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Review article

A review of the features and analyses of the solid electrolyte interphase in Li-ion batteries

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ABSTRACT

The solid electrolyte interphase (SEI) is a protecting layer formed on the negative electrode of Li-ion batteries as a result of electrolyte decomposition, mainly during the first cycle. Battery performance, irreversible charge “loss”, rate capability, cyclability, exfoliation of graphite and safety are highly dependent on the quality of the SEI. Therefore, understanding the actual nature and composition of SEI is of prime interest. If the chemistry of the SEI formation and the manner in which each component affects battery performance are understood, SEI could be tuned to improve battery performance. In this paper key points related to the nature, formation, and features of the SEI formed on carbon negative electrodes are discussed. SEI has been analyzed by various analytical techniques amongst which FTIR and XPS are most widely used. FTIR and XPS data of SEI and its components as published by many research groups are compiled in tables for getting a global picture of what is known about the SEI. This article shall serve as a handy reference as well as a starting point for research related to SEI.

Contents

Abbreviations: AAS, atomic absorption spectroscopy; AES, Auger electron spectroscopy; AFM, atomic force microscopy; ARC, accelerated rate calorimetry; ATR, attenuated total reflectance; BET, Brunauer–Emmett–Teller; DEC, diethyl carbonate; DMC, dimethyl carbonate; DSC, differential scanning calorimetry; EC, ethylene carbonate; EELS, electron energy loss spectroscopy; EIS, electrochemical impedance spectroscopy; ELSA, elemental line scan analysis; EMC, ethyl methyl carbonate; EQCM, electrochemical quartz crystal microbalance; ESCA, electron spectroscopy for chemical analysis; FIB, focused ion beam; FTIR, Fourier transform infrared spectroscopy; IC, ion chromatography; ICL, irreversible charge “loss”; IRAS, infrared absorption spectroscopy; *k*, rate constant; NMR, nuclear magnetic resonance; PC, propylene carbonate; PEO, polyethylene oxide; PVDF, polyvinylidene difluoride; PVDF-HFP, polyvinylidene difluoride-hexafluoropropylene; SEI, solid electrolyte interphase; SEM, scanning electron microscopy; SIMS, secondary ion mass spectroscopy; SNIFTIR, subtractively normalized interfacial Fourier transform infrared; SPM, scanning probe microscopy; STM, scanning tunneling microscopy; TEM, transmission electron microscopy; THF, tetrahydrofuran; ToF-MS, time of flight-mass spectroscopy; ToF-SIMS, time of flight-secondary ion mass spectroscopy; TPD, temperature programmed desorption; UHV, ultra high vacuum; VC, vinylene carbonate; XANES, X-ray absorption near edge structure; XPS, X-ray photoelectron spectroscopy; XRD, X-ray diffraction.

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1. Introduction

Li-ion batteries have replaced the conventional batteries like alkaline, Ni–Cd, and lead acid batteries in a wide range of applications, ranging from microelectronics to aerospace. The prime reason for this sweep is up to two times higher voltage of Li-ion battery (∼3.6 V) compared to aqueous batteries (∼1.2–2 V) and up to six times higher gravimetric specific energy of Li-ion battery (∼240 Wh/kg [1]) compared to lead acid battery (∼40 Wh/kg). After decades of intensive research on each component of Li-ion batteries, they can now be titled as one of the most widely used rechargeable systems. Li-ion batteries are also prospective candidates for use in electric vehicles. However, the very facts that give Li-ion batteries an edge over the alkaline and Ni–Cd batteries are also the bottlenecks of this technology. Wide voltage window demands the use of non-aqueous electrolytes. But the known non-aqueous solvents are thermodynamically instable in this voltage window.

The state of the art Li-ion battery is also called the “rocking chair” battery [2]. It comprises of insertion materials as active materials [3]. The Li-ions shuttle back and forth between the negative and positive electrodes during cycling. The electrochemistry of a typical Li-ion battery is shown in Fig. 1. By far, the most common active material used in the negative electrodes is graphite ($C_6 + x\text{Li}^+ + xe^- \rightleftarrows C_6\text{Li}_x$). However, there are innumerous other kinds of carbons which have also been used [4]. As positive electrode mostly transition metal oxides [5] and phosphates [6] have been employed, out of which LiCoO_2 [7], LiMn_2O_4 [8], and LiFePO_4 [9] are the most common ones.

During first charge of the Li-ion battery the electrolyte undergoes reduction at the negatively polarized graphite surface. This forms a passive layer comprising of inorganic and organic electrolyte decomposition products. In an ideal case this layer prevents further electrolyte degradation by blocking the electron transport through it while concomitantly allowing Li-ions to pass through during cycling. This essential passive layer has appropriately been named solid electrolyte interphase (SEI) [10]. Some solvents such as cyclic alkyl carbonates [11] form effective passive layers that ensure good cycling stability of the negative electrodes. An overview of the fundamental concepts and principles of the SEI was published in handbooks like “Handbook of Battery Materials” [12] and “Lithium-Ion Batteries: Solid-Electrolyte Interphase” [13].

This review describes some vital features of the SEI on graphitic carbons. Some fundamental questions are discussed, like what factors affect the SEI and how the SEI affects battery performance. Substantial work has been done in the past few decades on analyzing the SEI and spelling out its components. In this paper, the literature of SEI on graphite is compiled with a detailed compilation of the X-ray photoelectron spectroscopy (XPS) and Fourier Transform Infrared (FTIR) data of the SEI components.

2. Formation and features of the SEI

As lithiated carbons are not stable in air, a Li-ion battery is always assembled in its discharged state that means with graphite and lithiated positive materials. The electrolyte solution is thermodynamically unstable at low and very high potentials vs. Li/Li$^+$. Hence, on first charge of the cell the electrolyte solution begins to reduce/degrade on the graphite surface and forms the SEI.[2] There are competing and parallel solvent and salt reduction processes, which result in deposition of a number of organic and inorganic decomposition products on the surface of graphite. On the whole this layer imparts kinetic stability to the electrolyte against further reductions in the successive cycles and thereby ensures good cyclability of the electrode. The SEI also prevents solvent co-intercalation and hence exfoliation of graphites [14].

The onset potential of SEI formation is not a fixed value. Literature offers values such as 2 V [15], 1.7 V [16], or 1 V [14], but 0.8 V [17,18] is the most widely adopted practical value. SEI formation may also continue up to few cycles. However, this parameter cannot be normalized because it depends on a number of factors like nature and composition of electrolyte, nature of additives used in the electrolyte [19], sweep rates [20], etc. It is desirable to have complete SEI formation before Li-ion intercalation begins (>0.3 V [21]). It is more difficult to achieve this for disordered carbons as the intercalation begins from 1.5 V as compared to ordered carbons where it begins at 0.25 V [15].

SEI is a very complicated layer comprising of inorganic components which are normally salt degradation products and organic components which are partial or complete reduction products of the solvent of the electrolyte. The thickness of the SEI may vary from few Å to tens or hundreds of Å [18,22]. It is difficult to distinctly measure the SEI thickness as some of the components are partially soluble in the electrolyte [23]. But as formation of a new phase between active material and the electrolyte modifies the interphase resistance, the average thickness was estimated using electrochemical impedance spectroscopy (EIS) [24]. The picture of a real SEI inside the battery has always been blur. Models of the SEI on graphite were proposed by Peled et al. [25], Aurbach [21,24], and Edström et al. [18,26]. They all suggest SEI to be a dense layer of inorganic components close to the carbon, followed by a porous organic or polymeric layer close to the electrolyte phase. Sometimes crystals of LiF are also detected [27].

2.1. Components of SEI

The composition of the SEI is a highly debated subject. It is highly dependent on numerous factors, which are detailed in Section 3. Proposed composition of SEI varies from one research group to another as operating conditions in different laboratories can be different. Thus it is impossible to normalize or generalize the composition or even contents of SEI. Table 1 lists what various research groups believe to be the major components of the SEI. A large number of inorganic salts (precipitates) originating from salt reductions may be present in the SEI. Hence, all the possible (reported) inorganic components are not listed in Table 1. We list the most plausible and common SEI components along with their references to the best of our knowledge.

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[2] The reduction occurs on all surfaces at the same potential, in particular on the current collector too. However, because of the low surface area of the latter the reaction at graphite is predominant.