



Quantifying lithium in the solid electrolyte interphase layer and beyond using Lithium- Nuclear Reaction Analysis technique



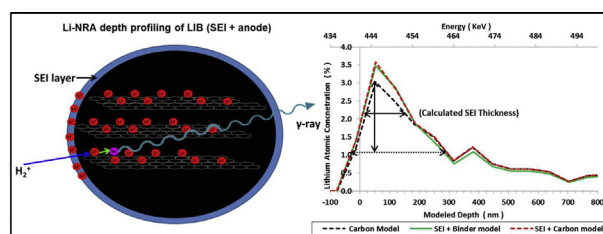
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HIGHLIGHTS

- Li Nuclear Reaction Analysis (Li-NRA) depth profiles of LIB electrode (SEI + anode).
- Studied anodes at various state of charge (SOC) & state of health (SOH) conditions.
- Quantified Li content in (SEI + anode) depth using 3 approximate composition models.
- Theoretical & experimental Li content at various SOC conditions match within 1.5%.
- 1st demonstration of accurate Li estimation using approximate materials composition.

GRAPHICAL ABSTRACT



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ABSTRACT

Accurate knowledge of lithium content within the solid electrolyte interphase (SEI) layer and anode would significantly enhance the current understanding of the lithium ion battery (LIB) degradation mechanisms, enabling knowledge-based improvements in the technology. For the first time, we have demonstrated the capabilities of highly selective Lithium Nuclear Reaction Analysis (Li-NRA) as a non-destructive depth profiling technique for quantifying Li within the SEI and anode without accurate knowledge of the composition, which is unavailable with other depth profiling techniques. The Li-NRA technique detects the gamma radiation resulting from a nuclear reaction at characteristic resonance energy between an incident high-energy proton and Li. The intensity of γ -ray is directly proportional to the Li content, and the energy of the incident proton is increased stepwise to depth profile the sample. We performed Li-NRA on the carbonaceous negative electrodes of commercial LIB coin cells at varying states of charge (SOC) and states of health (SOH) conditions. We used three simple models for the composition of SEI and anode material to show concurrence between theoretical and experimental value for Li content at varying SOC conditions, estimated the average SEI layer thickness, and correlated the residual Li content within the SOH samples with electrochemical data.

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1. Introduction

Lithium ion batteries (LIBs), coupled with increasingly efficient integrated circuits, have transformed the mobile electronics market over the past few decades [1]. Decreased cost, higher energy

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density, and improved operational lifetimes of LIBs may enable mass electrification of automobiles [2]. While incremental improvements in LIB performance have been made, LIB capacity loss still significantly impacts both mobile electronics and electric vehicles [3–5]. Charge capacity loss is frequently attributed to consumption of mobile lithium by solid electrolyte interphase (SEI) on the anode, growth of the SEI layer, and active material loss [6–8]. There are numerous sophisticated computational models that accurately fit LIB performance and aging data [9–14]; however, these models are independent of true materials states within the LIB. This in part is due to the dearth of data on lithium distribution within the SEI layer and beyond. Knowledge of accurate lithium distribution would allow LIB models to be based on true materials states, which would enable verification of capacity loss mechanisms, improving materials based LIB performance modeling, and imparting predictive capabilities for determining future performance.

In spite of the need for quantitative materials analysis, few lithium depth profiles of the graphitic electrode exist. Nagpure et al. have demonstrated accumulation of lithium within the anode using low resolution in-situ neutron depth profiling [15]. Takahara et al. and Waldmann et al. have recently reported depth profiles of elements within the solid electrolyte interphase (SEI) layer and bulk graphitic electrode using Glow Discharge Optical Emission Spectroscopy (GD-OES) [16–18]. GD-OES requires calibration by ion coupled plasma-optical emission spectroscopy (ICP-OES) of a separate area of the sample due to the destructive nature of the technique. The lithium concentration is frequently reported as a function of sputtering time, rather than depth, due to varying sputtering rates resulting from non-homogenous substrate composition.

Nuclear Reaction Analysis (NRA) is a highly-developed, largely non-destructive, ion beam analysis technique for materials characterization. Proton induced gamma emission (PIGE), a subset of NRA technique, has been used previously to study LIB components. Tadic et al. have examined gel/polymer electrolyte interphases [19,20]. Berger et al. studied graphite Li–Ca–C intercalation compounds [21]. Reddy et al., Swaitowska-Mrowieka et al., Andrade et al., Habrioux et al., and Mima et al. have studied LiNiVO₄, MoO₃, LiMn₂O₄, C–LiFePO₄, Li_xNi_{0.8}Co_{0.15}Al_{0.05}O₂ cathode materials by NRA respectively [22–26]. Perlado et al. recently fully reviewed the capability of the technique and characterized in three-dimensions lithium distribution in cathodes using ion beam analysis [27]. This body of work has significantly developed the study of LIB systems by ion beam techniques. Nevertheless, there are no reports of NRA studies on commercial composite carbon electrodes to the best of the authors' knowledge.

In this work, we evaluate the ⁷Li (p, γ)⁸Be nuclear reaction for depth profiling lithium within the SEI and anode. In the experiment, an incident proton beam reacts with the nucleus of lithium atoms on the sample surface at a characteristic energy of 441 keV. The resulting reaction forms a highly excited new element beryllium, which de-excites by emitting two characteristic high-energy (14.7 MeV and 17.7 MeV) γ-rays. Li– depth profiles are obtained by increasing the energy of incident proton beam in discrete steps and measuring γ-radiation. The γ-ray intensity is converted to lithium atomic percent (at. %) using a calibration sample with known Li content. The incident energy (*E*) is converted to depth (*x*) within the sample using knowledge of sample composition and thickness (in case of multilayered samples). The technique is described in detail by Bakhru et al. and Lanford et al. [28–30].

The accuracy of reported depth is dependent on a number of factors, including: variation in the ion beam energy, beam directionality, and inaccuracies within SRIM (Stopping and Range of Ions in Matter) software used for deriving the stopping range of ions

within the sample based on the sample composition. These factors can lead to a substantial variation (10–20%) in reported depth [31].

The composition and thickness of the SEI layer is most difficult to determine since it is a non-homogeneous mixture of a multitude of organic and inorganic phases. For this study, we used X-ray Photoelectron Spectroscopy (XPS) technique to measure the SEI layer composition in a similar LIB system [32]. This SEI layer composition was used in the SRIM software to calculate the stopping range.

The variability resulting from inaccuracy in sample composition was a non-issue for the analysis of Li-NRA depth profiles of our system, as will be evident from our results. Our samples were modeled as a bilayer, with SEI on top of graphitic carbon material and with constituents (hydrogen, lithium, carbon, oxygen, fluorine, and phosphorous) whose atomic size was comparable to the size of the incident ion (H⁺). The high-energy beam (0.43 MeV–0.56 MeV) was practically transparent to any compositional variation in SEI layer and microstructure.

We investigated the Li depth profile in the anodes of LIB coin cells at varying states of charge (SOC) or charged to varying degrees, and states of health (SOH) or varying degrees of performance loss. In all Li-NRA depth profiles, we observed an initial peak due to the presence of Li atoms within the SEI layer. The degree of overlap of these peaks with the Li content outside of SEI layer was significantly lower in the SOH samples as compared with the SOC samples, since they were in a fully discharged state.

We estimated the width of the SEI layer from this peak at the full width at half-maximum (FWHM) position for 100% SOH (or 0% SOC) sample. Multiple experimental variabilities including the spread in the incident beam energy, beam directionality, beam step size compromises the intrinsic depth resolution of Li-NRA technique. In addition, the sample related variabilities including sample roughness, unknown SEI composition (amorphous mixture of organic and inorganic phases), non-uniformity of Li distribution within the SEI layer, and variation in Li distribution as a function of charging and discharging cycle etc. add to the uncertainty. Hence, under all these uncertainties, the FWHM is the best possible approximation for estimating the width of the SEI layer. Various spectroscopic techniques including Raman, FTIR, XPS, UV-VIS, and SIMS etc. routinely use FWHM to estimate the linewidth.

We used three distinct models for the anode material based on the initial composition of the anode (per manufacturer's data sheet) and composition of SEI (from XPS analysis) to calculate the Li depth profile within the (SEI + anode) material post electrochemical cycling.

Using three simple models for (SEI + anode) composition, we demonstrated that it is possible to use Li-NRA technique to estimate the thickness of SEI layer and Li depth profile within the SEI layer and adjacent anode material without accurate knowledge of SEI layer thickness or composition. In addition, we demonstrated the concurrence between measured average Li content in various SOH and SOC samples with theoretical expectations.

2. Experimental

2.1. Cell description

We obtained commercial secondary LIBs (40 mAh CR2032) from EUNICELL (Schenzen Euni Battery Co. Ltd.) with SEI layers pre-formed. The LIB cells were comprised of LiCoO₂ based cathode; composite hard carbon and natural graphite mesoporous carbonaceous microbeads (MCMB) particles (~16 μm diameter, σ = 7.1 μm) and 4% SBR + CMC binder (Styrene-Butadiene Rubber and Carboxy-Methyl Cellulose) based anode; and 1 M LiPF₆ salt dissolved in 1:1:1 ratio of EC: DMC: EMC (ethylene carbonate:

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