Experimental Investigation to Evaluate $LiFePO_4$ Batteries Anode and Cathode Elastic Properties under Cyclic Temperature Loading Conditions

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Abstract: Experimental investigations and associated methods are provided to characterize the mechanical properties of a lithium-ion battery accounting for operating temperature variation and thermal effects. Material properties for $LiFePO_4$ cathode and anode samples taken from an off-the-shelf battery are evaluated in new and fatigued (subjected to charging and discharging cycles) conditions.

Key words: $LiFePO_4$ battery; cathode; anode; temperature; mechanical properties

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1 Introduction

The need to develop and deploy large-scale, cost-effective, renewable energy is becoming increasingly important. Lithium-ion batteries are one of the most popular types of rechargeable battery for portable electronics. Developing technologies to produce flexible batteries with good performance in combination with high specific strength is strongly desired[1]. Various approaches to fabricate structural electrodes to enhance the mechanical properties have been reported in Ref. [1]. When blends of traditional electrode with other materials are used, as is commonly the case, device performance directly depends on the nanoscale morphology and phase separation of the blend components. Both anode and cathode materials are layered structures, which allow lithium ions to stay in or pass through them. On the cathode side, intercalated lithium compound such as Lithium iron phosphate ($LiFePO_4$), lithium manganese oxide ($LiMn_2O_4$), and lithium cobalt oxide ($LiCoO_2$) are commonly used. $LiFePO_4$ is a promising candidate for high-energy-density low-cost batteries. This material has numerous advantages, among which, it is environmentally friendly and has minimal hazard with significantly higher safety[1-5]. Synthesis and electrochemical properties of $LiFePO_4$ and $LiFePO_4/C$ composite powders were investigated. The study involved the evaluation of temperature effect on specific capacity of battery and dependence on firing temperature at three temperatures associated with voltages varying between 2.5 V and 4.3 V. However, the cyclic charge/discharge process of a battery occurs between different temperatures, therefore the mechanical properties are also expected to change significantly within the operational range of temperatures, from room temperature to 600 °C. Li_xFePO_4 ($0<x<1$) is phase separating at room temperature and undergoes a phase transformation between heterosite $FePO_4$ and triphylite $LiFePO_4$ during the charge and discharge processes.

Nanoindentation method is extensively used to characterize the mechanical behavior of small

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volumes of material with spatial resolutions in the range from nanometer to micrometer. The technique relies on the local deformation induced on a material' s surface with an indenter of known properties under the application of a given load. The load applied on the indenter and the corresponding displacement of penetrated indenter into a sample is continuously monitored during the loading and unloading processes. In Lithiumion batteries, the technique has been used to study the changes in mechanical properties due to phase transformation of anode coating[6-9]. In order to better control the thermodynamical properties determining its electrochemical performance, a better understanding of its elastic properties is needed. At present, experimental data on mechanical properties such as elastic constants or bulk moduli are not available since Li_xFePO_4 is usually synthesized as sintered powder and the growth of larger crystals is known to be very difficult. To fulfill the gap in knowledge currently existing in lithium-ion battery material properties, the objective of this work is to apply characterization technique based on nanoindentation (NI) and scanning electron microscopy (SEM) methods to understand their nonlinear mechanical characteristics behavior and their primary dependence on temperature, which changes during charge/discharge process. While such materials could be exposed to high temperature during their lifecycle, the tests performed at ambient temperature would no longer predict the reliability with greater accuracy.

2 Experimental Methods

2.1 SEM measurements

A new off-the-shelf $LiFePO_4$ battery is used for this experiment. Anode and cathode constituents are carefully extracted from the new battery and tests are conducted on the individual constituents before and after the battery is subjected to cyclic loading by charging/discharging operations. The cathode and anode material characteristics are evaluated using SEM. Micrographs of the material morphology and structure are taken by SEM (JEOL JSM-7400F). Images are taken with a 15 kV accelerating voltage and working distances of 6—15 mm. It can provide constituent material characteristics along with structural composition and percentage of chemical elements. An example of $LiFePO_4$ cathode SEM picture is provided in Fig. 1. The olivine crystal structure is evident.

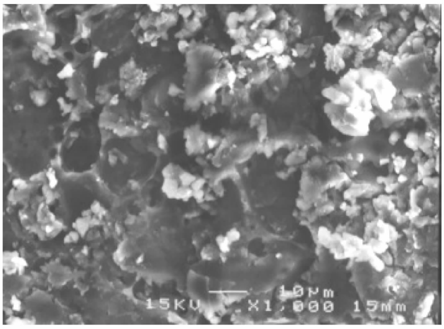

Fig. 1 SEM micrograph of new cathode

As indicated earlier, the $LiFePo_4$ battery was subjected to cyclic loading to follow a charge/discharge process 2 000 times. The battery was cycled between 2. 2 V and 3. 2 V, with an average of 2. 7 V. Charge continued until the voltage reached 3. 2 V, and then a discharge was initiated. The process was stopped after 2 000 consecutive cycles. SEM is used before and after this cyclic process to evaluate any change in the crystal structure and measure the quantities of chemical elements and the structure of the cathode constituent. In Fig. 2, an SEM image of the cycled cathode is provided. The thermo-electrical cyclic process has significantly changed the structure of the battery component.

Similarly, the new anode material (before cycling) is analyzed using SEM (Fig. 3) to evaluate both structural composition and percentage of chemical elements. After a similar charge/discharge process conducted for the cathode, the anode is also analyzed under SEM, and its structure is reported in Fig. 4.

The thicknesses of the cathode and anode

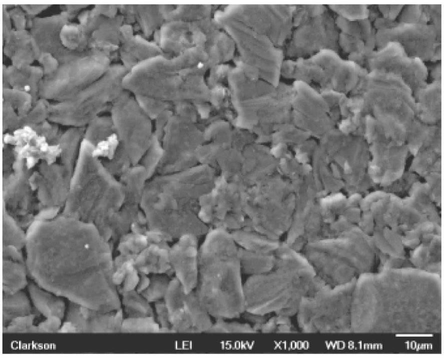

Fig. 2 SEM micrograph of cathode subjected to cyclic process(2 000 times)

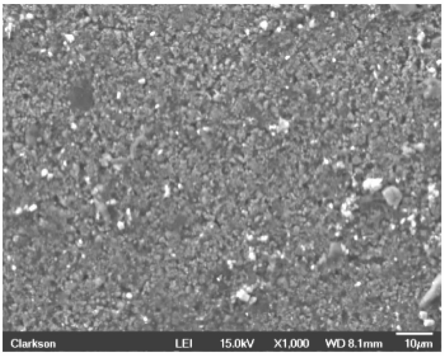

Fig. 3 SEM micrograph of new anode

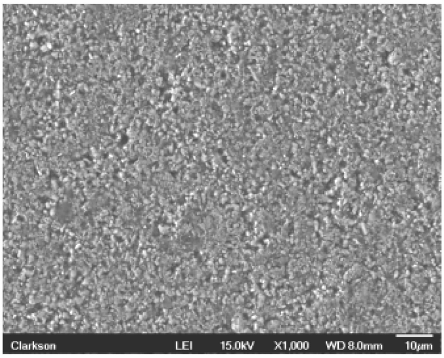

Fig. 4 SEM micrograph of anode subjected to cyclic process (2 000 times)

layers are also measured. In Fig. 5 the thickness of cathode is displayed. The two $LiFePO_4$ layers and copper substrate are about 93 μm.

Fig. 6 presents the thickness of the anode. Two $LiFePO_4$ layers and aluminum substrate are about 172 μm. The thickness information is used to plan the successive test to characterize the local mechanical properties.

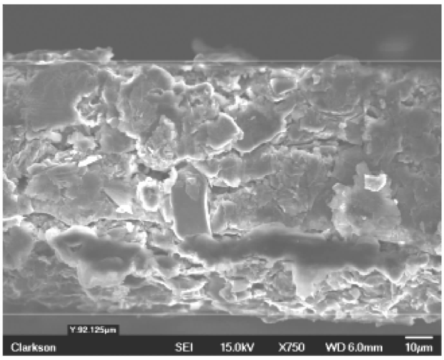

Fig. 5 Micrograph of cathode thickness

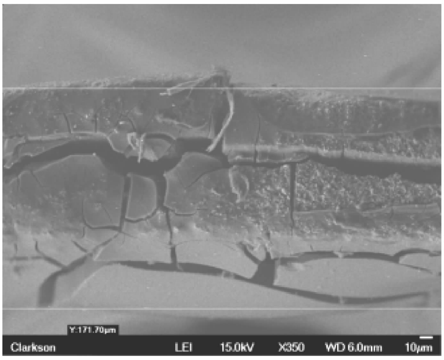

Fig. 6 Micrograph of anode thickness

2.2 Nanoindentation measurements

To characterize the local mechanical properties at different temperatures, high temperature quasi-static nanoindentation tests are performed using a TI-950 Triboindenter (Hysitron Inc., MN). It is also important to mention that the TI-950 Hysitron Tribolndentor can only measure up to 10 μm from the surface. In order to confirm the reliability of results, the machine is well calibrated before performing tests. A Berkovich tip (three-sided diamond pyramid) is used to indent the materials at different locations using a trapezoidal load function (Fig. 7), resulting in an average maximum indentation depth of 100—200 nm which is lower than 10% of the material thickness.

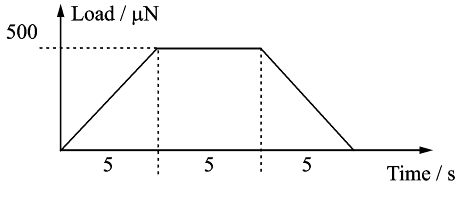

Fig. 7 Trapezoidal load function used for the tests

In quasi-static nanoindentation experiments, the Oliver-Pharr method[10] is used to extract the indentation modulus and hardness from the force-displacement curves. The reduced modulus (E_r) is calculated from the unloading portion of the force-displacement curve according to the relation

$$\frac{1}{E_r}=\frac{1-\nu_s^2}{E_s}+\frac{1-\nu_i^2}{E_i} \tag{1}$$

where E and ν are the Young's modulus and Poisson's ratio, respectively, and the subscripts correspond to the sample (s) and diamond indenter tip (i) elastic properties. Parameters for the indenter are $E=1\ 140$ GPa and $\nu=0.07$. Hardness (H) is the ratio of the maximum force to the contact area, namely

$$H=\frac{P_{\max}}{A_c} \tag{2}$$

On the specially designed heating stage, the samples are secured with compression clips in order to avoid slippage and obtain efficient thermal conductivity. Temperature is varied from 30 °C to 400 °C with the steps of 30, 50, 100, 200, 300 and 400 °C. Between each temperature increase, at least 30 min is allowed to elapse for the sample to equilibrate. Before initiating the indentations, the tip is brought in contact with the sample for 5 min in order to equilibrate the temperature at the specimen-tip contact.

3 Results and Discussions

Quantitative analysis of measurements for the cathode from SEM images is provided in Table 1. The presence of copper is explained by the fact that the cathode substrate material is copper. Quantitative measurements for the 2 000 times cycled material are presented in Table 2.

Table 1 Quantitative analysis of new cathode chemical elements

Element	Net counts	Weight/%	Atom/%
C	4 411	38.42	46.53
O	14 891	53.86	48.96
F	697	4.81	3.68
P	703	0.67	0.31
Cu	263	2.25	0.51
Total		100.00	100.00

Table 2 Quantitative analysis of cycled cathode chemical elements

Element	Net counts	Weight /%	Atom/%
C	20 785	97.95	99.51
P	555	0.48	0.19
Fe	33	0.13	0.03
Cu	170	1.44	0.28
Total		100.00	100.00

After 2 000 cycles of discharge-recharge the oxygen is fully fired, a large percentage of carbon remains. For the new anode the percentages of chemical elements are presented in Table 3. The presence of Aluminum and Magnesium is explained by the fact that the anode substrate material is Aluminum rich Magnesium. Alloys of Al-Mg system are characterized by a combination of satisfactory strength, good ductility, weld ability and very good corrosion resistance. Cycled material quantitative measurements of chemical elements are presented in Table 4. The evaluated Young's moduli for new and cycled $LiFePO_4$ cathode and anode materials are provided in Figs. 8,9, respectively. It was observed that, the materials

Table 3 Quantitative analysis of new anode chemical elements

Element	Net counts	Weight/ %	Atom/%
C	3 844	45.09	61.36
O	7 502	27.68	28.28
Mg	173	0.14	0.09
Al	149	0.11	0.07
P	13 426	9.84	5.19
Fe	5 516	17.14	5.02
Total		100.00	100.00

Table 4 Quantitative analysis of cycled anode chemical elements

Element	Net counts	Weight /%	Atom / %
C	2 057	34.42	50.95
O	8 466	31.32	34.80
Mg	238	0.23	0.17
Al	689	0.60	0.40
P	13 609	11.89	6.82
Fe	5 990	21.54	6.86
Total		100.00	100.00

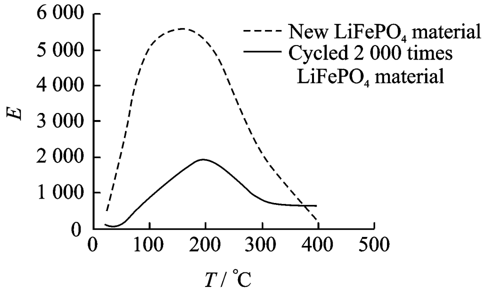

Fig. 8 Young's modulus for new and cycled 2 000 times LiFePO$_4$ cathode

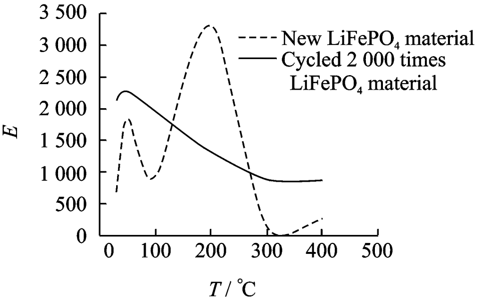

Fig. 9 Young's modulus for new and cycled 2 000 times LiFePO$_4$ anode

increase in reduced modulus with the rise in temperature up to 200 °C. However, for temperatures beyond 200 °C, the reduced modulus values start decreasing with increase in temperature. The material is composed of several base materials. Such variations in the reduced modulus could be from the response of different materials at elevated temperatures. The adhesion of the materials with the copper substrate at the higher temperatures could also considerably affect the reduced modulus values. The experimental results use Eq. (1) to compute the Young's modulus E using values of generalized gradient approximation (GGA) of Poisson's ration supplied to Eq. (1).

The results show that the cycled LiFePO$_4$ cathode material has modulus of elasticity around 2.5 times lower than a new material. This is explained by the fact that oxygen is fired during the cycles and softer carbon is mostly left on the samples. Interestingly, in both new and cycled cathode materials, the maximum value of the modulus of elasticity is found in the proximity of 200 °C, while after 250 °C the modulus of elasticity starts decreasing. The modulus of elasticity of new material is 5.87 GPa, while the cycled material has an elastic modulus of 2.18 GPa. On the other hand, the maximum value of the modulus of elasticity for the new anode, as it is for the cathode, is near 200 °C, while it is near 50 °C for the cycled material. The maximum value of the modulus of elasticity of new material is about 3.3 GPa while it is about 2.62 GPa for the cycled material.

The maximal hardness for the new and cycled cathode as well as for the new and cycled anode materials at room temperature, 50, 100, 200, 300 and 400 °C are reported in Fig. 10.

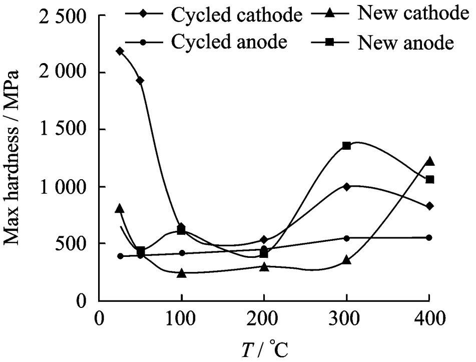

Fig. 10 Max hardness for new and cycled LiFePO$_4$ cathode and anode

Fig. 10 shows that a large variability in hardness is present at low temperature 25—100 °C, and at larger temperature above 300 °C. A minimum of hardness is reached around 200 °C for the new and cycled cathode and for the new anode, while the cycled anode hardness remains unchanged. These results show certain consistency.

4 Conclusions

This paper discusses the influence of temperature on the elastic properties of the cathode and anode of LiFePO$_4$ battery. Quantitative measurements including the chemical composition and structure by SEM, and elastic modulus and hardness by nano-indenter for new or cycled cathode and anode materials, are conducted. A peculiar behavior is noticed, namely the elasticity modulus has its maximum value for both cathode and anode materials near 200 °C, with the exception of the cycled anode material which has its maximum around 50 °C.

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