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In order to improve the electrochemical performance of Li-ion batteries, especially at the elevated temperature, we, for the first time, modifies the separator with the oxygen plasma method. The physical characterizations including the contact angle measurement and Fourier Transform Infrared Spectrometer analysis indicate that the O_2 plasma treatment can generate oxygen-containing groups on the surface of separator. The Li-ion battery using the O_2 plasma modified separator shows superior performance with higher initial capacity (135.7 $mAh{\cdot}g^{-1}$) and significantly improves cycling stability (maintaining 96.98% of its initial discharge capacity after 100 cycles), because of the presence of oxygen containing groups such as carbonyl and hydroxyl on the surface of the separator after the plasma modification. Moreover, when cycled at 1 C, the discharge capacity of Li-ion battery using normal separator is only 86.7 $mAh{\cdot}g^{-1}$, the Li-ion battery with the modified separator shows a much higher discharge capacity of 135.7 $mAh{\cdot}g^{-1}$, indicating an excellent rate performance owing to the electrostatic repulsion between electronegative oxygen functional groups on the surface of modified separator. When tested at the elevated temperature (55 °C), the capacity retention of the cell using the modified separator is much higher (85.39%) than that of the normal separator (53.69%). All the tests show that the oxygen functional groups on the surface of the separator by the oxygen plasma modification play a critical role in improving the electrochemical performance of the Li-ion battery.

1. Introduction

Li-ion batteries (LIBs) play an increasing role as a potential power source for electric vehicles (EV) and hybrid electric vehicles in the future[1-3], due to the fossil fuel crisis. As one of the most promising cathode materials for rechargeable lithium ion batteries, spinel $LiMn_2O_4$ composite materials has the superior characteristics of low cost, abundance, environmental affinity, low safety hazard and good rate capability, which are the key factors for a large scale EV battery [4-8]. Among the various components in Li-ion batteries, separators widely used in the commercial lithium-ion batteries made from polyolefins and polymer matrices in the gel electrolytes play a critical role in all batteries [9-10]. The separators act as a spacer between the positive and negative electrodes to prevent internal short-circuit[11-13]. However, the normal separator usually has low melting points and inferior mechanical strengths leading to the dimensional changes at elevated temperatures or the damage by lithium dendrite commonly formed at high rates or long-term cycling [14-15]. Especially, the low thermal stability of the separator gives rise to high thermal shrinkage around their melting or softening temperature [16-17]. In order to solve the disadvantages of the separator, novel separators with different components or modifications on the commercial separators have been widely reported. For examples, lots of organic materials were used to prepare novel separator has been reported, such as polyvinyl chloride[18], polyacrylonitrile[19], poly(methylmethacrylate)[20] and so on. But, the separators still have low melting points and lack enough mechanical strength or ionic conductivity for their application in commercial lithium ion batteries, which lead to poor affinity with the electrolyte, thus adversely affect the overall performances of the LIBs. On the other hand, the use of inorganic layers into the separator matrix has been extensively reported because of their excellent thermal stability and electrolyte wettability[21-22]. Embedding the inorganic layers, such as Al_2O_3, MgO, TiO_2, SnO_2, and SiO_2, into the separator matrix is an effective way to improve the properties of separator [23-25], which shows improved performances of the LIBs such as long-term stability, high capacity, high-power, rate capacity, high-temperature and low-temperature performances. Though, this method can to a large degree improve the performance of the separator, it involves the additional use of inorganic materials which need much energy consumption and long synthesis time[26-28], and it did not fundamentally solve the safety issues [29-30], hindering the large commercial application. Therefore, it is in significant demand to find a novel and efficient approach to modify the separator, expecting to have good mechanical strength, excellent affinity to the electrolyte and even ideal high temperature performance.

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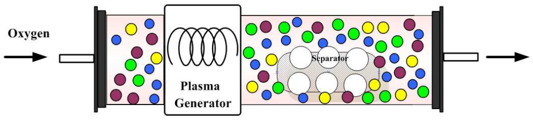
In this work, we, for the first time, reported a novel strategy to modify the commercial separator through the plasma surface treatment. Plasma, as one of the four fundamental states of matter, has very unique properties. In plasma environment, the positive and negative ions are completely free showing a high chemical activity. In this study, the normal separator (Celgard 2400, thickness 25 um) was modified by the oxygen plasma to enhance the surface energy of the separator and the compatibility with electrodes, which is vital for the superior electrochemical performance for commercial applications of lithium ion batteries. The oxygen functional groups were introduced onto the surface of separator by the oxygen plasma treatment through the cross-linking reaction between oxygen and carbon species on the surface of the polypropylene [31]. During the plasma treatment, the C-C and C-H bonds were broken and the oxygen functional groups such as –C=O, -OH were probably generated between the broken bond sites [32]. After the plasma treatment, the separator shows improved wettability with electrolyte to obtain high conductivities and satisfactory battery performances.

A plasma-enhanced tube furnace was used to prepare O_2 plasma treated separator, as illustrated in Scheme 1, which mainly consists of a vacuum pump, a plasma generator, and a pressure probe. The separator modified with the high efficiency oxygen plasma method is firstly used into the Li/$LiMn_2O_4$ batteries, which show excellent electrochemical performance in terms of capacity and cycling performance, especially at the elevated temperature for the Li-ion batteries.



Scheme 1. Illustration on the separator modified by the oxygen plasma method

2. Experimental Section

2.1. Preparation of the separator modified by oxygen plasma. The separator modified by oxygen plasma was prepared by a simple plasma treatment: firstly, the normal separator (Celgard 2400) was put in the plasma generator chamber. The oxygen gas was introduced into the reactor for about 20 min to remove the air in the tube. Then the pressure was controlled under 50 Pa. During the process, the applied RF power was set at 100 W. The plasma treatment time was from 30 to 90 seconds in order to control the extent of modification on the surface of separator. When plasma treatment time was beyond 90 second, the separator was easily destroyed, on the other word, which is over-modified.

2.2. Preparation of $LiMn_2O_4$ cathode, Cell Fabrication and Electrochemical Analysis. The spinel $LiMn_2O_4$ used as the cathode material is prepared by the conventional solid state method [33]. Lithium hydroxide as a lithium source and manganese sources (MnO_2-EMD) were used as starting materials. The two reagents were prepared with a stoichiometric molar ratio of 1:2, then ball-milled for 2 h. The mixture calcined at 800 ℃ for 8 h in air to obtain $LiMn_2O_4$. The positive electrodes were made by coating a slurry of the active material, Super-P carbon black, and polyvinylidene fluoride (PVdF) binder in N-methyl-2-pyrrolidone (NMP) at a weight ratio of 80:10:10 onto an aluminum foil, which was then dried at 120 ℃ for 12 h in a vacuum oven. The coin-cell with $LiMn_2O_4$ as a cathode, lithium foil as an anode and the separators untreated or plasma treated above was assembled into two-electrode CR2032-type coin cell in an argon-filled glove box. The electrolyte consists of 1.0 mol·L^{-1} $LiPF_6$ in ethylene carbonate (EC) and dimethyl carbonate (DMC) in a 1:1 (w/w) ratio. The cell with the normal separator and the separator modified by oxygen plasma were named with LMO-N and LMO-O, respectively. The galvanostatic charge and discharge cycle tests were carried out for the cell within the voltage range of 3.0 ~ 4.3 V at the current density of 0.2 C using a LAND CT2001A battery tester (Wuhan, China) at room temperature and 55 ℃ in order to estimate the discharge capacity, rate capability and cycling performance.

2.3. Physical and Electrochemical Characterizations. The contact angle with the polymer separator and the separator modified by oxygen plasma were tested by the contact angle tester (Kruss, dsa100). The wetting behavior of electrolyte consisting of 1.0 mol·L^{-1} $LiPF_6$ in EC and DMC in a 1:1 (w/w) ratio was tested at the room temperature. IR was measured by Fourier Transform Infrared Spectrometer (FTIR WQF-410), and the spectral range was 300-4000 cm^{-1}. The ionic conductivities of the separator infiltrated with the electrolyte were Determined by electrochemical impedance spectroscopy (EIS) on AUT85794 (made in the Netherland), an Autolab electrochemical workstation over the frequency range from 100 kHz to 10 mHz.

3. Results and Discussion

FTIR spectroscopy in attenuated total reflection (ATR) mode is used to characterize the medications caused by the oxygen plasma on the separator surface. The FTIR spectra of the treated (denoted as LMO-O) and the untreated (LMO-N) samples are shown in Fig.1. We can clearly find that the characteristic peaks of the normal separator are a tripe peak at 2975.62 cm^{-1}, 2919.70 cm^{-1} and 2846.42 cm^{-1}, single peak at 1442.49 cm^{-1}, 1386.57 cm^{-1} and 1166.72 cm^{-1} and a double peak at 992.02 cm^{-1} and 971.95 cm^{-1}. Comparing the untreated separator with the oxygen-treated separator (for 60 secs), it is seen that a broad band appears at 3419.17 cm^{-1} and the other is at 1716.34 cm^{-1}, which correspond to the hydroxyl group (–OH) and the stretching vibration (C=O) [32], indicating generation of oxygen functional groups after the oxygen plasma treatment. The FTIR results demonstrate the oxygen plasma treatment can modify the surface of the normal separator, introducing several oxygen-based functional groups like carbonyl and hydroxyl onto the surface of the separator.

It is interesting to observe the changes in the surface morphology of the separator after the plasma treatment. Fig. 2 shows the microstructure of the separator before and after the oxygen plasma treatment. Before the plasma treatment, the separator shows a stacked lamellar morphology with small space between the lamellae and there are some cracks on the surface of the separator. The separator modified by the oxygen plasma treatment for 60 s shows a different microstructure from the normal separator, which has some of the stacked lamellae separate to form a micro porous structure while others remain with their initial morphology. It is obvious that the surface of the modified separator is smoother than the normal one, which indicates the high-temperature resistance is better than that one, which is very important for the electrochemical performance of the lithium ion battery. It illustrates that the $LiMn_2O_4$/Li cell using the modified separator will probably have better electrochemical performance than that of the normal separator.

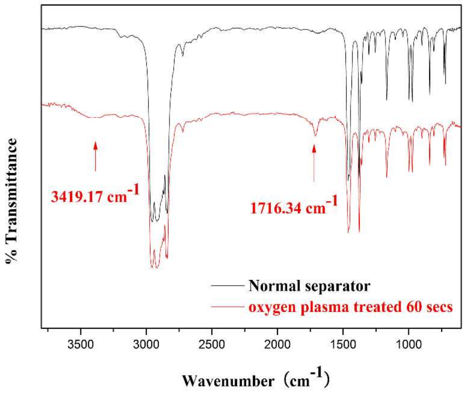


Figure 1. FTIR spectra of normal separator and separator modified by oxygen plasma treatment.

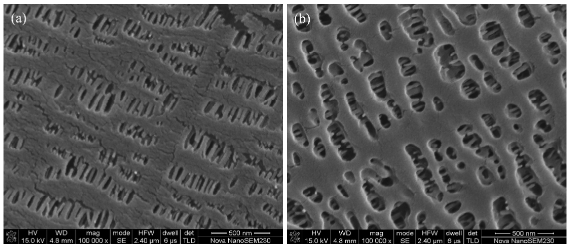


Figure 2. SEM images of the microstructure of normal separator (a) and separator modified by oxygen plasma treated for 60 s (b).

The affinity behavior of the separator with electrolyte could significantly affect the performance of the as-assembled batteries. Therefore, we investigated the wetting behavior of the separator by electrolyte before and after the oxygen plasma treatment. The contact angle measurement was performed by dropping an electrolyte onto the surface of the separators, as observed in Figure 3. As shown in Fig. 3a, the contact angle of the normal separator is as large as 119 °, due to its low ability to hold organic solvents with a high dielectric constant.[13] However, the contact angle of the separator modified by oxygen plasma treatment is only 41.5 ° in Fig. 3b. The separator modified by oxygen plasma treatment is highly effective in absorbing polar liquid electrolyte, compared to the normal separator. This superior wetting behavior may be attributed to the polar component like -OH and -C=O introduced onto the surface of the separator after the oxygen plasma treatment, where the liquid electrolyte can infiltrate preferentially through the well-connected interstitial fiber voids. The excellent wettability of the separator which can effectively maintain the electrolyte solutions and facilitate the electrolytes to diffuse well into the cell assembly plays a critical role in the electrochemical performance [16, 34]. The improving of polarity and higher surface energy of the separator modified by oxygen plasma can enhance the compatibility between electrodes and separator, which be beneficial to improve the cycling performance of the lithium ion battery.

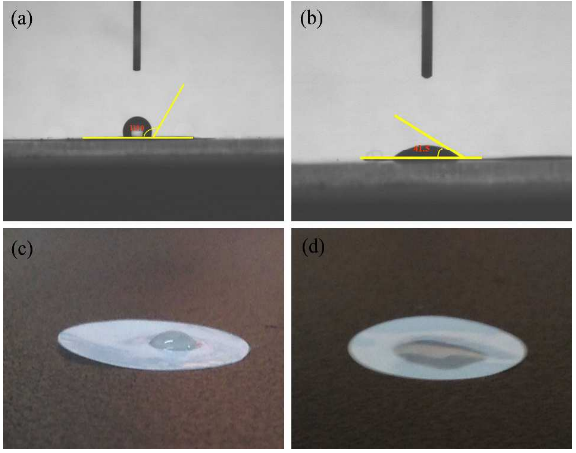


Figure 3. The contact angle measurement of (a) normal separator and (b) the separator modified by oxygen plasma treatment; Photographs of wetting behavior by dropping the electrolyte (1.0 $mol \cdot L^{-1}$ $LiPF_6$) on (c) the normal separator, (d) the separator modified by oxygen plasma treatment.

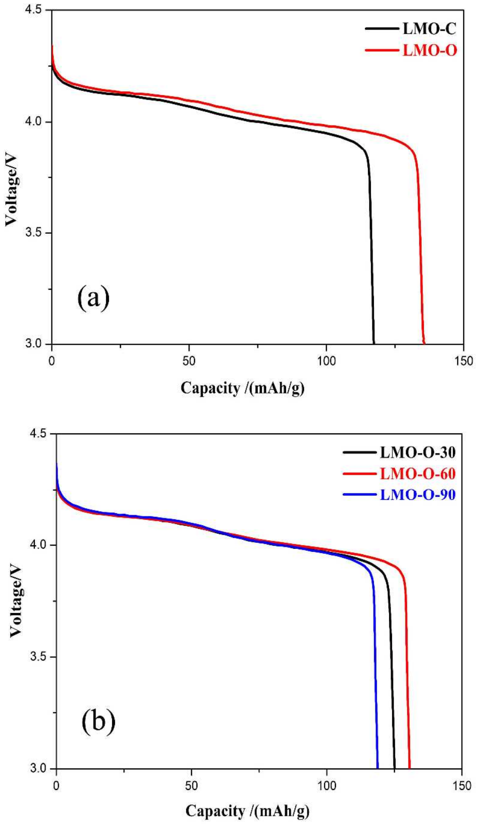


Figure 4. The initial discharge voltage profiles of the spinel $LiMn_2O_4$ batteries: (a) the normal separator and the separator modified by oxygen plasma treatment for 60 s; (b) the separator modified by oxygen plasma with different treatment time.

With the separators discussed above, we assembled the LIBs with $LiMn_2O_4$ as the cathode materials to investigate the effect of the plasma treatment on the separator and thus the electrochemical performance of the as-assembled batteries. Fig. 4a shows the initial discharge voltage profiles of the spinel $LiMn_2O_4$ batteries using the normal separator and the separator modified by oxygen plasma treatment at the 0.2 C rate within the voltage between 2.8 and 4.3 V. The cell using the normal separator and the separator modified by oxygen plasma treatment exhibit initial discharge capacities of 117.3 mAh·g^{-1} and 135.7 mAh·g^{-1}, respectively, which evidently indicates the higher initial discharge capacity on the plasma modified separator. Fig. 4b presents the initial discharge profiles using the separator modified by oxygen plasma with different treatment time (LMO-O-X, X represents the separator by the oxygen plasma treated time-seconds). The cell using the separator LMO-O-60 shows the highest initial discharge capacity of 135.7 mAh·g^{-1} compared with the others. The high initial discharge capacity of the cell might be due to the appropriate amount of the functional groups such as –C=O and -OH on the surface of the separator. The initial discharge capacity of the cell using the separator LMO-O-30 is 118.8 mAh·g^{-1}. As the plasma treatment time increased up to 90 s, the initial discharge capacity reached 125.1 mAh·g^{-1}. The initial discharge capacities of all the cells using the modified separators are higher than the cell with the normal one, which illustrates the importance of the oxygen plasma treatment on the separator to improve the performance of the LIBs.

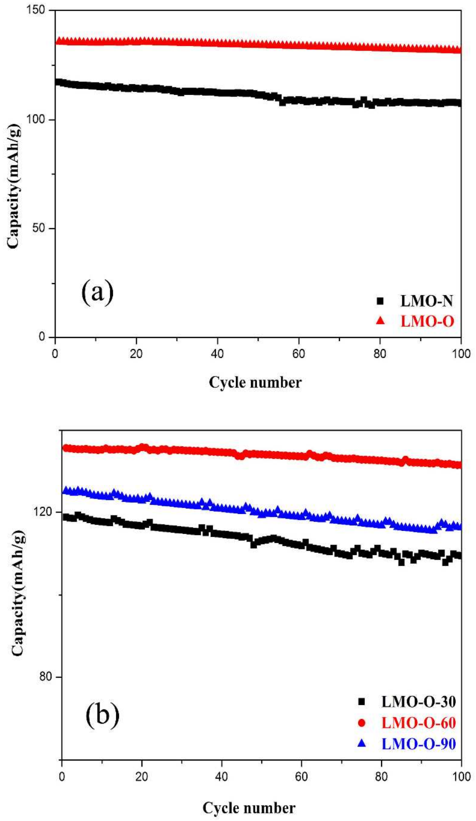


Figure 5. The cycling performance comparison of the Li-ion batteries with (a) the normal separator and the separator modified by oxygen plasma treatment for 60 s; (b) the separator modified by oxygen plasma with different treatment time.

The cycling performance is a key parameter of a Li-ion battery. We investigated the cycling performance of the as-assembled batteries, as shown in Fig. 5. Figure 5a shows the cycling behavior of LMO-N and LMO-O-60, which demonstrates that the cell using the separator LMO-O-60 always possesses higher discharge capacity and much better cycling performance than that of using the normal separator. After 100 cycles, the discharge capacities of the cell using the normal separator and the separator LMO-O-60 are 107.6 mAh·g^{-1} and 131.6 mAh·g^{-1}, respectively. The capacity retention of the cell using the separator LMO-O-60 (96.98%) is higher than that of the polymer separator (91.73%), which might be due to the presence of -OH and -COOH introduced onto the surface of the separator by the oxygen plasma treatment. The improvement on the cell cycling performances may be because of the reduced side reactions and the Jahn-Teller distortion[35-38]. When the oxygen functional groups are introduced onto the surface of separator, the ionic conductivities of the liquid electrolyte is improved, which results in the enhanced stability of the $LiMn_2O_4$/Li battery with the separator modified by oxygen plasma. The discharge cycling performance of the cells using the separator modified by oxygen plasma with different treatment times are shown in Fig. 5b. Capacity fading is observed after several charge/discharge cycles in three cases, but the retention of the discharge for the cell with the separator LMO-O-60 is better than any other sample with the capacity retention of 96.98%. However, the cell using the separator of LMO-O-30 and LMO-O-90 could only respectively contain 92.17 % and 92.97% after 100 cycles of their initial discharge capacities, which further demonstrates that the shorter treatment time could not introduce enough oxygen functional groups, while the longer treatment time could damage the structure of the separator. Therefore, the separator treated with the suitable oxygen plasma time can obviously enhance the cycling performance of the $LiMn_2O_4$/Li battery.

Discharge curves of the spinel $LiMn_2O_4$ batteries using the separators of sample LMO-N and LMO-O at different rates varying from 0.2 to 2 C are shown in Fig. 6a. Specific capacity of 135.7 mAh·g^{-1} is obtained at the rate of 0.2 C using the separator LMO-O then reduced to 133.5 mAh·g^{-1} at 0.5 C, 131.9 mAh·g^{-1} at 1 C, finally, 120.4 mAh·g^{-1} at 2 C, corresponding to 0.30%, 1.57%, 3.64% and 10.22% capacity fading, respectively. At the same time, the cell using the separators of sample LMO-O keeps 99.70% of its capacity compared with that at 0.2 C, which is larger than the cell using the separator of sample LMO-N even at 1 C. Moreover, this rate capability is much higher than the rate capability for the cell using separator LMO-N that the specific capacity is 117.5 mAh·g^{-1}, 100.8 mAh·g^{-1}, 86.7 mAh·g^{-1}, 61.5 mAh·g^{-1}, and their capacity retention were 98.47%, 96.03%, 88.93%, 70.89% at 0.2 C, 0.5 C, 1 C, 2C after 10 cycles, respectively, which indicates that the appropriate plasma treatment plays an important role on the improvement of the electrochemical performance in LIBs.

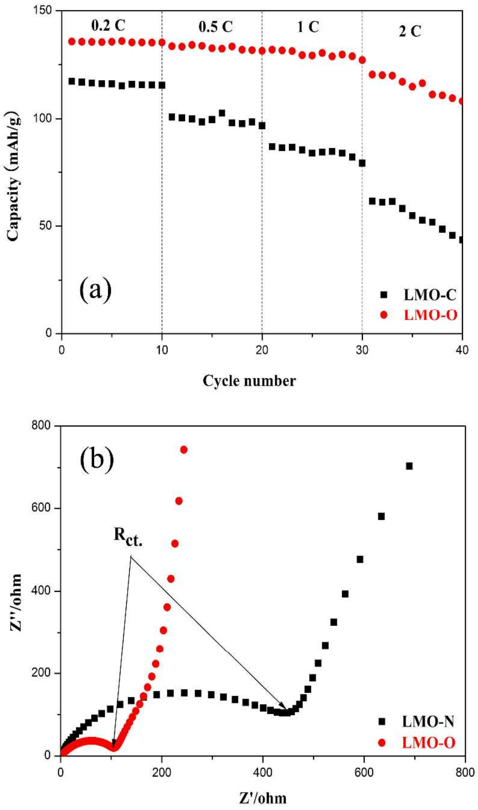


Figure 6. (a) Variation of discharge capacity vs. cycle number at different rates between 2.8 and 4.3 V using the separators of LMO-N and LMO-O. (b) Nyquist plots of the spinel $LiMn_2O_4$ batteries using the separators of LMO-N and LMO-O.

In order to further study and understand the electrochemical performance of the LIBs with the modified separator, the electrochemical impedance spectroscopy is recorded. The Nyquist plots of the spinel $LiMn_2O_4$ batteries using the separators of LMO-N and LMO-O are shown in Fig. 6b. It can be seen that both two cells have a similar ohmic resistance, but the semicircle of the cell using the separator of sample LMO-O is much smaller than LMO-N. From the fitted impedance parameters, the charge transfer resistance (R_{ct}) of the cell using the separator of sample LMO-O is smaller ($R_{ct} \approx 113.5\ \Omega$) than the sample LMO-N ($R_{ct} \approx 488.86\ \Omega$), indicating the inserting and de-inserting of lithium-ions of the cell using the separator of sample LMO-O is easier. The reduced charge transfer resistance could be due to the modified wetting properties and electrolyte retention properties of the separator by oxygen plasma treatment[39]. The larger charge transfer resistance leads to capacity decay for the $LiMn_2O_4$/Li cell using the LMO-N separator faster than that using the LMO-O separator [40], which indicates the rate performance of cell using the LMO-O separator might be better than that of the LMO-N separator. In other words, the cell using the modified separator with excellent electronic and ionic conductivities can greatly enhance rapid electron transport during the electrochemical lithium insertion/extraction process possibly due to the oxygen functional groups introduced onto the surface of separator after the oxygen plasma treatment. The impedance results of the cells using the two types of separators are consistent with the results from the other electrochemical measurements.

The major problem prohibiting $LiMn_2O_4$ from large-scale applications is its capacity fading seriously during charge and discharge process, especially at elevated temperature[41-42]. The cycling performance of the $LiMn_2O_4$/Li cell using the separators of LMO-N and LMO-O at the rate of 0.2 C at 55 ⍰ is shown in Fig. 7. The cell using the normal separator exhibits a discharge capacity fading from 106.4 mAh·g^{-1} to 45.8 mAh·g^{-1} after 60 cycles. The capacity retention of the cell using the LMO-O separator (85.39%) is much higher than that of the normal separator (53.69%). The excellent electrolyte retention of the oxygen plasma modified separator is mainly attributed to its oxygen functional groups such as –C=O and -OH on the surface of the separator and the capillary force due to the presence of many micropores in the LMO-O separator. The LMO-O separator can improve the cycling stability of $LiMn_2O_4$/Li cells probably because the modified separator can generate repulsion with trace HF in the electrolyte, avoiding HF accelerating manganese ions dissolving[43-44], which leads to the $LiMn_2O_4$ capacity fading at high temperature.

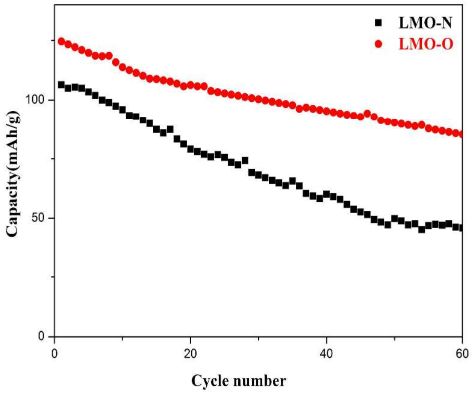


Fig. 7. Cycle performance of the $LiMn_2O_4$/Li cell using the separators of LMO-N and LMO-O at 55 ⍰ at the rate of 0.2 C in the voltage range of 2.8 ~4.3 V.

4. Conclusions

The $LiMn_2O_4$/Li battery firstly uses the separator modified by the oxygen plasma treatment, which exhibits better wettability with electrolyte and smaller contact angle than that of the normal separator. Electrochemical measurements show that the $LiMn_2O_4$/Li cell using the separator modified by the oxygen plasma delivers a high initial discharge capacity of 135.7 mAh·g^{-1} and excellent cycling reversibility that after 100 cycles, 96.98% of discharge capacity retained. The excellent performances of the $LiMn_2O_4$/Li cell developed in this work are benefit from the separator modified by the oxygen plasma method, which can induce oxygen functional groups on the surface of separator to enhance ionic conductivities. At the same time, the $LiMn_2O_4$/Li cell using the separator modified by the oxygen plasma method exhibits better rate performance and cycling performance at the elevated temperature. The capacity retention of the cell using the LMO-O separator (85.39%) is much higher than that of the normal separator (53.69%) at 55 . The electrochemical performance of the LiMn$_2$O$_4$/Li battery using LMO-O separator can be prominently enhanced by oxygen plasma technology, which can improve the high rate capability of LiMn$_2$O$_4$/Li battery, which is the key to the success of electric and hybrid electric vehicles (EVs and HEVs) technology. In conclusion, the separator modified by the oxygen plasma can be used in batteries to improve the electrochemical performance.

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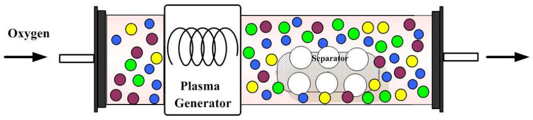
Graphical Abstract



Scheme 1. Illustration on the separator modified by the oxygen plasma method

A plasma-enhanced tube furnace was used to prepare O_2 plasma treated separator, as illustrated in Scheme 1, which mainly consists of a vacuum pump, a plasma generator, and a pressure probe. The separator modified with the high efficiency oxygen plasma method is firstly used into the Li/$LiMn_2O_4$ batteries, which show excellent electrochemical performance in terms of capacity and cycling performance, especially at the elevated temperature for the Li-ion batteries.