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Key electronic states in lithium battery materials probed by soft X-ray spectroscopy

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ABSTRACT

The formidable challenges for developing a safe, low-cost, high-capacity, and high-power battery necessitate employing advanced tools that are capable of directly probing the *key electronic states* relevant to battery performance. Synchrotron based soft X-ray spectroscopy directly measures both the occupied and unoccupied states in the vicinity of the Fermi level, including transition-metal-*3d* and anion-*p* states. This article presents the basic concepts on how fundamental physics in electronic structure could provide valuable information for lithium-ion battery applications. We then discuss some of our recent studies on transition-metal oxide based cathodes, silicon based anode, and solid-electrolyte-interphase through soft X-ray absorption and emission spectroscopy. We argue that spectroscopic results reveal the evolution of electronic states for fingerprinting, understanding, and optimizing lithium-ion battery operations.

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1. Introduction

Energy storage is one of the critical links in the chain of sustainable energy applications due to the increasing demand of portable energy carriers and the intermittent nature of green energy sources. It is believed that conventional chemical energy sources, mostly in the form of fossil fuels, leads to environmental impacts from the CO_2 emission. Therefore, a high-performance zero-emission electrochemical device is an essential element for realizing clean energy applications, such as plug-in electric vehicles (EVs) [1–4]. At present, among all different types of electrochemical devices, lithium-ion batteries remain the most promising short-term solution to low-cost, rechargeable, high-capacity, and high-power energy storage devices.

Li-ion batteries were first commercialized by Sony in 1991 [5]. The first generation of lithium batteries, based on $LiCoO_2$ cathode and graphite anode, have ever since conquered the electronic market requiring efficient energy storage, for example in wireless communications and laptop computers. Now, with emerging clean energy applications including EVs, the market of rechargeable Li-ion batteries is predicted to be exploded ten fold from 2010 to 2020 [6]. However, the current battery technology level is well below what is required for this second phase of large-scale energy storage.

The technological breakthrough in batteries is hindered by the complexity in the operation of electrochemical cells. Batteries operate under non-equilibrium states, which are often beyond the thermodynamic stability of the electrolyte, and sometimes the electrodes [4]. This complexity has been witnessed more than once in the history of developing commercial lithium batteries. For example, both lithium metal and graphite have been studied as anode materials since 1970s; however, lithium metal suffers the infamous dendrite issue from nonuniform Li plating until now, and cycling graphite causes parasitic electrolyte reduction [7]. Graphite anodes were eventually commercialized after the proper electrolyte system was developed for providing the necessary kinetic stability [8]. The complicated nature of the battery operation is manifest in the lengthy developments of almost all battery components. New strategies for speedy innovation of battery technologies require more and more fundamental understandings of the mechanism and guidelines for the optimization.

Unfortunately, such fundamental understanding is difficult to achieve without systematic and sustainable research effort. For the electrodes, the charge and discharge process involves both structural and electron state evolutions, which often interact with each other [9]. In addition to the most extensively studied electrochemical properties, more attention has been paid to study the structural evolution than measure the electronic states. These efforts on determining structures have been highly recognized, which motivated recent progresses on in situ microscopic [10] and hard X-ray techniques [11,12]. However, as for any electronic device, information on electronic state evolution is an indispensable part of the battery operation mechanism, but is limited partially due to the unavailability of suitable techniques for direct measurements. As reviewed below, the key electronic states in battery

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materials principally define the performance of batteries. For example, the occupied and unoccupied electron states of electrolyte determine the upper limit of the open-circuit voltage of a thermodynamically stable battery cell; the electron state configuration of transition-metal (TM) based cathodes fundamentally defines safety and intrinsic voltage limit [13,14], as well as the phase stability and transformation [9].

In this review, we focus on electronic states in some of the Li-ion battery materials studied by soft X-ray spectroscopic tools and methodologies developed at the Advanced Light Source (ALS). The purpose is to demonstrate the power of soft X-ray spectroscopy for tackling some long-standing problems of battery materials. The outline of the paper is as follows. In Section 2, we elaborate the basic principles of the key electronic states involved in Li-ion batteries. Critical energy levels associated with TM *3d* states and anion *p* states will be elaborated. Section 3 briefly summarizes the soft X-ray techniques employed in this work. A recently developed methodology for aligning the TM and anion valence states on a common energy scale is emphasized. Sections 4–6 present our recent soft X-ray absorption studies on $LiFePO_4$ cathodes, Si based anodes, and electrolyte-electrode interface respectively. We then provide our conclusions and perspectives in Section 7. This review is by *no* means to cover the much diversified issues in Li-ion battery materials, which has been constantly summarized and updated through many books, e.g., [4,15], and reviews, e.g., [1,2,6,16–24]. Instead, we focus on soft X-ray spectroscopy that could probe directly the key electronic states pertaining to the battery operations. Emphases are not on solving specific battery issues, but the basic principles on how synchrotron based soft X-ray spectroscopy could help fingerprinting the battery operations, understanding the fundamental mechanism, and more importantly, providing guidelines for material optimizations.

2. Key electronic states

From the fundamental physics point of view, all electronic devices operate with evolving electronic states. The potential and kinetics of these electronic states defines the transportation of the charges in either electrons or ions. The functionality of the electronics is essentially realized by this controlled/guided motion of charges. Fig. 1 shows the overall energy diagrams of open-circuit battery cells. The interplay of the energy levels determines both the performance and stability of a battery cell. Furthermore, the electronic states in each of the battery elements evolve with the battery charge/discharge process. In reality, the evolving states lead to complicated electronic structure in individual battery component, other than the simple levels shown in Fig. 1. In this section, we elaborate the fundamental concepts on the connection between these *key electronic states* and battery operations, and argue that probing, understanding, and tailoring these key states could lead to more rational and speedy developments of battery materials.

Architecturally, there are different types of commercially available Li-ion batteries [6]. All consist of three essential components, the anode (negative electrode), cathode (positive electrode), and electrolyte with separator. The architecture design of a battery cell is not a topic here, but it is noteworthy that all electrodes and electrolyte layers are very thin (typically < 100 μm) with large surface areas. This is an intrinsic requirement due to the much lower Li-ion conductivity comparing with the electric conductivity, i.e., the Li-ion diffusion and the electrode phase transformation with (de)lithiation are often more of a problem for designing high power/rate Li-ion batteries. As a matter of fact, a clear picture of phase transformation in some electrode materials, e.g., $LiFePO_4$, is still under hot debate [25–27].

Fig. 1 shows the schematic energy diagrams of the so-called “rocking-chair” battery and outlines the basic principle for developing and optimizing battery materials. The operation of the batteries is based on the principle of Li-ion insertion (extraction) in anode (cathode) during charge process, and vice versa for the discharge. Li-ions diffuse through the electrolyte that is electrically insulating, in concert with electrons shuttling through the external circuit. In general, the anode sits high in electron energy level as the reductant, while cathode is the oxidant. The open circuit voltage, V_{OC}, of a battery cell is determined by the difference of Li chemical potential of the anode and cathode. In order to be thermodynamically stable, the anode electrochemical potential has to be located below the lowest unoccupied molecular orbital (LUMO) of the electrolyte, otherwise the electrolyte will be reduced. On the other hand, the cathode electrochemical potential should be above the electrolyte highest occupied molecular orbital (HOMO) to avoid electrolyte oxidation effect.

In reality, a thermodynamically stable battery cell as described above is hardly commercially viable. One example is the cell with carbon coated $LiFePO_4$ cathode and $Li_4Ti_5O_{12}$ anode. The cell is thermodynamically stable, thus with outstanding safety and cyclability performance at very fast charge/discharge rate [28]. However, the voltage is limited to 1.55 V, which reduces the power density almost by half. In order to achieve a thermodynamically stable but high power-density battery device, development of electrolyte systems with large energy window and electrodes with matching energy levels is under intensive investigation [16].

The alternative way to achieve high power batteries is to form a passivating layer on the surface of the electrodes. This passivating layer, typically about 20–50 nm thick, is known as solid-electrolyte interphase (SEI). SEI protects electrolyte from further reduction/oxidation. The protection from SEI is critical in the commercial $LiCoO_2$/Graphite batteries (Fig. 1b). The graphite based anode tends to reduce the electrolyte because its electrochemical potential sits above the $LiPF_6$/Ethylene carbonate (EC) + diethyl carbonate (DEC) electrolyte LUMO [8]. It is now clear that, the EC based electrolyte could decompose and form a passivating SEI layer on the surface of the carbon anode during the initial cycle. Although this SEI layer consumes electrolyte during its formation, it provides the kinetic stability for protecting the electrolyte from further decomposition (Fig. 1). An ideal high-voltage battery cell could be realized with SEI forming on both cathode and anode surfaces, leaving a much larger energy window for electrode selections (Fig. 1c). However, this is only feasible if stable SEI layers could be controlled on both electrodes, which is not possible at present. Nonetheless, almost all current Li-ion batteries on the market rely on such SEI mechanism for achieving relatively stable batteries. The dual-functionality and controlling of SEI in batteries remain elusive and a formidable challenge [2,15,16,29–33].

With the kinetic stabilization from SEI, Sony eventually commercialized Li-ion batteries with graphite based anodes. However, because the electrochemical potential of graphite is close to lithium (about 0.2 eV), during a high-rate (fast) charge, the internal voltage may conquer and lithium may plate over the SEI defects and form metallic lithium dendrites. The detailed mechanism of Li dendrite formation is still unclear. But it is known that the dendrites, once form, will likely keep growing across the separator, leading to internal short-circuit and catastrophic consequences. While the carbon based anode has been the most mature anode technology for portable electronics such as mobile phones and laptops, further improvements on both safety and capacity of anodes are necessary for large-scale energy storage. Understanding and controlling the SEI, as well as enabling other types of anode technologies, e.g., Si- or Sn-based anodes, has been one of the central topics in the battery research.