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Discovery of lithium in copper current collectors used in batteries

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Aging studies of Li-ion batteries have been concentrated on degradation of cathode, anode and electrolyte materials with very limited attention to degradation in current collectors. Our data shows the presence of lithium beyond the active material and in the copper current collector (CCC). The lithium impurity in the CCC will lead to degradation in its thermal and electrical behavior and thus cannot be ignored for overall efforts in understanding the aging mechanisms predicting the life and performance of the batteries.

Keywords: Li-ion batteries; Aging; Current collector; Degradation mechanism

The world energy consumption is expected to double in next 50 years. Environmental concerns have stressed the use of clean renewable sources to satisfy this increasing demand. Batteries play an important role in storage of electrical energy obtained from these renewable sources. The automotive application of batteries has led the development of high energy and power density Li-ion battery technology. Aging characteristics of Li-ion battery systems for hybrid electric, plug-in hybrid electric and electric vehicles must be understood and quantified for the commercial success of these vehicles. Several studies on the degradation mechanisms for cathode, anode and electrolyte materials have been published [1]. For a better understanding of the aging mechanisms, all the components in a battery, including the separator and current collector, have to be tested under real-life driving conditions. Even as new anode and cathode materials are developed, certain components, such as the current collectors, are made of the same material in the new generation of Li-ion batteries. In the case of Li-ion batteries, copper is used as the current collector for the anode and aluminum is used as the current collector for the cathode. The corrosion of the current collectors has already been studied to demonstrate their electrochemical stability; however, these studies were not performed on the current collectors extracted from real-life Li-ion batteries. Degradation in the performance of current collectors is never anticipated when predicting the cycle life of the battery.

In a Li-ion battery Li is the single most important element as it directly participates in the electrochemical reactions during the cycling of the battery. Measuring the Li concentration in the electrodes is crucial for understanding the migration of Li across the battery. Electron-based techniques are unable to measure the Li due to the presence of a thin beryllium window on the detectors that blocks the low-energy X-rays from any element with an atomic number less than five. We have successfully applied neutron depth profiling (NDP) to measure the Li concentration profiles in the anode and cathode of unaged and aged batteries [2]. We adopted a similar approach to measure the effect of aging and Li migration on a copper current collector (CCC). The data presented here suggests that the degra-

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dation of current collectors cannot be ignored in the overall effort to understand the aging of Li-ion batteries.

NDP is a non-destructive analytical technique based on the nuclear fission reaction between a beam of neutrons with certain elements, such as lithium, throughout the sample. The cold neutrons are delivered through a neutron guide to the NDP facility. In this work, the "cold" neutrons refer to neutrons with energy of less than 5 meV. Since cold neutrons have extremely low energy and momentum, there is no center-of-mass motion in the neutron–lithium reaction. Furthermore, the neutron event rate is not sufficient to cause a significant temperature rise in the sample, nor is there significant radiation damage to the sample during the measurement period. All NDP experiments were conducted at the NIST Center for Neutron Research (NCNR).

A schematic of the NDP chamber at the NIST-NCNR facility is shown in Figure 1. The sample is attached to an aluminum disk (Fig. 1) and held vertically in the center of a vacuum chamber by the alignment grooves provided on the sample mount. The sample mount is oriented facing a surface barrier-type charged particle detector. The chamber is maintained at a vacuum of less than 1.33 mPa (10^{-6} torr). An ~0.8 cm^2 area of the sample is exposed to the cold neutron beam long enough for the statistical error in counting the energy particles to be no greater than 3%. Upon absorption of the neutron by the Li in the sample, monoenergetically charged ^{4}He and ^{3}H particles are emitted, as per the reaction below. These particles travel diametrically opposite from the site of the reaction.

$$^6\text{Li} + \text{n} \rightarrow {}^4\text{He}(2055\ \text{keV}) + {}^3\text{H}(2727\ \text{keV}) \tag{1}$$

The energies of the ^{4}He and ^{3}H particles at the reaction site are known to be 2055 and 2727 keV, respectively [3]. These heavy charged particles lose energy via a stochastic collision with electrons along their outward path towards the surface. The count rate and the residual energy are simultaneously measured from all sample depths for the particle species emerging in the direction of the detector (Fig. 1). The charged particles do not lose any energy after leaving the surface of the sample as they travel through the vacuum towards the detectors.

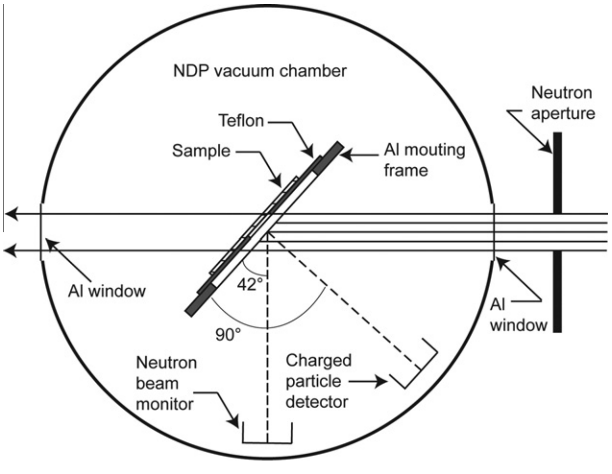

Figure 1. Schematic layout of the cold neutron depth profiling chamber at NIST.

The reaction center of mass is coincident with the site of the lithium atom. Thus the ^{4}He and ^{3}H particles originate from the same location as the original lithium atom, and their respective energies are directly related to the location of the lithium atom in the sample. The energy loss of the charged particle per unit length traveled through the sample is given by the stopping power function of the sample. Mathematically, to the first-order approximation, the depth is related to the stopping power by Bragg's law, which is given as:

$$x = \int_{E(x)}^{E_0} \frac{dE}{S(E)} \tag{2}$$

Here x is the path length traveled by the particle through the material, E_0 is the initial energy of the particle, $E(x)$ is the energy of the particle emerging from the surface and $S(E)$ is the stopping power of the sample material [4]. The Stopping and Range of Ions in Matter (SRIM) code developed by Ziegler et al. [5] is then used to obtain the stopping power of copper, and to assign the residual energies of the charged particle to the corresponding depth in the sample. The concentration of ^{6}Li within the sample is determined by comparing the count rate observed from the sample with that of a well-characterized boron concentration standard, labeled as N6 [6]. Since the natural abundance of ^{6}Li in the sample is only 7.5%, the total Li elemental concentration is obtained by dividing the determined ^{6}Li concentration by 0.075. The full-width-half maximum resolution of the NDP system had geometric and energy contributions corresponding to 0.27 μm in Cu.

Figure 2a shows the dissembled commercial Li-ion battery used in this experiment. This commercial Li-ion battery has a graphite anode, a cathode comprising LiFePO_4 nanoparticles (40–50 nm) and lithium hexafluorophosphate salt in 1:1 ethylene carbonate and dimethyl carbonate as the electrolyte. Each electrode has an active material bonded onto the current collector using a polyvinylidene difluoride binder. In the case of the anode, graphite is bonded onto a CCC, as shown in Figure 2b. For cathode layers of LiFePO_4, nanoparticles are bonded onto an aluminum current collector (ACC) (Fig. 2c). The anode and cathode strips, with a separator in between, are rolled and then packed into a can to form a cylindrical cell. The battery has an operating voltage of 3.3 V and a nominal discharge capacity of 2.3 Ah. It was cycled from 65% to 75% state of charge with an average of ~6 C-rate at a temperature of 45 °C until it reached ~80% of its rated capacity. At this residual capacity the battery was considered to be dead for automotive applications, consistent with the definition of a dead battery used by the automotive industry [7]. The cell was completely discharged after it reached ~80% of their rated capacity. The cylindrical cell was then opened in a glove box filled with an argon atmosphere. The oxygen level was maintained at ~88 ppm and the dew point was ~−34 °C. The cell was unrolled, and the long anode and cathode strips were separated. The total surface area of the CCC was 0.193 m^2 (length = 1520 mm, width = 63.5 mm). As such, the current density in CCC with ~6 C-rate cycling is 71.5 A m^{-2}. A small area of the anode where the CCC