Experimental Study on Lithium Ion Diffusion of Graphite Anode Based On In-Situ Optics

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Abstract: During charge and discharge of the lithium-ion batteries (LIBs), the graphite electrode will produce a color change behavior. In view of the difficulty in in-situ observation of the current lithium ion concentration distribution in real batteries. An in-situ optical experimental method is reported in this paper, which realizes an in-situ observation of the color change of the graphite anode electrode section, and obtains the diffusion path of lithium ion in the graphite anode electrode section. Base on colorimetric method the results show that the surface of the graphite electrode is priority region during lithiation/delithiation, and the lithiation characteristics are discrete. At the same time, the optical image was further analyzed by the MATLAB program ,obtains three color (RGB) variations at different lithiation concentrations (SOC). This method can be used to qualitatively analyze the basic color change mechanism of graphite electrode during lithiation /delithiation.
Keywords: Lithium-ion battery, Graphite anode, Diffusion, Colorimetric method.

I. INTRODUCTION

Lithium-ion batteries (LIBs) are the most common energy storage components in consumer electronics, portable devices and hybrid and electric vehicles[1, 2].One of the main challenges of their development is to meet the application and safety requirements of new energy electric vehicles. Therefore, research on lithium-ion batteries from battery to module-level design to electrochemical mechanism is essential. In order to evaluate the mechanismof color change during lithiation and delithiation of graphite anodes, many theoretical and computational models have been established at the particle and electrode levels[3, 4].Graphite has a layered structure, and the process of intercalating lithium is a process in which lithium ions are intercalated between graphite layers--Intercalation reaction. By observing the graphite discoloration macroscopically, the lithiation state of the graphite negative electrode can be obtained. However, it should be noted that the above lithium intercalation stage is in a completely ideal state, and the lithium intercalation state inside the actual graphite is relatively complicated, and is often a mixture of various stages. One of the possible methods to in situ observe the Li diffusion in the electrodes is the colorimetric method, which is widely applied to graphite electrodes. The Li intercalation into the crystal lattice of the graphite electrodes would change the visible absorption spectra of the LiC_x compounds[5-10].In situ colorimetry, a technique that correlates the color of an electrode with the state of charge(SOC) to measure the distribution of lithium ions in a battery electrode[5, 11]. A calibration curve of the three color values of red, green, and blue are obtained and used to map the distribution of lithium in the battery electrode. In-situ optical experiments and in-situ colorimetry were used as a fast, low-cost measurement method to study the lithium content in various lithium-ion battery electrodes. The apparent diffusion coefficient and activation energy of the porous graphite electrode were obtained by experiments. The distribution of lithiation of the negative electrode of aged lithium ion batteries is highly heterogeneous. The color change process of Li transport in the surface of the graphite electrode material during charge and discharge was studied by in-situ optics, and the effective lithium ion diffusion coefficient was extracted[12, 13].

At present, what the researchers observe is only the surface condition of the electrode[14]. The actual process inside the electrode is more complicated than the simple diffusion, which has certain limitations on the vertical condition of the real battery. In particular, there is a lack of in-depth study on the actual situation of the internal charge and discharge process of the soft pack battery. The lithium ion is captured in the whole process of the cross-section of the electrode, and the lithiation process is effectively analyzed. An in-situ optical experimental method is reported in this paper, which realizes an in-situ observation of the color change of the graphite anode electrode section, and obtains the diffusion path of lithium ion in the graphite anode electrode section. Base on colorimetric method the results show that the surface of the graphite anode electrode is priority region during lithiation/delithiation.

II. EXPERIMENTAL SECTION

As shown in Figure 1 and Figure 2(b), an in-situ battery device similar to a sandwich structure was designed. The structure of the battery is clamped by a glass slide with a graphite anode electrode in the middle,and the diaphragms and thecathode electrodes on both sides. Figure 2 shows the experimental process , and graphite electrode supplied by soft pack battery (502030 battery), and LiFePO$_4$ (LFP) electrode as cathode electrode , and the glass fiber film as separator (supplied by Whatman). In order to obtain a clear and flat cross section for observing the graphite stacking configuration, graphite-based electrode was cut using a scalpel. Assemble the battery (excessive positive electrode) and seal it in the in-situ cell. The in-situ cell sealing device prevents the battery from contacting the air. It is made of PTFE material (no reaction with electrolyte, good sealing), as shown in Figure 2c. The upper end of the in-situ cell is made of glass, and the test sample can be clearly displayed at one end.Inject electrolyte infiltration (~ 1 ml) at the edge of the battery separator before sealing, and the electrolyte is made of commercial lithium iron phosphate (LiFePO$_4$=LFP, 99%). The above sample preparation process was carried out in a glove box (Ar gas environment, H$_2$O<0.1, O$_2$<0.1).
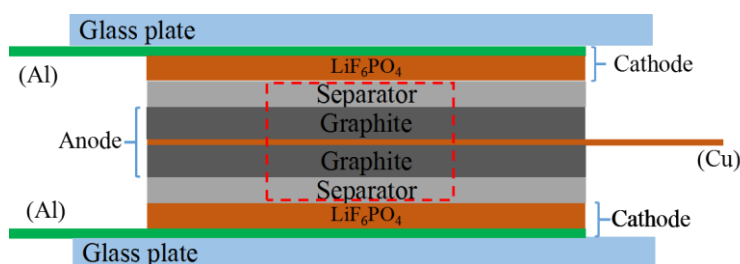

Figure 1: Cross-sectional schematic of the full battery sample(Red frame is the observation area)
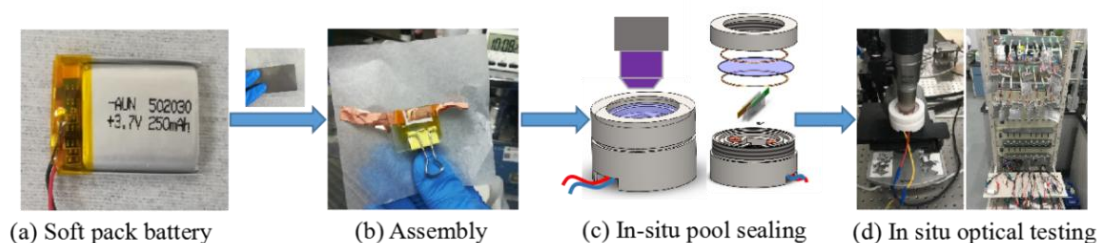

Figure 2: Flow chart of sample preparation

As shown in Figure 2(d), the experimental platform consists of optical microscopy (KEYENCE, VHX-S90) combined with a battery test system (Neware, BTS 2000). All electrochemical tests were performed at the temperature of 25℃. The full-cell was tested at the current density of 330mA/g (1 Cate). The test area was magnified 500 times using optical microscopy and continuously photographed with the interval of 30s. The series of optical images were developed in Photoshop software with a resolution of 1600×1200, and the 50μm area of the images corresponds to 130 pixels.

III. RESULTS AND DISCUSSION

As shown in Figure 3, the initial thickness of the double-coated graphite anode before the test is 130μm. The initial color of the graphite electrode is black. As shown in Figure 4, the multi-cycle test was performed by charging/discharging at a constant current of 0.5 mA, and it is a stable cycle of voltage and current. Since the battery does not reach the upper limit voltage due to the excess of the LFP cathode electrode, the charging time is set to 1h. During the cycle test, pictures were taken at different times by optical microscopy.

During the insertion of lithium ions into the graphite particles, the formation of LiC$_x$ leads to a change in lattice spacing and a presentation of different colors. The microstructure evolution of the graphite electrode during charge/discharge process as shown in Figure 5. The color change state of the graphite electrode under different state of charge (SOC) can be obtained by in-situ colorimetry. The study found that the surface of the graphite electrode is a preferential region of lithiation, and the lithiation process is star-shaped and discrete. The lithiation process of the graphite electrode: subjectively, the color changes continuously from black gray to gold; the delithiation process: lithium ions are successively removed from the graphite electrode, and the color gradually fades. The lithium intercalation state inside the graphite is complicated, and it is often a mixture of various stages. It was found that there was a phenomenon of lithium deposition phenomenon between the graphite electrode and the separator.
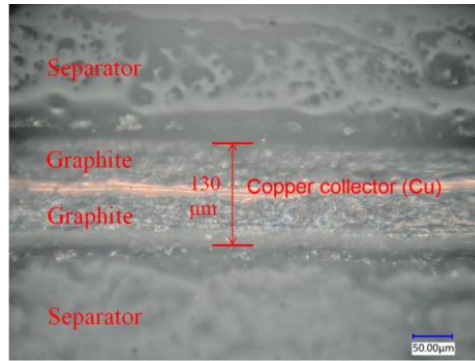
Figure 3: Initial cross-section of the full battery
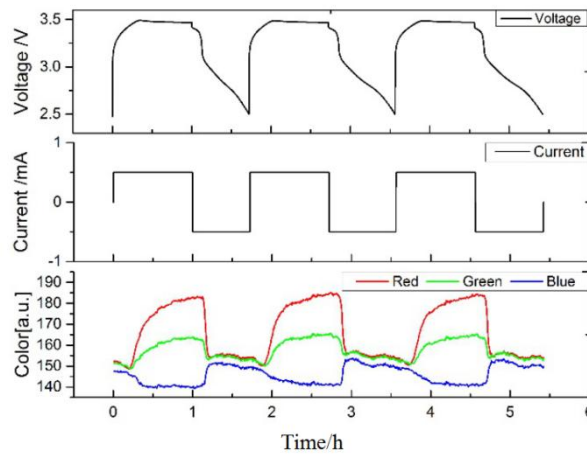
Figure 4: Current and voltage cycles of full cell
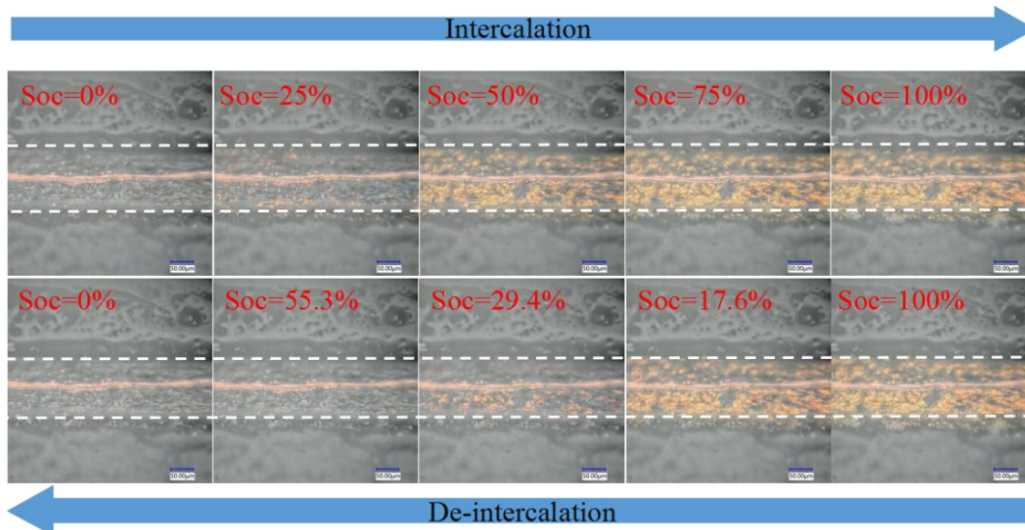
Figure 5: .color change on the cross-section of graphite electrode
(white line frame is the RGB analysis area)

As shown in Figure 3 and Figure 6(a), three color evolution values of red, green and blue (RGB) are extracted from the experimental optical digital image of graphite electrode (the white frame portion shown in Figure 4 by MATLAB programming. In the process of cycling, RGB forms stable intervals and trends. For further quantitative analysis, the correspondence between the state of charge (SOC) and the color (RGB) is calibrated, and the calibration result is shown in Figure 6(b). In the initial stage of lithium insertion, the RG values arereduced firstly , and then the fast response is positively correlated with the SOC. The delithiation process is the reverse process of lithiation, and the RGB values are relatively more responsive. The B values is negatively correlated with SOC, and the interval of R value is the largest.
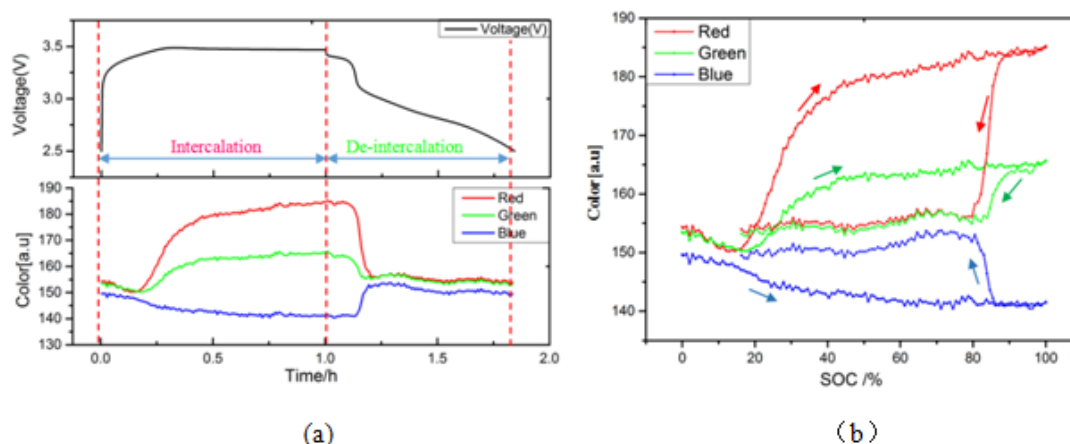
Figure 6: The second cycle: (b)curves of voltage and colorsand (b)curves of SOC and colors

IV. CONCLUSION

In this paper, the in-situ optical experiment was used to report the inside of the real battery, revealing the lithium ion diffusion mechanism. The following main conclusions were obtained through experiments: The lithiation process of the graphite electrode is obtained based on the in situ colorimetric method. The electrode-separator interface is the preferential region for lithiation and delithiation, and the lithiation process is discrete. At the same time, At the same time, there is a phenomenon of uneven lithiation, and a place where the electrode material has high activity has a concentrated lithium intercalation region.The RGB values were extracted from the optical digital pictures by MATLAB programming and corresponded to the lithiation process, and the semi-quantitative characterization of the lithiated color change in the electrodes.

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