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Short communication

Surface potential measurement of aged Li-ion batteries using Kelvin probe microscopy

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ABSTRACT

In lithium-ion batteries, several electrical and physical parameters are responsible for the degradation of the electrode materials. Here the application of Kelvin probe microscopy (KPM) is demonstrated to measure the charge sustaining capability of the $LiFePO_4$ cathode under aged and unaged conditions. The aged sample shows lower surface potential than the unaged sample, which can be attributed to changes in physical and chemical properties including particle size, phase of the surface layer and nanocrystalline deposits.

1. Introduction

Advanced Li-ion batteries with high energy and power density are favored for automotive demands. While the operation of the Li-ion cell is well established, the aging mechanisms still need to be investigated as the aging of a Li-ion battery is still the weak link in the development of long lasting hybrid vehicles [9]. The harsh duty cycles (high current demand, low state of charge, deep depth of discharge, and high temperature profiles) in hybrid/electric vehicles cause the loss of capacity (range) and power (performance) in the battery system faster than normal rate. The degradation or "aging" is a result of several simultaneous physiochemical processes that occur within the electrode, electrode–electrolyte interface, and within the electrolyte.

The aging of a battery causes a decrease in capacity and a subsequent increase in the internal resistance. The degradation in these system level parameters is due to damage in the cathode, anode, and electrolyte within the cell. The surface electrical properties need to be evaluated for a better understanding of the damage mechanisms of the electrodes. Surface resistance properties have been measured for $LiFePO_4$ unaged and aged cathodes using scanning spreading resistance microscopy (SSRM) [10].

Another technique of interest is KPM, which has been used in a variety of applications to measure surface potential. Because of the sensitive nature of silicon to charge buildup and subsequent discharge which can damage small silicon parts, surface potential measurement has been of interest in the semiconductor industry. The technique has also been used successfully to detect wear precursors from wear at very low loads using atomic force microscopy (AFM) based Kelvin probe methods [5–7].

The use of the Kelvin probe method is now extended to the study of Li-ion batteries. The KPM technique is based on the contact potential difference method for measuring the electronic work function (EWF) [14]. Since EWF is strongly influenced by the surface chemical composition and Fermi level of the material KPM can detect the structural and chemical changes of the surface and provide vital information about the onset of damage. Using KPM large areas of the entire cathode electrode can be scanned quickly giving spatial information of its surface. In this study, KPM is used for the first time to characterize aging of the cathode surfaces by measuring the change in the surface potential which can be attributed to physical and chemical changes of surface.

2. Experimental details

2.1. Kelvin probe microscopy

Nanoscale surface potential measurements were taken with a Dimension™ 3100 AFM. A schematic of this instrument with KPM setup is shown in Fig. 1. The KPM measures the surface poten-

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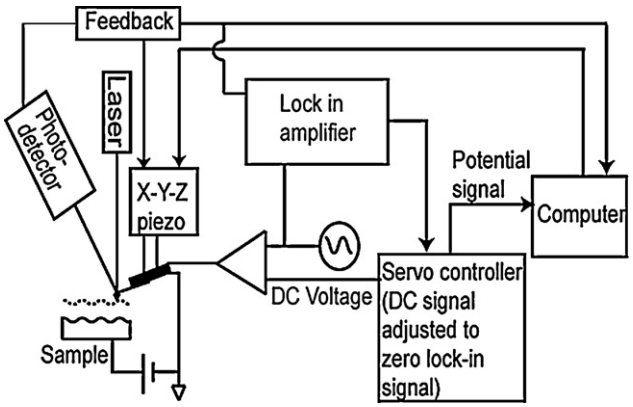

Fig. 1. Schematic of the two pass interleave scan method used in KPM. (Adapted from Rice, 2002 [12].)

tial of the samples in interleave mode. Along one scan line on the sample, in first pass, the surface height image is obtained in tapping mode. In second pass the tip is lifted off the sample surface and a surface potential map is obtained. Both images are obtained simultaneously [12]. During the first pass, the cantilever is mechanically vibrated by the *X–Y–Z* piezo near its resonance frequency. The amplitude of the tip vibrations (not shown) is maintained at a constant value by the feedback loop as the tip scans the surface of the sample. The signal from the feedback loop is used to construct the height map of the sample surface (Fig. 1). During the interleaved scan, the *X–Y–Z* piezo is switched off. Instead, an AC signal is applied directly to the conductive tip which generates an oscillating electrostatic force on the tip. The tip is scanned along the surface topography line obtained in the tapping mode with a certain lift off the sample (dotted line in Fig. 1).

To briefly describe the operating principle of KPM, consider a tip and sample interaction as seen in Fig. 2. When the tip and sample are electrically connected (Fig. 2a) electrons flow from the material with the lower work function to the material with the higher work function. Due to the difference in the work function of the electrically connected tip and the sample an electrostatic contact potential difference (or surface potential difference) is created between the tip and the sample [14]. The value of this surface potential ($\Delta\Phi$) is given by the following equation:

$$\Delta\Phi = \frac{\Phi_{tip} - \Phi_{sample}}{e} \tag{1}$$

where Φ_{tip} and Φ_{sample} are work functions of the tip and the sample, respectively, and e is the magnitude of the charge of one electron. $\Delta\Phi$ will be affected by any adsorption layer and the phase of the material near the surface. Electrostatic force is created between the tip and sample under the influence of this surface potential difference and the separation dependent local capacitance C of the tip and sample. This force is given by:

$$F = \frac{1}{2}(\Delta\Phi)^2 \frac{\partial C}{\partial z} \tag{2}$$

where z is the distance between the tip and sample.

Along with $\Delta\Phi$, in the operation of the KPM a compensating DC voltage signal (V_{DC}) and AC voltage signal, $V_{AC}\sin(\omega t)$ (Fig. 2b and c) is applied directly to the tip. Thus the electrostatic force between the tip and the sample becomes:

$$F = \underbrace{\frac{1}{2}\frac{\partial C}{\partial z}\left\{(\Delta\Phi + V_{DC})^2 + \frac{V_{AC}^2}{2}\right\}}_{\text{DC-term}} + \underbrace{\frac{\partial C}{\partial z}(\Delta\Phi + V_{DC})V_{AC}\sin(\omega t)}_{\omega\text{-term}}$$

$$- \underbrace{\frac{1}{4}\frac{\partial C}{\partial z}V_{AC}^2\cos(2\omega t)}_{2\omega\text{-term}} \tag{3}$$

The cantilever responds only to the forces at or very near its resonance frequency. Thus, only the oscillating electric force at ω acts as a sinusoidal driving force that can excite oscillations in the cantilever. The DC and the 2ω terms do not cause any significant oscillations of the cantilever. In tapping mode, the cantilever response (RMS amplitude) is directly proportional to the drive amplitude of the tapping piezo. Here, in the interleave mode the response is directly proportional to the amplitude of the ω term [12]. The servo controller applies a DC voltage signal equal and out of phase with $\Delta\Phi$ so that the amplitude of the tip becomes zero ($F = 0$). This compensating signal from the servo controller creates the surface potential map of the sample [6].

The conductive AFM tip is necessary for the KPM experiments. The tips used in our experiments had an electrically conductive 5-nm-thick chromium coating and 25-nm-thick platinum coating on both sides of the cantilever (Budget Sensors, Model # Multi75E-G). The resonant frequency of the tips was 75 kHz, and the radius was less than 25 nm. The interleave height was optimized to 150 nm for a good surface potential signal.

2.2. Demonstration sample

The operation of the KPM technique is demonstrated with a sample shown in Fig. 3a. A single crystal silicon (1 0 0) wafer with a high resistivity of about 3.3 kΩ cm is chosen as a substrate. A SiO_2 layer of about 200 nm is grown on the substrate with thermal oxidation process. Then, using an evaporation process two distinct rectangular pads of Ti/Au with a separation distance of 15 μm are deposited on the sample. The thickness of the Ti coating is about 50 nm, and the thickness of the Au coating is about 200 nm. Electrical connections are made to the pads using micro-probes available from Accuprobe™.

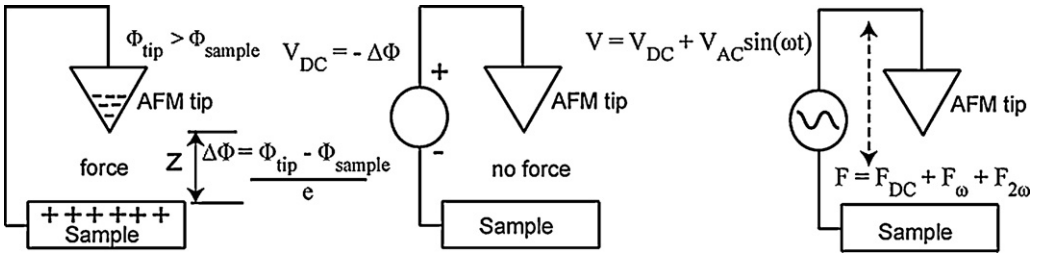

Fig. 2. (a) Electrostatic potential and interaction force between a conducting tip and a sample (for illustration $\Phi_{tip} > \Phi_{sample}$ is assumed), (b) external DC voltage applied to nullify the force, and (c) external AC voltage with adjustable DC offset is applied to the tip which leads to its vibration. (Adapted from Bhushan and Goldade, 2000 [6].)