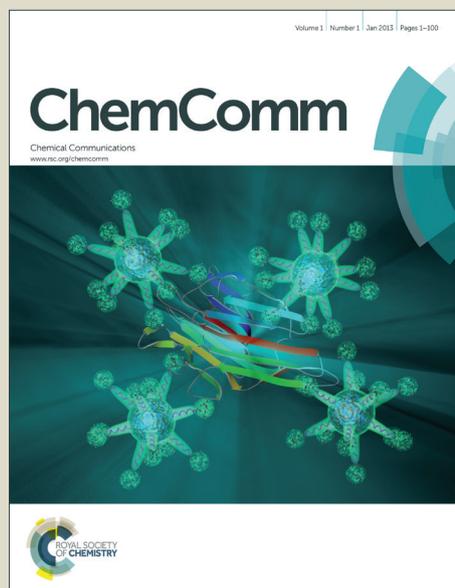


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COMMUNICATION

Modified Secondary Lithium Metal Batteries with the Polyaniline/Carbon Nanotube Composite Buffer Layer

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A modified secondary lithium metal battery inserted with a polyaniline/carbon nanotube nanoporous composite buffer layer was fabricated. This unique and simple design of battery has the great potential to decrease the safety risk of the secondary Li metal battery in cycles of recharging processes and improve its cycle life in the future.

Nowadays, the lithium ion batteries (LIBs) have extensive applications in equipment such as portable electronic devices and electric vehicles because of their higher energy density and longer cycle life than other rechargeable batteries.¹⁻³ The traditional LIBs use graphite or other carbon materials as anodes, where exists the reversible intercalation and removal of Li ions. However, carbon based anodes have a higher electrode potential compared with the Li metal. Li metal has a quite low electrode potential (-3.045 V vs. H_2/H^+) resulting in a higher working voltage of the Li metal batteries that directly using Li metal as anodes compared with the traditional LIBs with carbon materials as anodes. Moreover, the highest theoretical specific capacity (3862 mAh/g) of Li metal among all the anode materials leads to a much higher specific capacity of Li metal batteries compared with the traditional LIBs. Therefore, Li metal is theoretically the best choice for an anode material of the rechargeable Li-based batteries.⁴⁻⁷ In fact, the Li metal batteries have been widely investigated in the past 40 years, but they are now only commercially used as the primary batteries because of some negative problems in their recharging processes for long cycles. The main problem is the growth of Li dendrites during cycles of charging and discharging.⁸⁻¹² The Li dendrites can pierce through the separator and then cause the short circuits between anode and cathode, which will lead to the explosion or cell failure. Many methods have been presented to suppress the growth of the Li dendrites, such as the modification of the electrolyte,¹³⁻¹⁵ the use of pulse charging,¹⁶ the special treatment of the lithium electrode,¹⁷⁻¹⁹ etc.

In this work, we try to insert a buffer layer into the Li metal battery to fabricate a modified secondary Li metal battery. It is our expectation that this method can solve the abovementioned safety problem caused by the Li dendrites in the future. We envisage that this buffer layer is a thin, tough and flexible polymer film and especially that it has an excellent electrical conductivity. Polyaniline

(PANI)^{20,21} is a very common conducting polymer showing a remarkable conductivity and good electrochemical activity, but it usually exists in the powder form with a bad mechanical property. As a nanoporous material, carbon nanotube (CNT) has a large specific area, very high conductivity and good mechanical strength.²² Hence, the combining of PANI with CNT may create a material with merits of both of them. In our laboratory, we have fabricated a polyaniline/carbon nanotube (PANI/CNT) film nanoporous composite that combines the excellent conductive and mechanical properties of CNTs and the high pseudo capacitance of PANI. This PANI/CNT composite retains the advantages of the PANI and owns a superior porous character compared with PANI.²³ We have used this composite as the electrodes of supercapacitors showing enhanced electrochemical performances.^{24,25} We also have used this composite to successfully improve the electrochemical performances of the lead acid batteries,²⁶ which can be attributed to the synergic effect of batteries and supercapacitors.^{27,28} Here, the fabrication of the modified Li metal battery with PANI/CNT composite buffer layer is a notably new attempt having never been previously reported. In this work, we report some preliminary results on this aspect of research.

First, we fabricated the $LiCoO_2/CNT$ composite by the ultrasonication and co-deposition of the $LiCoO_2$ powders and the super-aligned CNTs.²⁹⁻³¹ The $LiCoO_2/CNT$ and Li metal was set as the

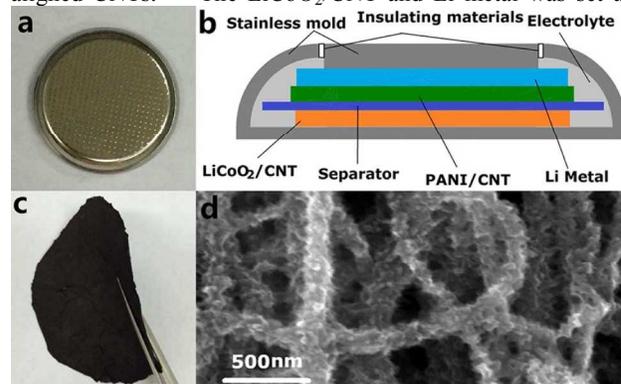


Figure 1. (a) Photograph of the coin cell used for packaging the modified battery. (b) Schematic of the structure of the modified battery. (c) Photograph of the PANI/CNT film. (d) SEM images of the PANI/CNT film.

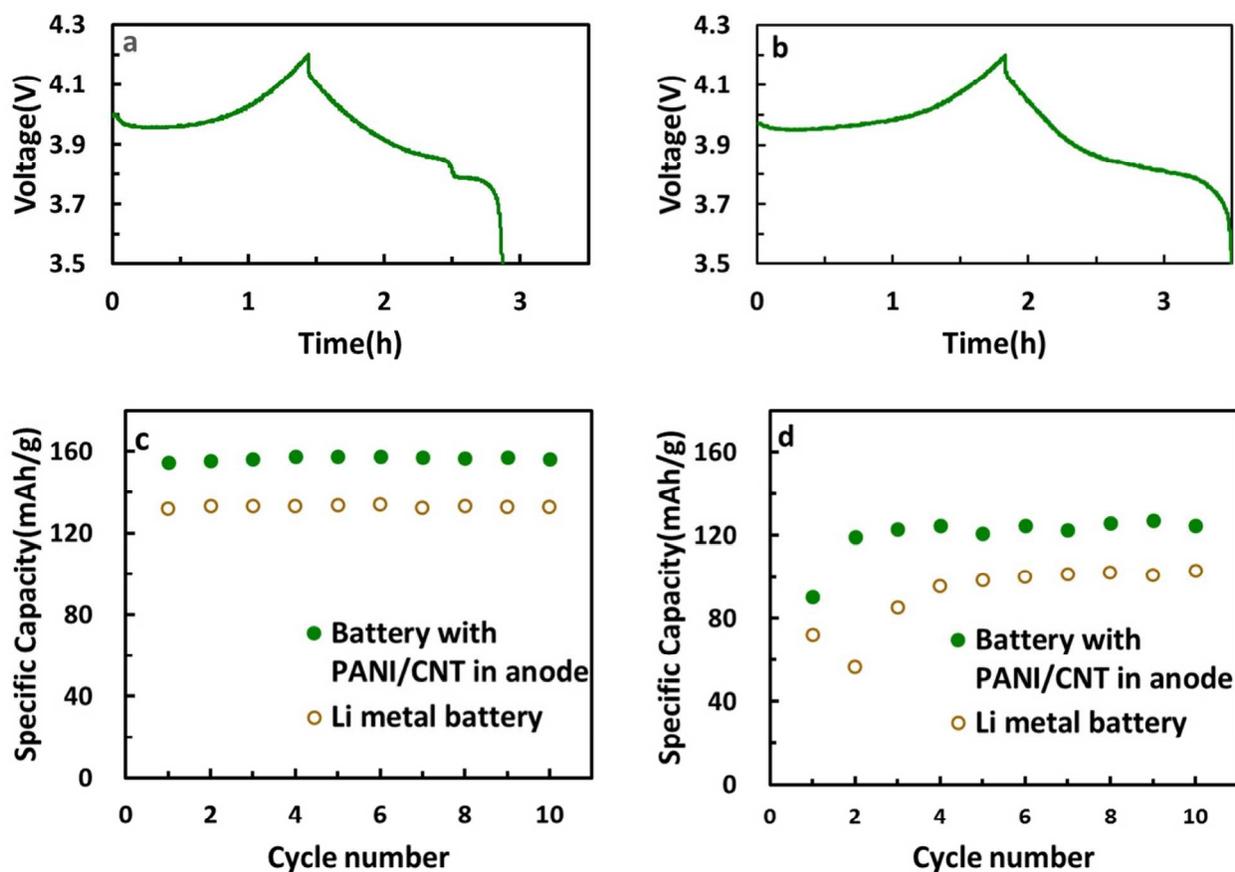


Figure 2. The galvanostatic charge-discharge curve of (a) the Li metal battery and (b) the modified battery with PANI/CNT in anode, respectively, at the rate of 0.4 C with the voltage from 3.5 V to 4.2 V. Comparison of the specific capacity of the Li metal battery and that of the modified battery with PANI/CNT in anode within initial 10 cycles of charge-discharge at the rate of (c) 0.4 C and (d) 4 C, respectively.

cathode and the anode respectively. Then, we fabricated the PANI/CNT film composite through an in situ chemical solution method reported previously.²³ The specific surface area and pore volume of PANI/CNT were about 25.4 m²/g and 2.59 cm³/g, respectively. Third, we inserted the PANI/CNT film between the Li metal and the separator (shown in Figure 1b). Finally, the modified battery was assembled as a coin cell shown in Figure 1a. Detailed processes for the fabrication of the LiCoO₂/CNT cathodes and PANI/CNT electrodes, assembly of the cells, characterization and electrochemical measurement are described in Supporting Information.

The photograph of the PANI/CNT film (Figure 1c) shows the flexible character of this ultrathin film with a thickness of 45 μm. The Figure 1d shows the scanning electron microscope (SEM) image illustrating a uniform and thin coating of the PANI on the CNT network, so that the nanoporous structure is well retained. Meanwhile, the combining of the PANI can enhance the compactness of the CNT network.

As shown in Figure 2a and Figure 2b, initial electrochemical characterization of this modified battery with PANI/CNT in anode is carried out by galvanostatic charge-discharge studies with a potential window range from 3.5 V to 4.2 V at the rate of approximately 0.4 C. During the charging processes of the Li metal battery and the modified battery, the voltage rapidly increased to about 3.9 V and then stayed stable at approximately 4.0 V. The two batteries show the similar characteristics of charging-discharging curves. Hence, the fundamental electrochemical performances of the modified battery

have not changed after we put the PANI/CNT in the anode of the Li metal battery. However, the modified battery shows a longer discharging time compared with the Li metal battery, which results in an increase in capacity.

Figure 2c and Figure 2d show the comparison in the specific capacity between the modified battery and the Li metal battery during the first 10 cycles at the rate of 0.4 C and 4 C, respectively, where the calculated specific capacity is based on the mass of LiCoO₂ in cathode. As Figure 2c demonstrates, the specific capacity of the modified battery at 0.4 C increases during the first two cycles and keeps stable in 157.8 mAh/g within the rest of cycles, which shows a 17.7% increase compared with Li metal battery (134.0

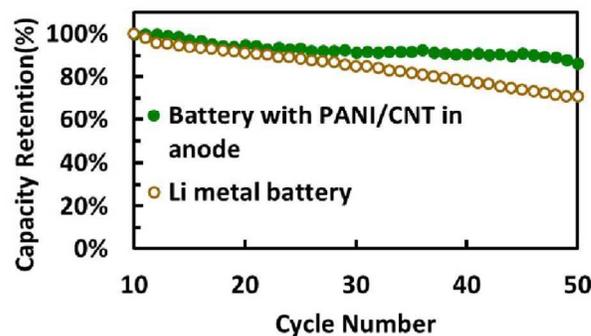


Figure 3. Retention of specific capacity of Li metal battery and the modified battery with PANI/CNT in anode for 50 cycles.

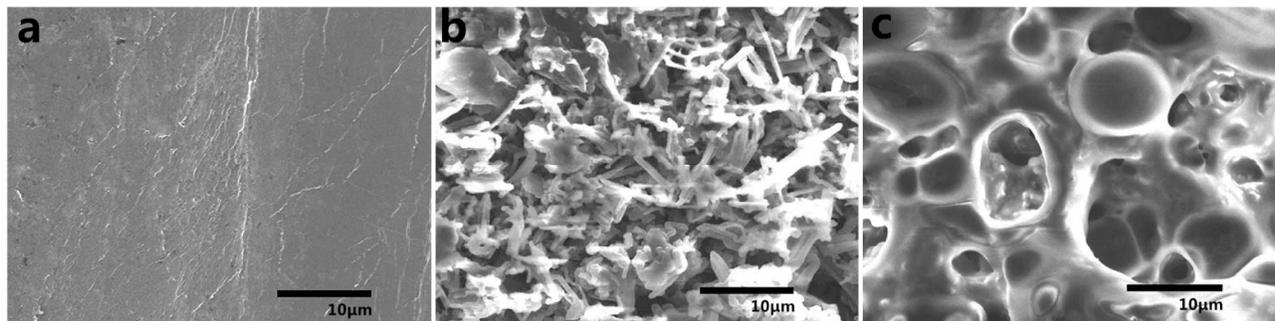


Figure 4. SEM images of the surface morphologies of (a) the original Li metal lamina. (b) disassembled the Li electrode of the Li metal battery after 50 recharge cycles. (c) the Li electrode of the PANI/CNT modified battery after 50 recharge cycles.

mAh/g). As shown in Figure 2d, the specific capacity of the two batteries at 4 C is low and unstable at the first several cycles, which is a common phenomenon because a newly fabricated battery need to be activated before tests especially in high rate. The stable specific capacity of the modified battery and the Li metal battery at 4 C is 127.0 mAh/g and 103.1 mAh/g, respectively, where the increase in specific capacity is 23.2%. The typical specific capacity of LiCoO_2 in the Li-based batteries is about 140 mAh/g,⁷ to which our results has a similar level.

Then, the cycling performance of the two batteries was also compared. After the initial 10 cycles of charging-discharging, the two batteries were activated completely reaching the highest specific capacity, so Figure 3 shows the specific capacity retentions of the Li metal battery and the modified battery from 10 to 50 cycles at the rate of 4 C. The curves indicate that, after 50 cycles of charge-discharge, the retention of the modified battery (86%) is larger than that of the Li metal battery (71%), which increased by 21%. Larger number cycles will take a very long time, and will be carried out in the future.

The abovementioned results indicate that the modified battery has better electrochemical performances in high rate and cycling performances compared with the Li metal battery. Here we'd like to make a preliminary interpretation on this improvement. First, the introducing of the PANI/CNT composite has no negative effects on the working voltage and specific capacity of the Li metal battery, because the good conductivity and porous structure of the PANI/CNT composite can provide suitable channels for ion transport without the remarkable increase in the internal resistance. Second, the transport rate of ions in electrostatic adsorption and desorption on the nanoporous PANI/CNT is much higher than that of the Li ions in redox on the Li anode of the Li metal battery. When the battery is charged and discharged in a high current, the PANI/CNT can first mainly bare the charge transport and then make a slower transition to the Li anode, so the Li anode has more time to storage and release charges. Consequently, the modified battery with PANI/CNT in anode shows a higher specific capacity in high rate compared with the Li metal battery. Third, the PANI/CNT nanoporous film plays a role as a buffer layer in the charging and discharging process of the modified battery. When the conventional Li metal batteries are recharged, the Li-ions move to the surface of the Li electrode and then the deposition of Li forms after the reduction of the Li ions. After cycles of charge-discharge, Li dendrites form gradually on the surface of the Li electrode owing to its preferential crystal growth on Li metal. However, in the modified battery, the PANI/CNT nanoporous film covering on the Li metal is not fit for the preferential crystal growth of Li. There are two possible reasons. First, the Li dendrites were more likely to grow on

the surface of crystals but PANI/CNT was polymer. Second, even if some Li-dendrites growth existed, it would be obstructed easily by the network of PANI/CNT. So this film has the potential to impede formation of the Li dendrites.

Scanning electron microscopy (SEM) observation confirmed above conjecture. SEM images of the surface morphologies of the original Li metal lamina, and the disassembled Li electrode of Li metal battery and the modified Li battery are shown in Figure 4 respectively. From Figure 4a, the surface of original Li metal lamina is flat and smooth. But after 50 charging-discharging cycles, it has a remarkable change. From Figure 4b, we can see obvious Li dendrite formations. The surface is rough and has many sharp dendrites. The Li dendrites may pierce through the separator easily. Figure 4c shows an irregular network structure, but it is more smooth than the image in Figure 4b and without sharp dendrites so clearly has almost no threat to the separator. Obviously, the insertion of PANI/CNT composite layer led to the distinctly different surface structures of Li electrodes of the two battery, i.e., one is danger to the separator and one is relatively safe.

Conclusions

In summary, through inserting the PANI/CNT nanoporous composite into the anode of the Li metal battery, a modified secondary battery has been manufactured with a potential in solving the safety problem of Li metal batteries. This modified battery also has an obvious larger specific capacity at high current compared with the usual secondary Li metal battery. Meanwhile, it shows a better cycle performance in high rate. The results here demonstrate that the PANI/CNT composite plays a buffer layer role during charging and discharging in the modified battery, and can notably impede the formation of Li dendrites on the Li electrode surface.

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