Zhu, H.B. Qiao, *J. Phys. Chem. Sol*. 71 (2010) 1236.
16. C.H. Chen, B.J. Hwang, C.Y. Chen, S.K. Hu, J.M. Chen, H.S. Sheu, J.F. Lee, *J. Power Sources* 174 (2007) 938.
17. N. Imanishi, M. Fujiyoshi, Y. Takeda, O. Yamamoto, M. Tabuchi, *Solid State Ionics* 118 (1999) 121.
18. Q. Lin, Q. Li, K.E. Gray, J.F. Mitchell, *Cryst. Growth Des*. 12 (2012) 1232.
19. Y. Takahashi, N. Kijima, K. Dokko, M. Nishizawa, I. Uchida, J. Akimoto, *J. Solid State Chem*. 180 (2007) 313.
20. S.J. Yan, X. Liu, W.H. Qiu, Y.M. Tian, *J. Univ. Sci. Technol. B*. 29 (2007) 45.
21. S.J. Yan, M.G. Zhang, Y.M. Tian, G. Sun, W.H. Tian, *Chin. J. Inorg. Chem*. 25 (2009) 491.
22. Y. Baba, S. Okada, J. Yamaki, *Solid State Ionics* 148 (2002) 311.
23. Y. Wang, J. Jiang, J.R. Dahn, *Electrochem. Commun*. 9 (2007) 2534.