Effects of pre-charge temperatures on gas production and electrochemical performances of lithium-ion batteries

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Abstract. Pre-charge as a key step in the battery manufacture processes, which has a great impact on the film-forming properties and electrochemical performances, especially the Li-rich system batteries. As a key influence factor, it is necessary to clarify the effect of pre-charge temperature on battery performance. In this paper, we mainly studied the influence of different pre-charge temperatures (25°C, 40°C, 60°C) on the gas production and electrochemical performance of the batteries. The results show that the increase of the pre-charge temperature will result in the increase of gas production, and the gas components are mainly CO_2, H_2. After the long-term cycle, the sample under 40°C maintains the highest capacity retention rate, and as the pre-charge temperature increases, the median voltage of the battery can be effectively increased. In addition, compared with room temperature pre-charge, high pre-charge temperature samples have more excellent rate performance.

1 Introduction

Recently, due to the advantages of high working voltage, high energy density, long cycle life, and low environmental pollution, lithium-ion batteries have been widely used in mobile electronic equipment, electric vehicles, large power plants and other fields[1,2].

There are many production processes for lithium-ion batteries, among which pre-charge is critical to the performance of the battery. Pre-charge means that after the battery has been manufactured, let it stand for an appropriate period to allow the electrolyte to fully infiltrate the electrodes and separator, and then charge the battery with a smaller current density. During the first charging process, as the charge voltage increases, the additives in the electrolyte begin to reduce on the surface of the anode, and a passivation film is formed between the electrode material and the electrolyte solution, which is called the solid electrolyte interface (SEI) layer[3,4]. Then, the charging voltage continues to rise, some components added in the electrolyte are decomposed, resulting in the release of gas inside the battery[5,6].

The parameters of pre-charge process include charging voltage, current density[7], temperature[8]. The voltage mainly affects the path of the film-forming reaction, while the current density and temperature mainly affect the rate of the film-forming reaction. An[9] proved that the decomposition reaction of electrolyte is different under different charging voltage. When the voltage is above 1.0 V vs. Li^+/Li, $LiPF_6$ will decompose to produce amount of LiF, while the reduction reaction

of solvents or additives will take place between 0.2 V and 0.8 V. In addition, Bhattacharya[10] and his team found that the film-forming characteristics of the negative electrode are significantly affected by temperature, as shown in Figure 1, there are fewer holes on the surface of the negative electrode under high temperatures, this also illustrates that a dense SEI layer can be formed inside the battery. In order to form a stable SEI on the surface of the negative electrodes and slow down the destruction of SEI during cycling, in this article, we will study the influence of different pre-charge temperatures on the gas generation and electrochemical performance of the battery.

2 Experimental

2.1 Batteries manufacture

First, mix the lithium-rich cathode material, conductive agent (SP, CNTs, Ks-6), and binder (PVDF) in a certain proportion, and add an appropriate amount of solvent (NMP) to stir to make a slurry. Then, the mixed slurry is coated on the aluminium foil by a coater. After drying, the electrode is rolled according to the calculated compaction density, and use a punching machine to cut the electrode into electrode pieces with the same size. Finally, the electrode pieces were dried in a vacuum oven at 100°C for 12 hours. Use the same method to prepare the negative electrode slurry. Mix the Si@C
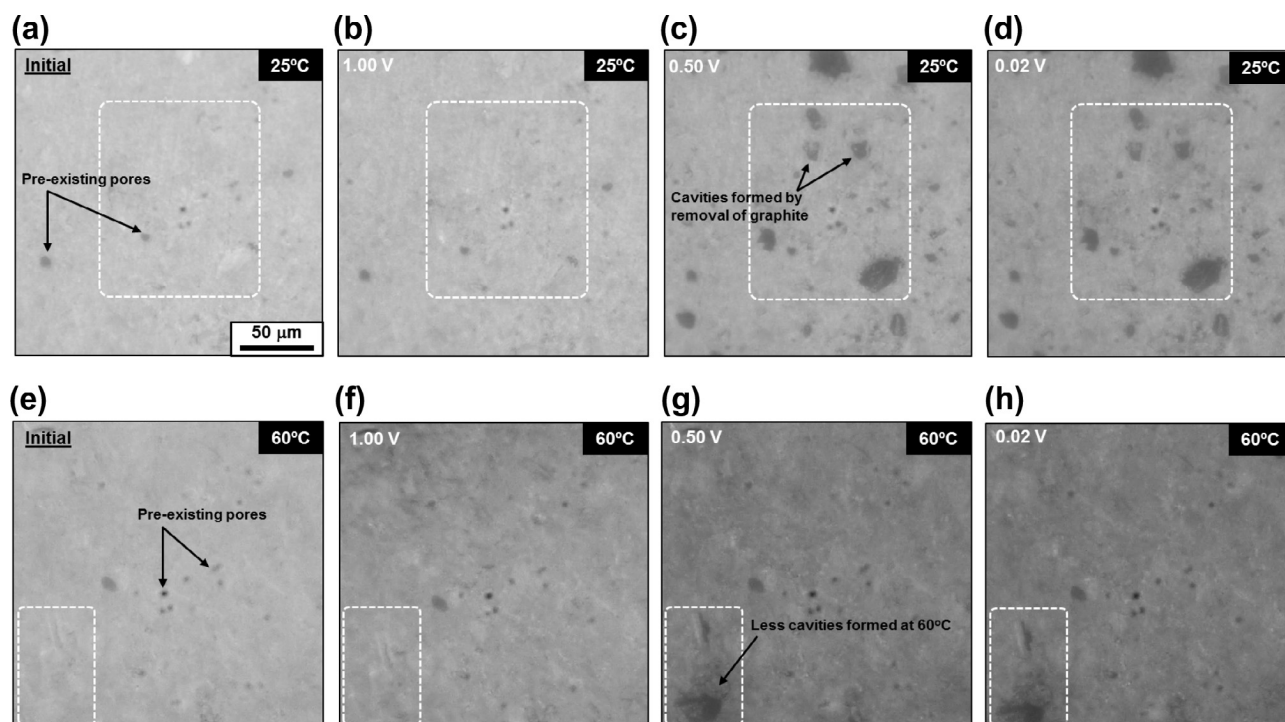

Fig. 1. Optical microstructures of graphite electrodes during the first cycle at different temperature [10].

anode material, conductive agent (SP and Ks-6), binder (PVDF) and solvent (NMP), and stir to make slurry. The difference is that the negative slurry should be coated on the copper foil. The separator is Celgard (16 μm, PP/PE/PP). After the core is made, it can be packaged with aluminium-laminated film, injected with electrolyte, sealed and left for a period of time before test.

2.2 Gas component test

GC-MS(Gas Chromatography-Mass Spectrometer) was used to test the composition of the gas. After the pre-charge is complete, the collected gas is injected into the equipment. The target substance is ionized into gas ion at the ionization source and then enters the mass analyzer. The ions of different mass-to-charge ratios are sequentially separated and arrive electron multiplier tubes generate electrical signals, so that we can obtain accurate information and clarify the composition of the gas.

2.3 dQ/dV curves

In the charge-discharge curve, the change of voltage with capacity contains information about the electrochemical process, but this change is generally small and not easy to observe. The differential processing of the curve is to amplify the change of the curve, so as to facilitate observation and processing. The dQ/dV curve can reflect the change of the capacity with the voltage under different voltages. At the voltage plateau during the charge and discharge, the voltage change is small while the capacity change is large, the characteristic peak will appear on the dQ/dV curve. Through the capacity differential curve, the capacity contributed by each electrochemical reaction under

different voltages can be more intuitively expressed. In this paper, in order to distinguish the various electrochemical reactions of active material in the process of pre-charge, the charge discharge curve is differentiated. Before the differential treatment, we need to filter the data, and then the capacity differential calculation will be carried out.

2.4 Electrochemical tests

After the batteries were pre-charged at different temperatures, we used the Neware test system (BTS-4008) for electrochemical performance test. In the study of the cycle performance of the battery, the charge and discharge currents are 0.3 C and 1 C respectively. In the study of the rate performance, the charge current of the test current is 0.3 C, 0.5C, 1 C, 1.5 C, 2 C, 2.5 C, 3 C respectively, and the discharge current is 1C. The temperature in the electrochemical tests is room temperature, and the voltage range is 2 V to 4.6 V.

3 Results and discussion

The pre-charge current and time are 0.01 C and 24 h, respectively. The pre-charge temperature is 25°C, 40°C, and 60°C. When the temperature is 25°C and 40°C, the cut-off voltage of pre-charge is 3.7 V, and when the temperature is 60°C, the cut-off voltage is 3.6 V.

3.1 The amount and composition of the gas

During the first charge of lithium-ion batteries, the potential of negative electrode material decreases continuously due to the increase of charging voltage, which leads to the electrochemical reduction of

electrolyte on the negative electrode surface and the generation of gas. After pre-charge, by comparing the reserved air pouches, it can be found that different temperatures have a significant effect on the gas production. Figure 2 shows the comparison of air pouches after pre-charge. Since the gas production of samples at room temperature is not obvious, it is not shown in the figure.
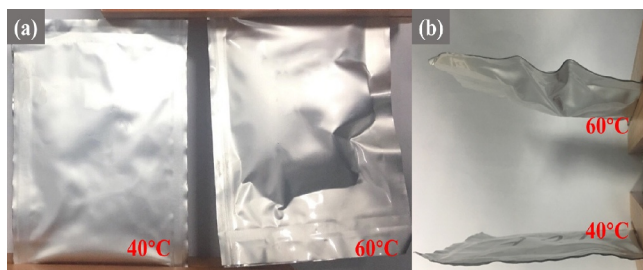

Fig. 2. Gas production in air pouches after pre charging at different temperatures.

We can clearly find that the gas production of the sample at 40°C is significantly less than that of the sample at 60°C. This is related to the infiltration and reaction between the electrolyte and the electrode at high temperature. At high temperatures, the reaction inside the battery is more intense, resulting in producing more gas. In addition, the gas produced in the 60 °C battery was analysed by GC-MS. The gas component and content are shown in Table 1. From the result, it can be found that the organic components of the generated gas are mainly C_2H_4, which indicates that a large amount of solvent EC is decomposed at this stage. The inorganic components are mainly CO_2, H_2, which indicates that a large amount of $LiOCO_2R$ and Li_2CO_3 have been decomposed[11]. The decomposition of EC will change the film formation state of the anode surface, thereby will affect the subsequent electrochemical performance.

Table 1. Components and content of gas produced after pre-charge at 60 °C.

	Component	Content/%
Organic gas	CH_4	0.078
	C_2H_6	0.102
	C_2H_4	0.304
Inorganic gas	H_2	15.100
	CO_2	72.533
	N_2	8.906
	CO	2.977

3.2 dQ/dV curves

The charging curves at different temperatures of 25 °C, 40 °C and 60 °C are shown in Figure 3. The effect of the pre-charge temperature on the charge capacity is not obvious, as shown in the figure, the charge capacity at 25°C, 40°C and 60°C is 576 mAh, 573.8 mAh, and 574.1 mAh, respectively.
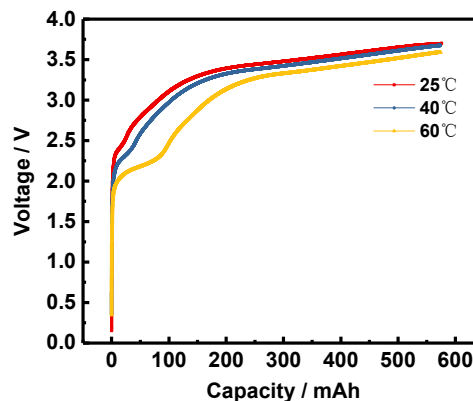

Fig. 3. Voltage-capacity curves of batteries at different pre-charge temperatures.

In order to more clearly understand the variation of each electrochemical reaction with temperature during charge, the capacity differential curve is shown in Figure 4. There are three oxidation peaks in the capacity differential curve during charge, and the influence of temperature on the electrochemical reaction of each peak is different. The peak O1 and O3 showed obvious differences with the change of temperature, while the peak O2 did not change significantly. When the pre-charge temperature increased from 25 °C to 40 °C, the position of peak O1 hardly changed. When the temperature continue to increase to 60 °C, the position of peak O1 obviously shifts to the low potential, the peak voltage decreased from 2.403 V at 25°C to 2.168 V, and the intensity increased sharply. Since the position of peak O2 is difficult to define, it is considered that it does not change with the change of pre-charge temperature. As the pre-charge temperature increases, the peak position of O3 gradually shifts to a lower potential. The peak voltages at 25°C, 40°C and 60°C are 3.468 V, 3.389 V and 3.334 V, respectively.
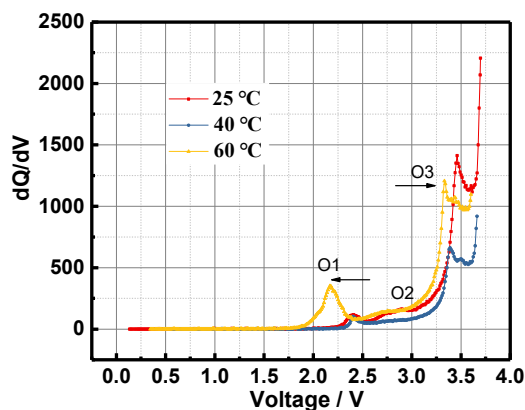

Fig. 4. dQ/dV curves of batteries at different pre-charge temperatures.

3.3 Electrochemical performance

During the cycle of lithium-ion batteries, as cycle number increases, the polarization will increase due to various reasons. We usually use the reduction of the capacity retention rate and the median voltage to characterize the cycle performance of the battery. The cycle curve is shown in Figure 5. It can be seen from the figures that at the beginning of the cycle, the capacity retention rate of the sample pre-charged at 60 °C is higher than that of the sample at 25 °C and 40 °C. However, after the cycling performance of all batteries decays rapidly, the sample at 40 °C has the best capacity retention rate. After 230 cycles, the capacity retention rate of 25 °C, 40 °C and 60 °C samples were 71.9%, 73.1% and 72.6% respectively.
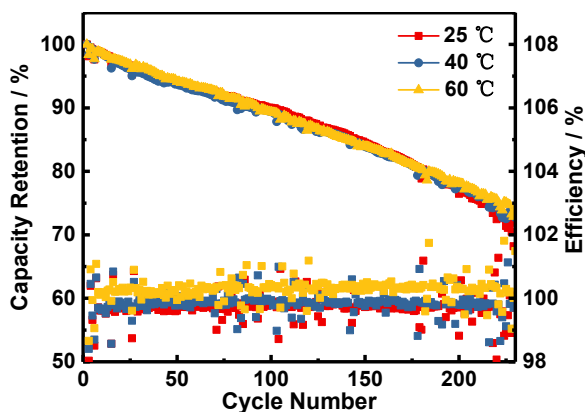

Fig. 5. The capacity retention rate of batteries pre-charged at different temperatures during cycling.

Figure 6 is the median voltage curve. From the figure, we can see that during the cycle, the median voltage of the samples after high temperature pre-charge is always higher than that of the room temperature. After 230 cycles, the median voltage of the 25°C, 40°C and 60°C samples were 2.929 V, 2.954 V, and 2.946 V, respectively. The results show that increasing the pre-charge temperature can effectively improve the discharge median voltage of the battery. The main reason would attributed to that the SEI film is more uniform and compact after high temperature pre-charging.
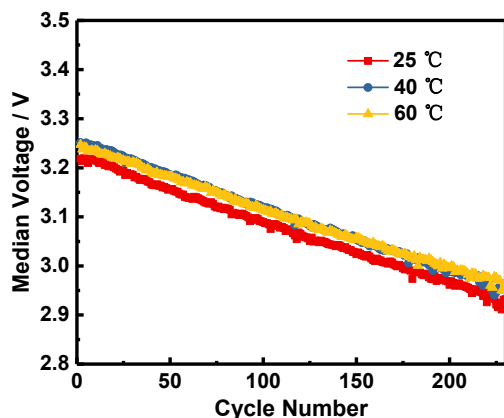

Fig. 6. The median voltage of batteries pre-charged at different temperatures during cycling.

In addition, we also tested the rate performance of the battery, and the tested current densities were 0.3 C, 0.5 C, 1 C, 1.5 C, 2 C, 2.5 C, and 3 C. It can be seen from Figure 7 that the high-temperature pre-charged samples have more excellent rate performance. The rate performance of the 40°C sample is better than the 25°C sample at each current, and the capacity retention rate of 3 C is increased by 11%. The specific capacity retention rate of the battery under different currents is shown in Table 2.
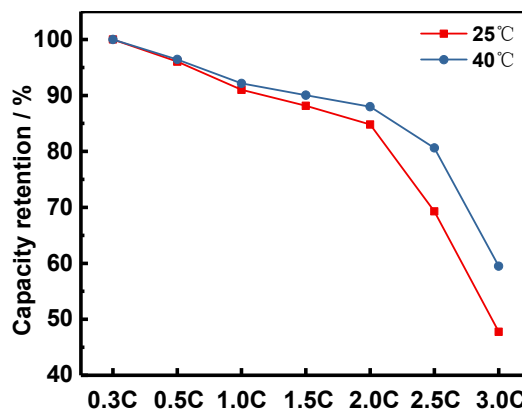

Fig. 7. The rate performance of batteries pre-charged at different temperatures.

Table 2. Specific capacity retention at different temperatures and currents.

Temp.	Capacity retention/%						
	0.3C	0.5C	1.0C	1.5C	2.0C	2.5C	3.0C
25°C	100	96.0	91.0	88.1	84.8	69.3	47.8
40°C	100	96.4	92.2	90.0	88.0	80.6	59.5

4 Conclusion

In this paper, we mainly studied the effects of different pre-charge temperature on the gas production and cycle electrochemical performance of the lithium-ion battery. It is proved that as the temperature increases, the amount of gas generated during the pre-charge process also gradually increases. The main reason is that high temperature can promote the film-forming reaction of SEI layer, which will produce gas. In addition, high temperature pre-charging could effectively improve the cycle electrochemical performance of the battery. The cycle and rate performance of the battery pre-charged at high temperature are higher than that at room temperature. In particular, the rate performance above 2.5 C can be improved by 10%. In subsequent research, we will study other key factors that affect the pre-charge process, including pre-charge current and time, and try to improve battery performance by optimizing pre-charge parameters.

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