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Electrochemical performance of $\text{LiAlCl}_4/\text{SOCl}_2$ electrolyte with 2, 2'-bipyridine in Li/SOCl_2 batteries

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Voltage delay of Li/SOCl_2 battery doped with 2, 2'-bipyridine is investigated by the galvanostatic discharge tests and the electrochemical impedance spectra. The results indicate that a certain amount of 2, 2' – bipyridine can be adsorbed on the Li anode surface, leading to the change of LiCl layer, which is beneficial to improve voltage delay of Li/SOCl_2 battery in effect.

Keywords: Voltage delay; 2, 2'-bipyridine; Li/SOCl_2 batteries

1. INTRODUCTION

Li/SOCl_2 battery is widely used in civil and military areas, due to its high energy density (600Wh Kg^{-1}), flat discharge profile (voltage stability over 95% of the discharge), wide operating temperature range ($-55\text{ }^\circ\text{C}$ to $200\text{ }^\circ\text{C}$), low self-discharge (2% per year) and long service life (10 years) [1-4]. However, passivation on lithium surface induce voltage delay of Li/SOCl_2 battery that batteries's operating voltage decrease fleetly to a low level, which is caused by the protective layer of lithium salts that forms on the Li surface in the course of prolonged storage and high temperature [2, 5-7]. The voltage delay limits its application field. Therefore, it is critical to solve voltage delay problem for improving electrochemical performance of Li/SOCl_2 battery.

Voltage delay is a phenomenon that cell voltage drops to certain value and recovers as the discharge progresses when a load is applied to Li/SOCl_2 battery. Especially, the phenomenon is serious under the circumstances such as discharge at room temperature after high temperature storage and temperature at low temperature with high power output. A protective film is formed on the Li anode surface due to reaction Li anode with SOCl_2 electrolyte. The main component of the passive film is LiCl constituted by the compact layer and porous layer [6, 8]. The transportation of electron and Li

ions will be hindered by the LiCl layer ascribed to lattice defect. Furthermore, the passive film on the surface of Li anode will split as the discharge progresses. Therefore, voltage delay is greatly influenced by thickness, mechanical strength and porous characteristic of the passive film and morphology and size of LiCl crystal [9].

Much effort have devoted to overcoming the above problem. For instance, modifying the electrolyte with PVC was attempted to change the structure of LiCl crystal, proven ineffective owing to insoluble of PVC [10]. SO_2 was added in the electrolyte to react with LiAlCl_4 for solve voltage delay problem. However, the addition of SO_2 would cause safety issues [11]. $\text{Li}_2\text{B}_2\text{Cl}_{10}$ and LiGaCl_4 were employed as electrolyte salts with some progress [12]. The Li anode coated with MEEP and PMMA were utilized to prevent the contact between Li anode and electrolyte. However, it is unrealistic for large-scale industrial production. Super capacitor was connected with Li/ SOCl_2 battery in parallel to overcome the problem by utilizing the priority of super capacitor discharge, but only with limited success [13].

Bipyridine was employed as brightening agent for electroplating due to adsorption of bipyridine on the electrode surface [14]. The coordination compound formed by the reaction the electrode with bipyridine is beneficial for grain refinement of the product of the electrodeposition and detailed light of clad layer. Bipyridine had been successfully utilized as additive for LiMn_2O_4 electrode to improve cycling stability of Li anode, which was attributed to the change of Li anode structure dut to the reaction the electrode with bipyridine. Here we firstly use 2, 2' – bipyridine in Li/ SOCl_2 battery, and the influence of 2, 2' – bipyridine for voltage delay is discussed in detail.

2. EXPERIMENTAL

2.1. Electrolyte Preparation

In a typical synthesis, 2, 2'-bipyridine added in a certain amount of Li foil and 1.5 mol/L $\text{LiAlCl}_4/\text{SOCl}_2$ electrolyte was refluxed for 5 h to get rid of water. If Li foil did not become darken, it was supposed that water had been evaporated absolutely. Molar ratio of 2, 2'-bipyridine and LiAlCl_4 in electrolyte were 0.05:1, 0.1:1, and 0.5:1, respectively. 1.5 mol/L $\text{LiAlCl}_4/\text{SOCl}_2$ electrolyte without 2, 2'-bipyridine was also used for comparison.

2.2. Battery Assemble

The AA-size (ER14505) spirally wound Li- SOCl_2 batteries were assembled in a glove box with an inert atmosphere of argon. The batteries consisted of a porous carbon cathode, lithium anode, and borosilicate glass fiber separators. The assembly is rolled together (anode, separator, cathode, and then separator), and the roll is inserted into a 304 stainless steel cell can with a prewelded burst disk in the base. The cell can is equipped with a 304 stainless steel cap assembly with prewelded nickel tabs for the Li anode. The cells were filled with 8 mL of electrolyte.

2.3. Electrochemical test

Test batteries were placed at room temperature 25 °C (RT) and 60 °C (HT) for 6d, 31d and 63d, respectively. The all batteries were placed at 25 °C for 2h before testing. Then the galvanostatic discharge tests at the current of 10 mA and 100 mA with 2.0 V cut-off voltage at 25°C were performed on BT2000 Arbin battery tester. Different depth of discharge (DOD) for test batteries was obtained that were discharged for 10S, 100S and 1000S at 10mA.

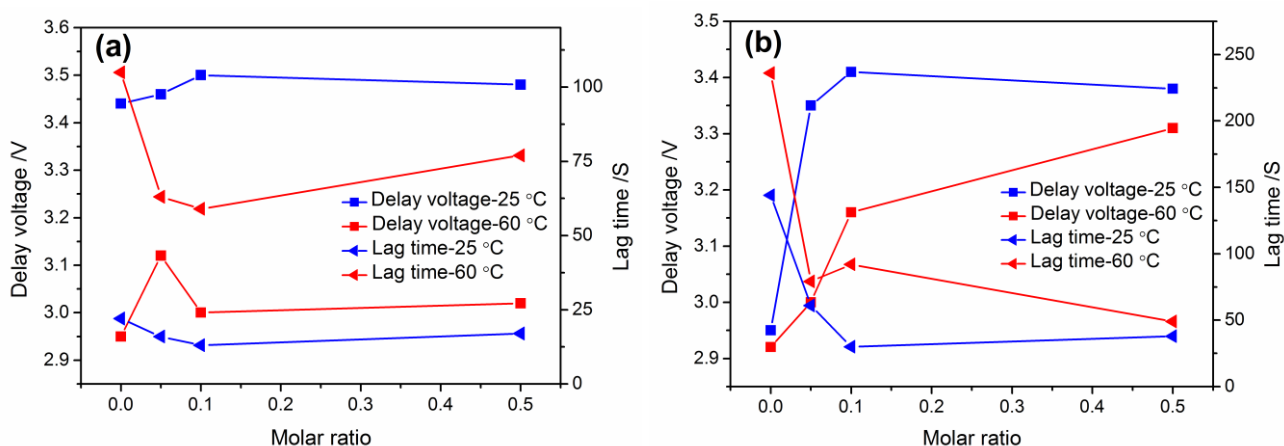
The delay voltage represents the lowest voltage before battery operating voltage recovers to 3.45 V when batteries discharging. The lag time denotes the time of battery operating voltage recovering to 3.45V. Multiple experiments were conducted for the same conditions, and the data reported in this work are an average of three or more.

The electrochemical impedance spectra (EIS) were measured using the VMP3 electrochemical workstation over frequency range from 10^5 Hz to 10^{-2} Hz at potentiostatic signal amplitudes of 5 mV.

3. RESULTS AND DISCUSSION

Fig.1 shows the delay voltage and lag time on the dependence with storage temperature, storage time and discharging current. As shown in Fig.1.a, all batteries exhibit no apparent voltage delay phenomenon placed at 25 °C. However, the batteries stored at 60 °C show lower delay voltage and higher lag time compared to these batteries stored at 25 °C. The phenomenon is also observed in other batteries stored for long time and discharged with large current (100 mA).

The batteries stored for 31 d show lower delay voltage and longer lag time shown in Fig.1.c and Fig.1.d compared to these batteries stored for 6 d shown in Fig.1.a and Fig.1.b. Furthermore, the batteries stored for 63 d possess serious voltage delay. Even the batteries stored at 60 °C for 63d can not recover to 3.45V forever in Fig.1.f. It is conclusion that voltage delay is influenced by the storage temperature and storage time, which is attributed to the passive film on the surface of Li electrode. The film becomes compact and thick as the increase of the storage temperature and storage time, leading to more serious voltage delay for Li/SOCl₂ battery.



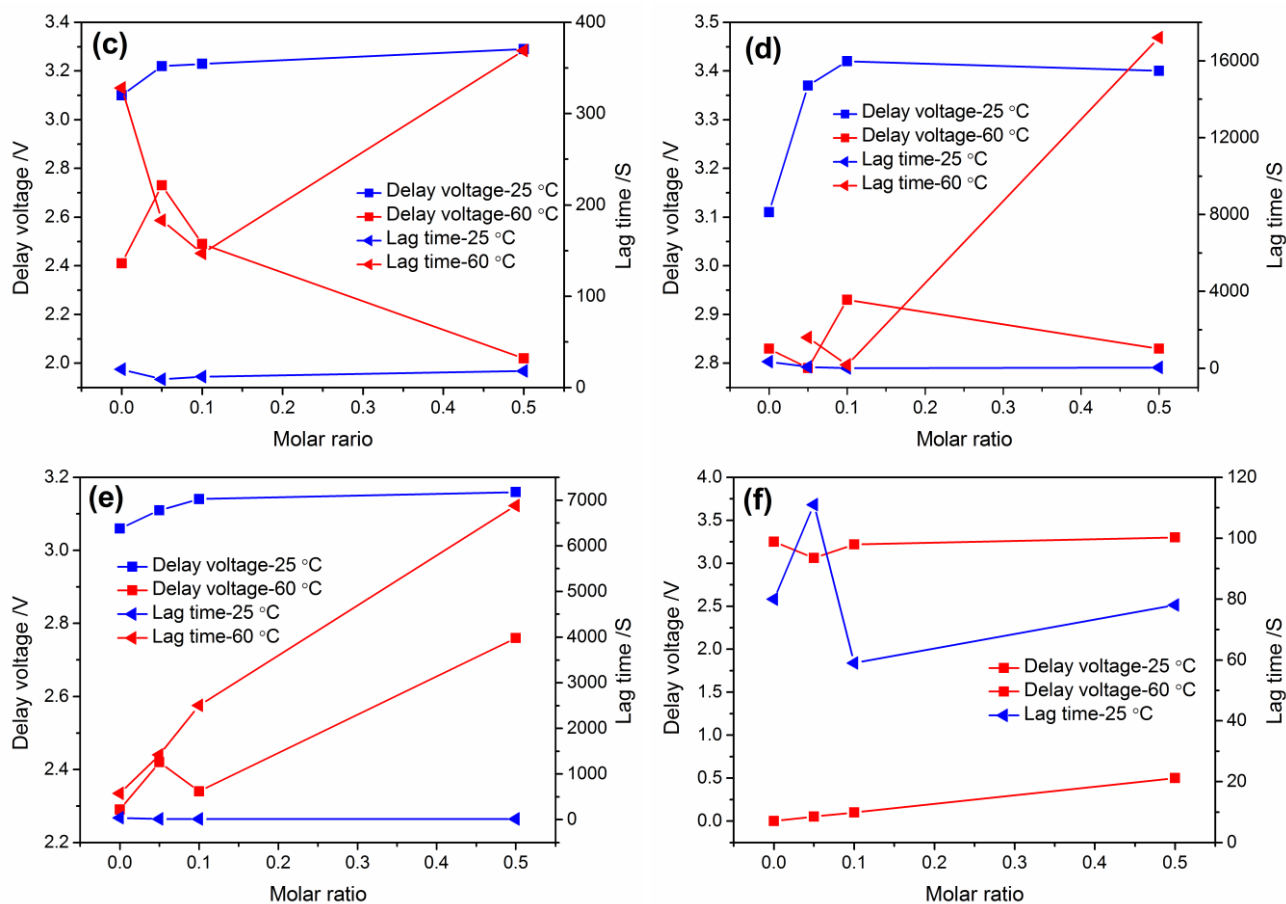


Figure 1. The delay voltage and lag time on the dependence with storage temperature, storage time and discharging current. (a) batteries discharging on 10 mA after storage 6 d at 25 °C and 60 °C; (b) batteries discharging on 100 mA after storage 6 d at 25 °C and 60 °C; (c) batteries discharging on 10 mA after storage 31 d at 25 °C and 60 °C; (d) batteries discharging on 100 mA after storage 31 d at 25 °C and 60 °C; (e) batteries discharging on 10 mA after storage 63 d at 25 °C and 60 °C; (f) batteries discharging on 100 mA after storage 63 d at 25 °C and 60 °C. Lag time of different molar ratios except molar ratio of 0.5 are not listed in Fig.1.a, due to the batteries with different molar ratios exhibit no apparent voltage delay phenomenon placed at 25 °C. In contrast, Lag time of the batteries stored at 60 °C for 31 d and 63 d are not shown in Fig.1.d and Fig.1.f which is attributed to the cell voltage can not recover to 3.45 V forever.

The batteries stored for 6d and added with 2, 2'-bipyridine exhibit no apparent voltage delay phenomenon compared the batteries without 2, 2'-bipyridine electrolyte shown in Fig.1.a and Fig.1.b. The batteries stored for 63 d and added with 2, 2'-bipyridine show higher minimum voltage and less lag time compared to these batteries without 2, 2'-bipyridine. Therefore, it is indicated that 2, 2'-bipyridine can improve the voltage delay problem for Li/SOCl₂ battery. It is supposed that 2, 2'-bipyridine can be adsorbed on the surface of Li anode, leading to LiCl crystal hardly form on the Li surface [15-18]. As a result, 2, 2'-bipyridine is proved to improve voltage delay problem, which is ascribed to 2, 2'-bipyridine can reduce the contact between Li anode and SOCl₂ and change Li anode surface structure due to the reaction of the electrode with bipyridine. The batteries stored at 60 °C for

31d without 2, 2'-bipyridine can not recover to 3.45 V with current of 100mA in Fig.1.c and Fig.1.d. However, the batteries stored at 60 °C for 31d and added with 2, 2'-bipyridine possess less lag time. Especially, the batteries added with molar ratio of 0.1:1 of 2, 2'-bipyridine exhibit less voltage delay compared to the batteries with other molar ratios. It is assumed that the surface of Li anode is covered by 2, 2'-bipyridine with high molar ratio, hindering the transportation of Li ions and electrochemical reaction. LiCl layer will be formed on the surface of Li anode with low molar ratio, which also prevents good transportation of Li ions. There is presence of pore volume between the adsorption layer of 2, 2'-bipyridine and LiCl layer due to the appropriate ratio of the adsorption layer of 2, 2'-bipyridine and LiCl layer, facilitating the transportation of Li ions and enabling electrochemical reaction to participate in completely. LiCl layer becomes fragmentation owing to reaction of the adsorption layer of 2, 2'-bipyridine and LiCl layer with Li anode, which allows good electrolyte penetration and complete electrochemical reaction, enabling to improve voltage delay problem.

The additive of 2, 2'-bipyridine shows little influence for improvement for voltage delay of the batteries stored at 60 °C for 63 d with current of 10 mA and 100 mA, respectively. Especially, the batteries operating voltage can not recover to 3.45 V with current of 100 mA forever. It is assumed that LiCl layer becomes thick as increase of storage time. The growth rate of LiCl crystal accelerates with the increase of temperature, leading to LiCl layer becomes thick [19-20]. Furthermore, the adsorption of 2, 2'-bipyridine become weak attributed to the increase of temperature, which causes 2, 2'-bipyridine show little influence for the change of Li anode morphology structure, leading to little improvement for voltage delay. Therefore, the batteries discharging at large current exhibit serious voltage delay problem which is ascribed to the passive film on the surface of Li anode is too thick to transport for Li ions compared to the batteries discharge current.

In summary, the additive of 2, 2'-bipyridine can be adsorbed on the surface of Li anode and change the Li anode morphology structure, which facilitates the improvement of voltage delay problem especially under large current circumstance. The adsorption of 2, 2'-bipyridine is also related with temperature.

The EIS for the batteries before discharging and after discharging with 2.0 V cut-off voltage are illustrated in Fig.2. All impedance results show a semicircle at high frequencies corresponding to the SEI layer of electrode surface and a short inclined line in low frequency due to the Li ion diffusion within the cathode [21-23]. It is noted that the resistance of SEI layer of the batteries stored at 25 °C for 6 d and 31 d after discharging is higher than before discharging, while the phenomenon is just opposite for the batteries stored at 60 °C. However, it is apparent that the resistance of SEI layer of the batteries stored at 25 °C and 60 °C for 63d after discharge is lower than before discharge. The resistance of SEI layer will reduce ascribed to the passive film split after discharge. However, the resistance of SEI layer of the batteries stored at 25 °C for 3d and 31d after discharge increases, which is attributed to EIS is not performed on the batteries in time after discharging, due to the change of SEI layer of the batteries occurring during the period. The batteries stored at 60 °C exhibits high resistance of SEI layer. Therefore, the change of SEI layer of the batteries due to the EIS tests not performed in time show little influence for high resistance. The resistance of SEI layer of the batteries stored at 25 °C and 60 °C for 63 d after discharge is lower than before discharging which is also attributed to high resistance of SEI layer before discharging. It is shown that the resistance of SEI layer of the batteries

with additive of 2, 2'-bipyridine is lower than the batteries without additive before discharging and after discharging. It is indicated that the additive of 2, 2'-bipyridine can change the Li anode morphology structure and reduce the SEI layer thickness, which facilitates the improvement of voltage delay. Especially, the batteries added with molar ratio of 0.1:1 of 2, 2'-bipyridine exhibit least resistance.

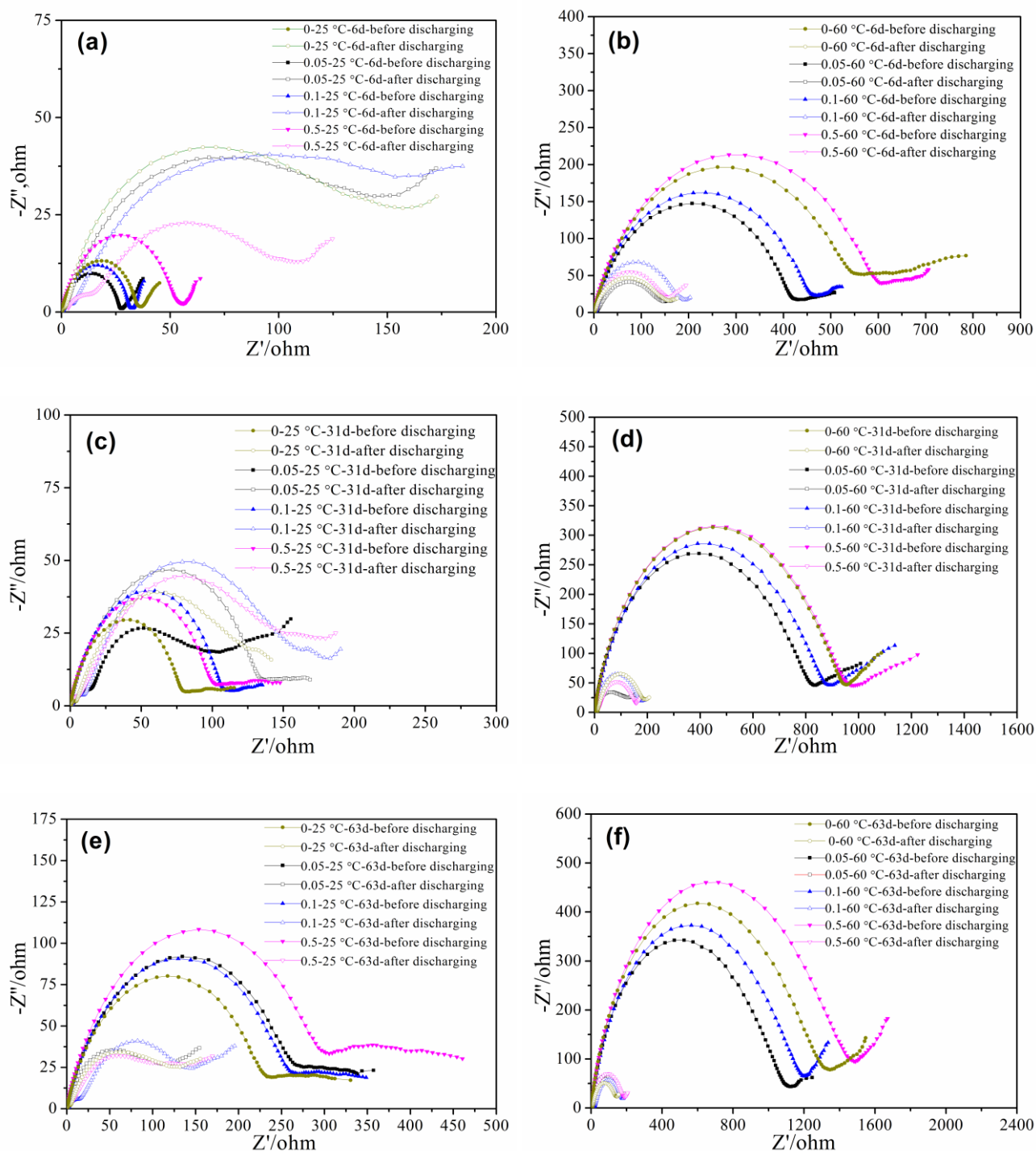


Figure 2. EIS of batteries with different storage time and temperature before discharging and after discharging with 2.0 V cut-off voltage.

The EIS for the batteries on the different DOD are presented in Fig.3-8. The depressed semicircles in high frequency region become small with increase of DOD. The passive film on the surface of Li anode splits gradually which is attributed to Li ions diffuse to the interface between Li anode [24]. Therefore, the resistance of SEI layer exhibits reduction trend.

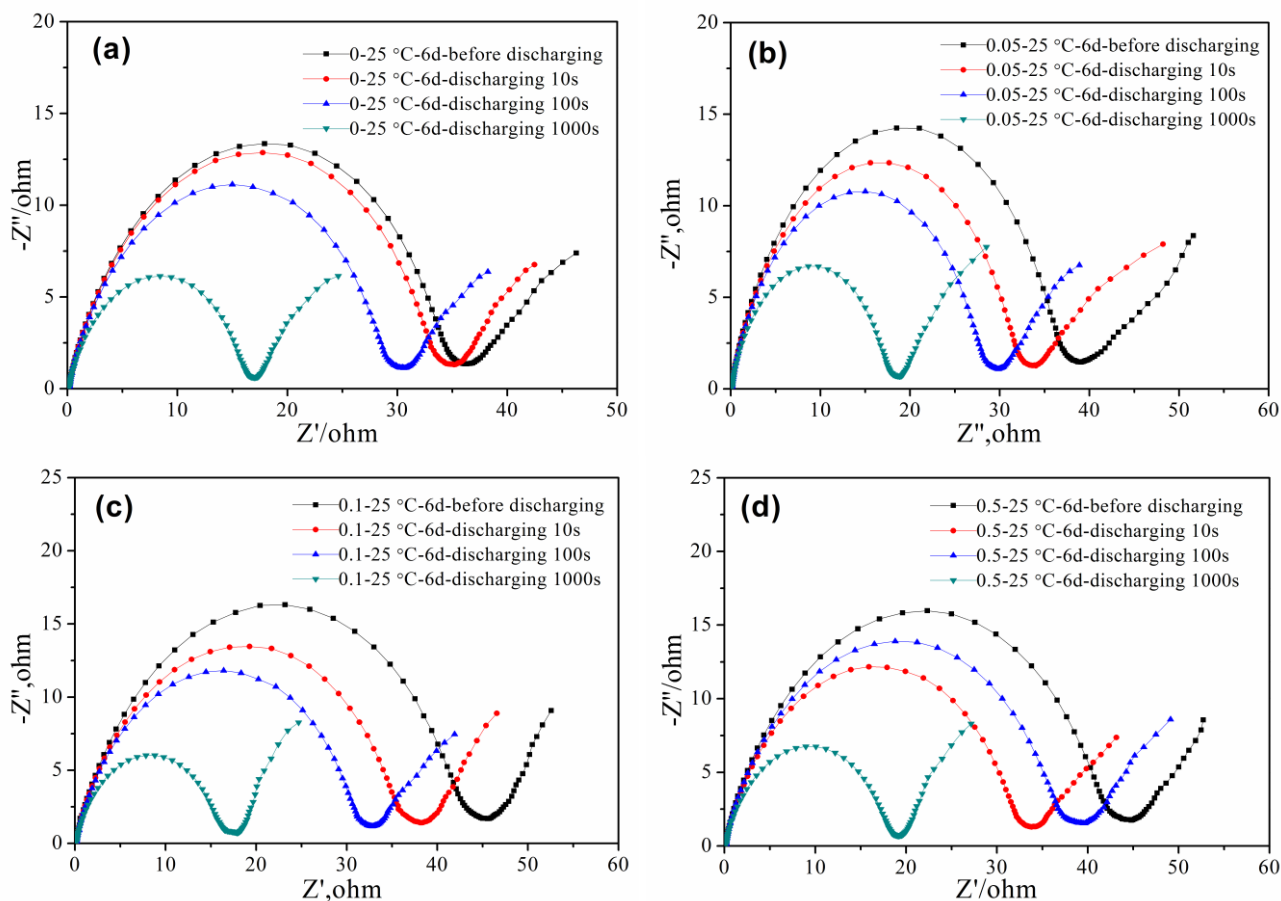
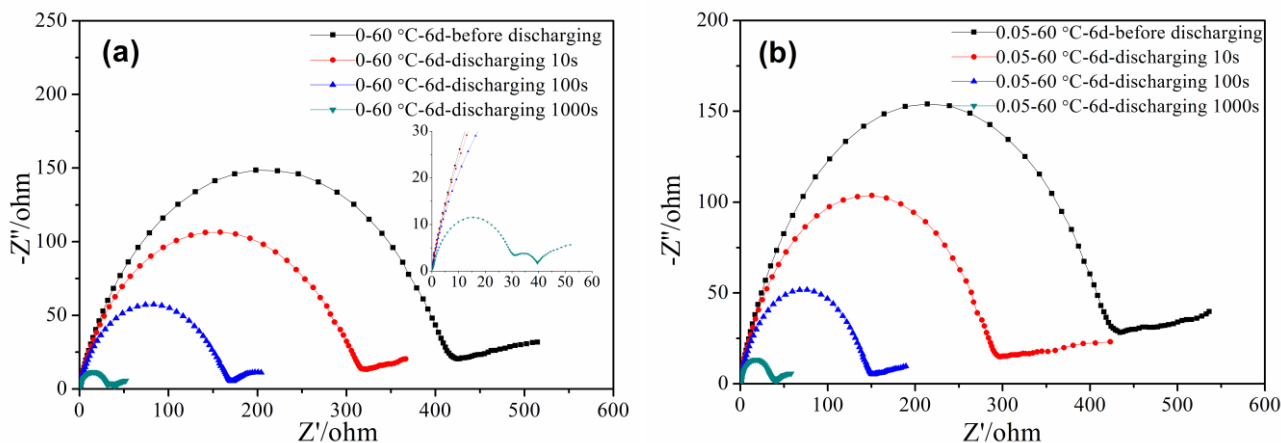


Figure 3. EIS of the batteries stored at 25 °C for 6d on the depth of discharge, (a) 0, (b) 0.05, (c) 0.1, (d) 0.5.



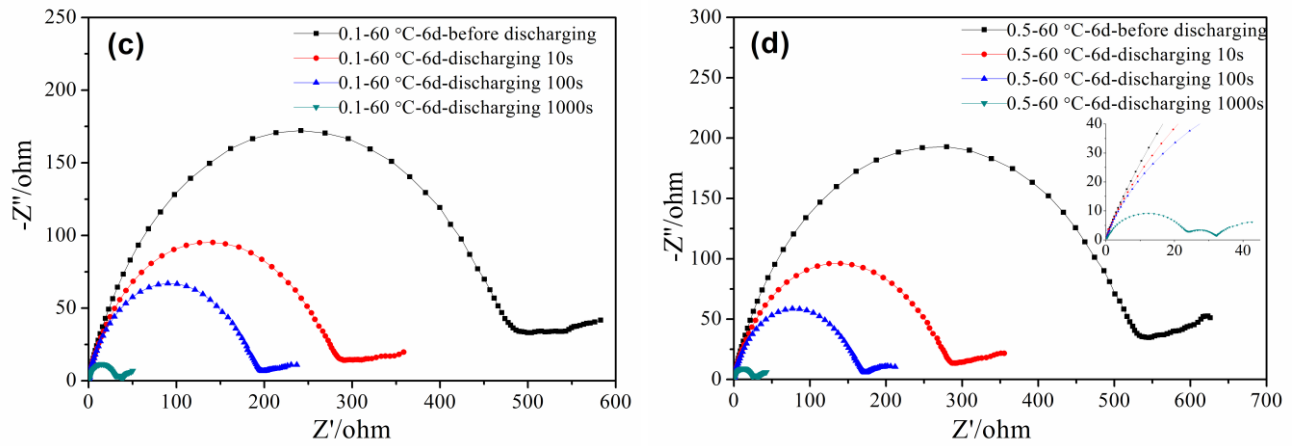


Figure 4. EIS of the batteries stored at 60 °C for 6d on the depth of discharge, (a) 0, (b) 0.05, (c) 0.1, (d) 0.5.

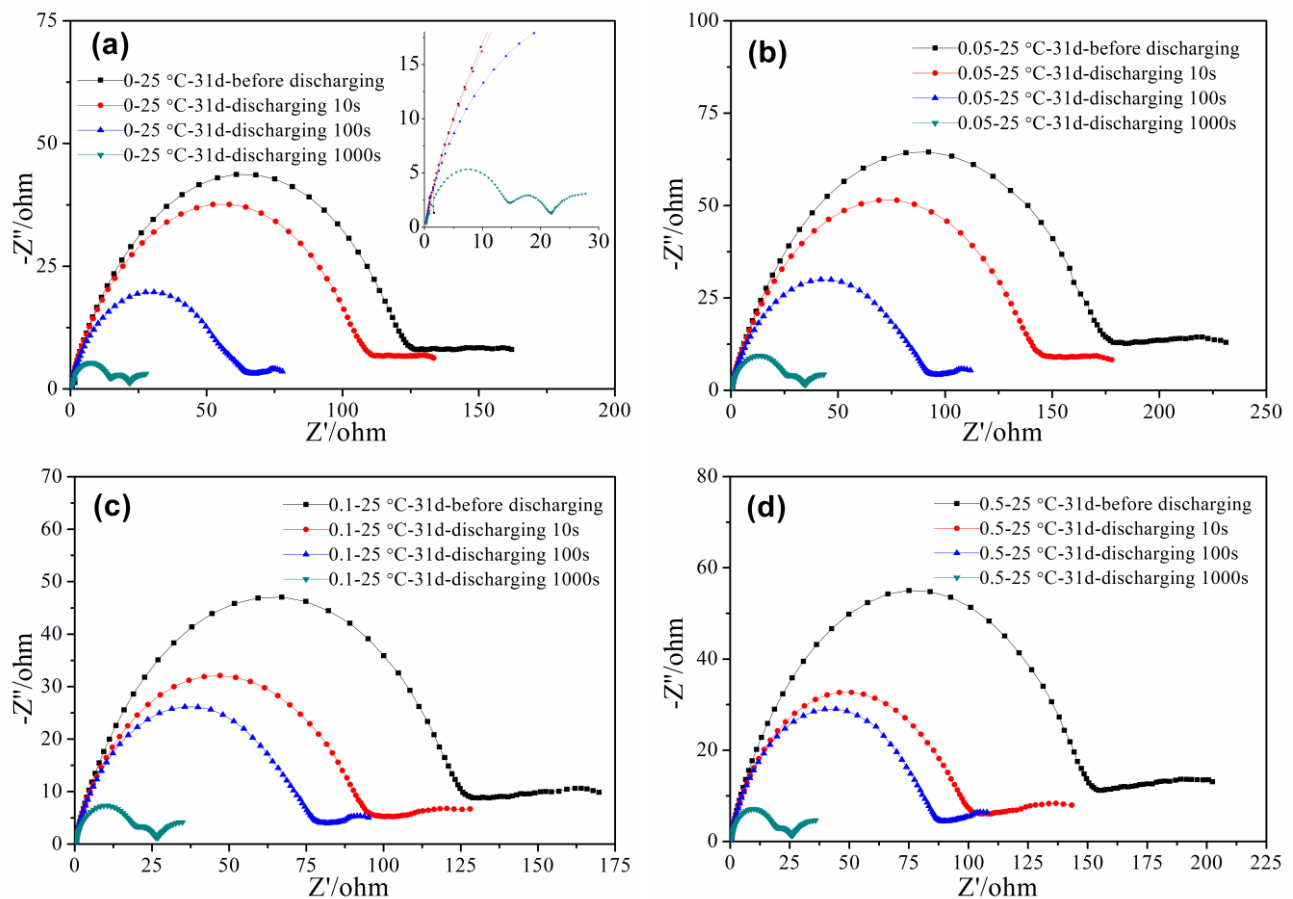


Figure 5. EIS of the batteries stored at 25 °C for 31d on the depth of discharge, (a) 0, (b) 0.05, (c) 0.1, (d) 0.5.

Especially, the EIS of the batteries exhibit two depressed semicircles in high frequency region and in middle frequency region followed by a short inclined line in low frequency region at DOD of

1000 s with the least the resistance of the passive film. It is assumed that the passive film on the surface of Li anode splits gradually with increase of DOD, which facilitates the transportation of Li ions. Therefore, the impedance spectra show a depressed semicircles in middle frequency region, which is related with the distribution of time constant [11].

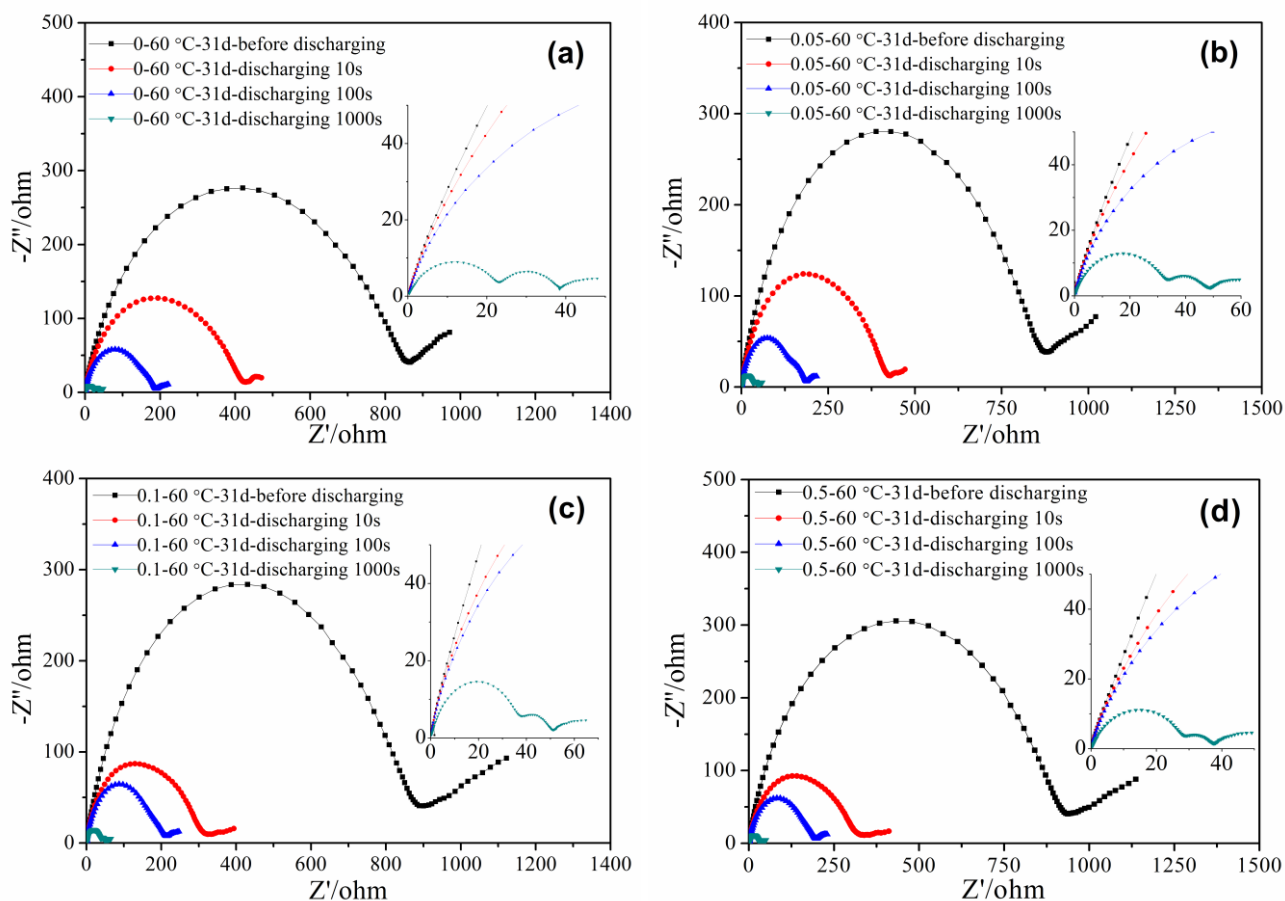
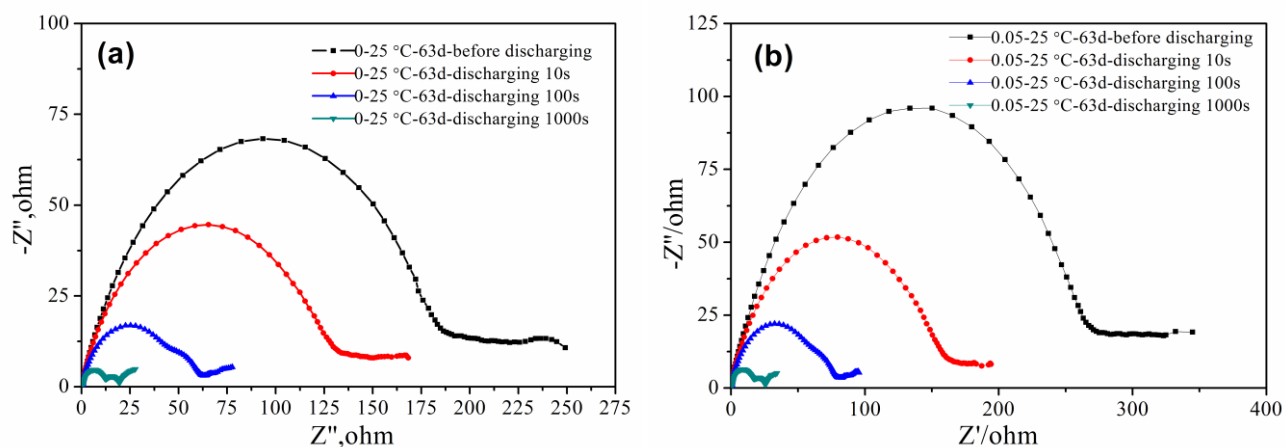


Figure 6. EIS of the batteries stored at 60 °C for 31d on the depth of discharge, (a) 0, (b) 0.05, (c) 0.1, (d) 0.5.



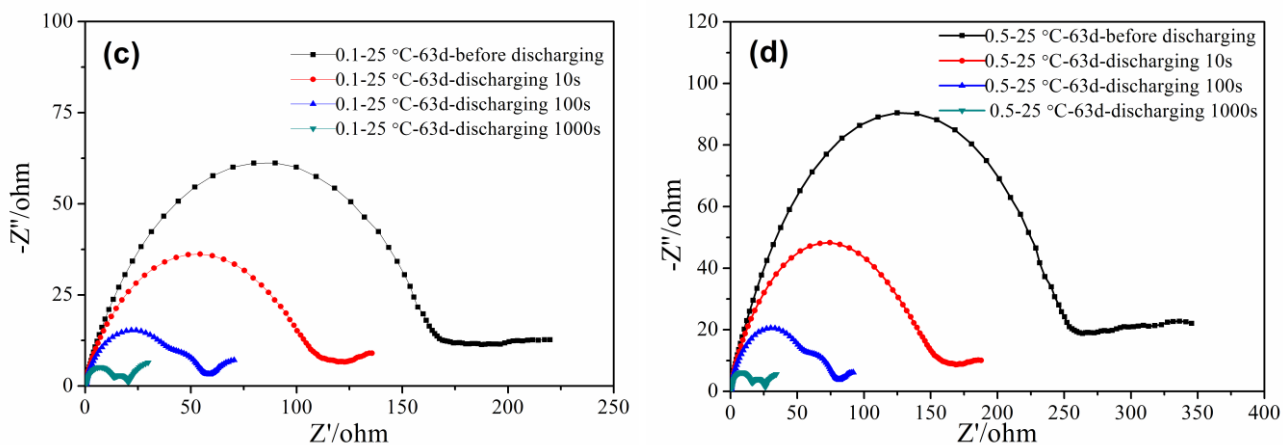


Figure 7. EIS of the batteries stored at 25 °C for 63d on the depth of discharge, (a) 0, (b) 0.05, (c) 0.1, (d) 0.5.

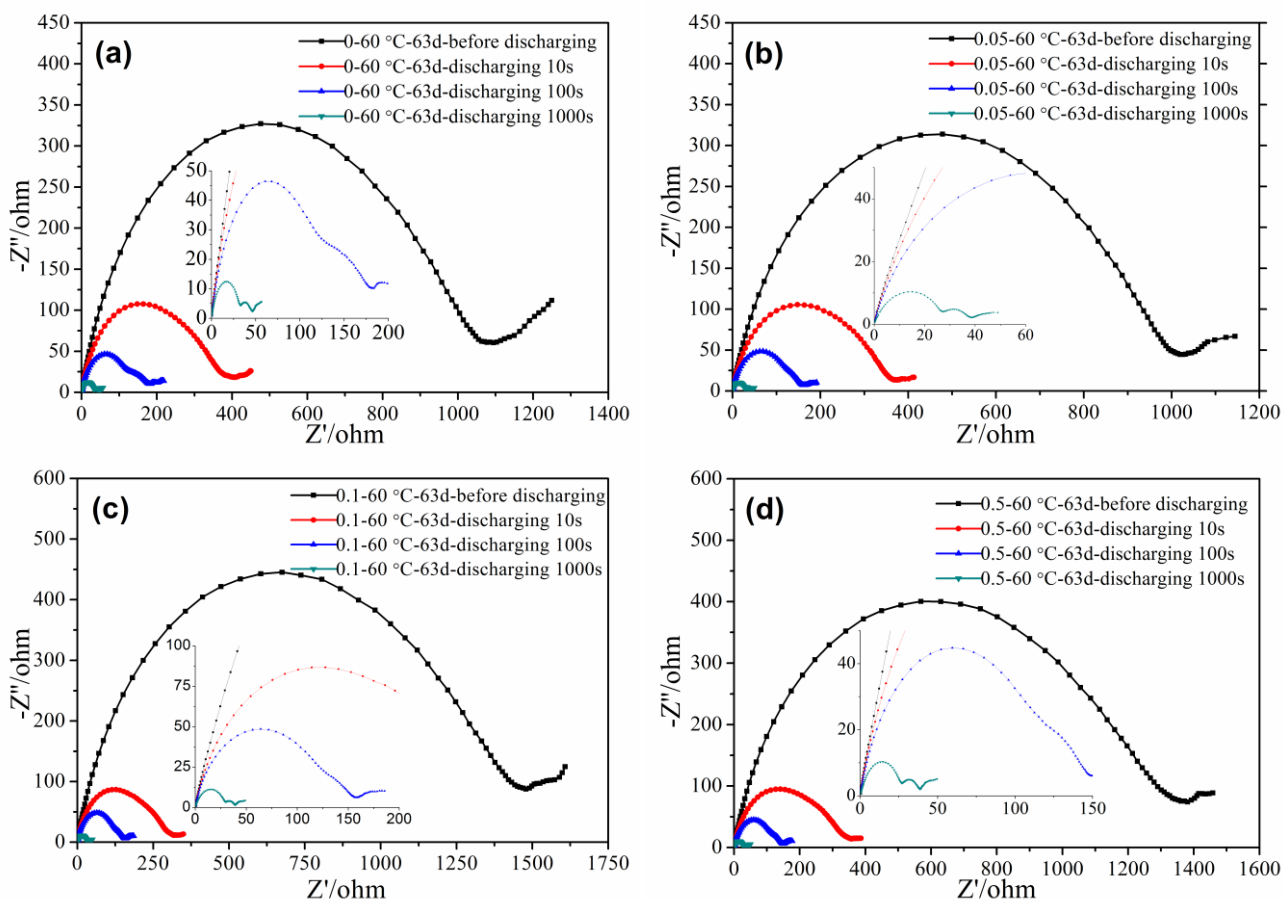


Figure 8. EIS of the batteries stored at 60 °C for 63d on the depth of discharge, (a) 0, (b) 0.05, (c) 0.1, (d) 0.5.

The shape of EIS for the batteries with and without additive of 2, 2'-bipyridine exhibits no apparent difference, meaning that 2, 2'-bipyridine will not alter the oxidation reaction mechanism of

Li. As shown in Fig.3 - 8, the depressed semicircles in high frequency region of the batteries with additive of 2, 2'-bipyridine become smaller than the batteries without additive of 2, 2'-bipyridine before discharging and at DOD of 10s. It is suggest that the additive of 2, 2'-bipyridine can change the compact passive film to the porous passive film. The porous passive film can be damaged more easily compared to the compact passive film at initial state of discharge [25-26]. Especially, the reduction of the resistance of the passive film for the batteries added with molar ratio of 0.1:1 of 2, 2'-bipyridine exhibit obvious trend. Furthermore, the angles of a portion of inclined lines in low frequency region of the batteries with additive of 2, 2'-bipyridine is larger compared to the batteries without additive of 2, 2'-bipyridine. The angles of a portion of inclined lines in low frequency region of the batteries with additive of 2, 2'-bipyridine increases as the increase of the DOD. It is indicated that porous passive film on the surface of Li anode facilitates the transportation of Li ions ascribed to the additive of 2, 2'-bipyridine.

4. CONCLUSIONS

In summary, a certain amount of 2, 2'-bipyridine added into the electrolyte can be adsorbed on the surface of Li anode and change the Li anode morphology structure, reduce the SEI layer thickness and allow the SEI layer to be porous, which facilitates the transportation of Li ions, leading to great improvement of voltage delay for Li/SOCl₂ battery. Especially, the batteries added with molar ratio of 0.1:1 of 2, 2'-bipyridine exhibit optimal performance.

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