



Neutron depth profiling of Li-ion cell electrodes with a gas-controlled environment



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HIGHLIGHTS

- Measurement of lithium concentration with neutron depth profiling (NDP) in electrodes of aged commercial Li-ion batteries.
- Demonstration of a modified NDP facility with a gas-controlled environment for air-sensitive Li-ion battery samples.
- Evaluation of measurement of lithium concentration during the operation of the Li-ion cell containing a liquid electrolyte.
- Monte-Carlo simulations to optimize the pressure of the inert gas in the NDP chamber for high measurement accuracy.

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ABSTRACT

Neutron depth profiling (NDP) is a nondestructive technique that has been applied to characterize the lithium concentration in the electrode materials of Li-ion batteries as a function of depth. NDP measurements have been traditionally performed ex-situ, under vacuum of the order of 10^{-6} Torr to avoid any change in the residual energy of the charged particles as they emerge from the sample surface. In this work, we describe the design of the NDP measurement facility that allows for conducting tests at variable pressure conditions, through an inert gas atmosphere. This study enhances the ability of the conventional NDP instrument to measure lithium concentration of air-sensitive materials without exposure to atmospheric conditions and under inert gas atmosphere. Furthermore, it provides the opportunity to conduct in-situ NDP on Li-ion cells using liquid electrolytes that would otherwise evaporate at high vacuum conditions.

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1. Introduction

Lithium ion batteries are the energy storage technology that has enabled the commercialization of electric and plug-in hybrid vehicles. This advanced battery technology has emerged over other chemistries due to its high energy and power density, excellent rate capabilities and safe operation under various environmental and operating conditions [1]. Nevertheless, the commercial success of electric and plug-in hybrid electric vehicles will ultimately depend on the ability of the battery to retain performance and reliability after many usage cycles. While the operation of Li-ion batteries is well understood, considerable research effort is today focused on understanding the mechanisms and fundamental causes that lead to the aging and degradation of the battery materials. To this extent,

several measurement and characterization techniques have been adopted (and in some case developed) to analyze the effects of degradation mechanisms on the morphological and electrochemical properties of Li-ion battery materials [2,3]. It is well understood that measuring or predicting the lithium concentration within the electrodes or electrolyte solution is the key to characterize the transport and electrochemical reactions that occur during the charging and discharging process of a cell. This is particularly critical for the operation of aged Li-ion batteries, where several complex physiochemical phenomena affect the intercalation/deintercalation mechanisms and the transport in solid and liquid phase, ultimately resulting in loss of capacity and power.

However, developing quantitative and direct measurement methods characterizing the lithium concentration within a sample has been extremely challenging. For instance, electron-based techniques such as energy dispersive X-ray spectroscopy (EDS) or electron energy loss spectroscopy (EELS) have been used in the past to measure the lithium bonding with its neighboring atoms in the

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structure of electrode materials [2]. Unfortunately, electron based techniques fail to detect light elements (such as lithium) because of the low energy of the X-rays emitted from light elements, which can not escape the beryllium window on the EDS or EELS detector systems. Thus direct measurement of lithium concentration is difficult with electron-based techniques.

On the other hand, neutrons have high penetration power for most of the elements but is almost opaque to light elements such as lithium. Exploiting the interaction of neutrons with lithium, several techniques have been applied to study the structure of Li-ion electrode materials, including neutron diffraction, radiography, imaging and small angle scattering [4].

Among others, Neutron Depth Profiling (NDP) is a nondestructive technique that is able to provide a quantitative measure of the concentration profiles of lithium within the host material, as a function of the thickness of the sample. Ziegler et al. [5] was the first to use a nuclear reaction experiment to determine the concentration of boron impurities in silicon wafers. The sample was bombarded with a well-collimated beam of low energy neutrons in vacuum, and the emitted energized particles were analyzed using a charged-particle spectroscopy for the concentration profile of the ^{10}B in the sample. Later, Downing et al. [6,7] and Biersack et al. [8] used this technique extensively to measure the concentration profiles of other neutron sensitive light-weight isotopes.

More recently, Whitney et al. [9] and Nagpure et al. [10,11] have demonstrated the application of NDP to measure the lithium concentration in the near surface region of commercial Li-ion battery materials, providing a wealth of information on the effects of degradation on the lithium concentration profiles in cathode and anode electrodes. Recently, in-situ neutron depth profiling experiments have been conducted to provide a measurement of lithium concentration in the electrodes during utilization of the cell. For instance, Oudenhoven et al. [12] have used NDP for in-situ characterization using an all solid state Li-ion cell tested under vacuum conditions. The need to establish a vacuum environment during the measurement process limits considerably the options for designing in-situ Li-ion cells, particularly preventing the use of liquid electrolytes that are common in commercial cells. In fact, the conventional alkylene-based electrolytes do not have suitable vapor pressure (Table 1) if the in-situ studies are to be conducted in vacuum [13].

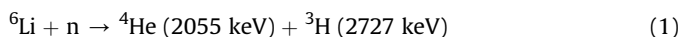
This work attempts to overcome the aforementioned limitations by proposing a novel NDP experimental setup that allows one to prepare and conduct tests in a controlled inert gas atmosphere.

This paper aims at benchmarking the ability of the OSU-NDP instrument to measure the lithium concentration profiles in the near-surface region of commercial electrodes. To this extent, several samples of cathode and anode materials were harvested from samples of commercial Li-ion batteries, both new and aged after accelerated cycling. The benchmarking was conducted by comparing the results to experimental tests previously conducted at the NDP facility at the National Institute of Standards and Technology (NIST) [10]. Furthermore, a preliminary evaluation was conducted to verify the ability of the OSU-NDP facility to measure the Li-ion concentration under an inert gas environment at ambient pressure conditions. Based on the preliminary experimental results, Monte-Carlo simulations were conducted to determine how the inert gas affects the measurement accuracy at different pressures, establishing a trade-off between system pressure and measurement accuracy. The paper is structured as follows. First, a discussion of the NDP operating principles and the required signal processing to measure the lithium concentration is presented. Then, the OSU-NDP facility fitted with the new design implementations is discussed. The benchmarking of ex-situ OSU-NDP (on dry samples) is then conducted to evaluate the accuracy of the instrument. Finally, a description of how the pressure of inert gas in the chamber affects

the instrument accuracy and range in measuring the Li-ion concentration based on experimental and simulation data is discussed.

2. The basic principles of NDP

The NDP technique is based on the energy release of nuclear reactions between certain light elements and the incident neutrons. The counts and the residual energy of the charged particles generated in this reaction are used to generate the concentration profile of the sampled element. When a sample is irradiated with a well collimated beam of thermal or cold neutrons, isotopes such as ^6Li , ^3He , ^{10}B etc. undergo an exoergic charged particle reaction. Based on the reacting element either a proton or an alpha particle and a recoiling nucleus are generated. Using the Q -value of the reaction the energies of the emitted particles can be determined and the element can be identified. In Li-ion battery samples, the reaction proceeds as:



When a sample is illuminated with a beam of low energy neutrons ($<10^{-2}$ eV) uniformly, most of the neutrons pass through the sample without any interference (Fig. 1). At some sites within the sample the reacting atoms capture the neutrons based on their reaction cross-section and generate monoenergetically charged particles. The isotropically emitted charged particle and recoil nucleus lose energy via mainly electronic interactions while travelling through the sample host material. Since both the sample and charged particle detectors are housed in vacuum, the particles do not lose energy after emerging from the sample surface. By measuring the residual energy of charged particles, the path length of the charged particles from the reaction site can be determined using the material's stopping power and the equation

$$x = \int_{E(x)}^{E_0} dE/S(E) \quad (2)$$

where x is the path length, E_0 is the particle's initial energy, $E(x)$ is the residual energy after leaving the sample, and $S(E)$ is the stopping power of the sample material. The stopping power of the sample material can be determined using the stopping and range of ions in matter (SRIM) code of Ziegler et al. [14]. By measuring the number of particles traversing a given path length, the concentration of that parent isotope can be determined for a known neutron flux and detector efficiency or by way of comparison to a certified standard material.

3. Description of the OSU-NDP setup

3.1. Experimental set-up

Fig. 2 shows the OSU-NDP chamber as described in Ref. [15]. The vacuum chamber is a 61 cm \times 61 cm right circular cylinder made of stainless steel 304, connected to a turbomolecular vacuum pump able to reach an operating pressure below 10^{-6} Torr. The neutron beam enters and exits the chamber through 80 μm thin aluminum windows. The charged particles are detected by an array of 8 silicon

Table 1
Liquid electrolyte vapor pressure [13].

Solvent (formula)	Vapor pressure (Pa)
Ethylene carbonate ($\text{C}_3\text{H}_4\text{O}_3$)	1.33 (20 °C)
Propylene carbonate ($\text{C}_4\text{H}_6\text{O}_3$)	4 (25 °C)
Dimethyl carbonate ($\text{C}_3\text{H}_6\text{O}_3$)	5300 (20 °C)
Diethyl carbonate ($\text{C}_5\text{H}_{10}\text{O}_3$)	1400 (25 °C)

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