

## CHAPTER 1

# SEI ON LITHIUM, GRAPHITE, DISORDERED CARBONS AND TIN-BASED ALLOYS

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### 1 Introduction

It is well known that in contact with both liquid and polymer electrolytes, lithium is thermodynamically unstable toward the solvents and salts and becomes covered by a passivating film that slows the corrosion of the lithium. It is now generally accepted that the existence and successful operation of most lithium battery systems, as primary and secondary power sources, are due solely to this anode-surface layer.

In the 1960s and early 1970s it was generally believed that, although some passivating film covers lithium, the metal is kinetically stable to many organic solvents.<sup>1</sup> It was assumed that the rate-determining step (r.d.s.) of the deposition-dissolution process for lithium is the electron charge transfer between the metallic electrode and the lithium cation in solution. In 1970, in a study of the electrochemical stability of propylene carbonate (PC), Dey suggested that lithium is covered by a passivating film, probably composed of lithium carbonate, which protects the metal from further chemical attack and imparts stability. This film was presumed to conduct lithium cations.<sup>2</sup>

On the basis of a study of the electrochemical behavior of magnesium electrodes in thionyl chloride (TC) solutions, Peled *et al.*<sup>3</sup> concluded that it is the migration of  $Mg^{2+}$  ions through the passivating layer that limits the total rate of deposition/dissolution of magnesium. In addition, it was concluded that the deposition of magnesium on an inert nickel cathode begins only after the nickel is covered by a passivating layer ( $MgCl_2$ ) that blocks the electronic current and enables only ionic current to pass. It was further proposed by Peled *et al.*<sup>4</sup> that this passivating-layer model is valid for all alkali metals in non-aqueous battery systems.

The layer formed instantaneously upon contact of the metal with the solution, consists of insoluble and partially soluble reduction products of electrolyte components. The thickness of the freshly formed layer is determined by the electron-tunneling range. The layer acts as an interphase between the metal and the solution and has the properties of a solid electrolyte with high electronic resistivity. For this reason it was called a “solid-electrolyte interphase” SEI.<sup>3,4</sup> The batteries, consisting of SEI electrode, were called SEI batteries.<sup>3,4</sup>

SEI determines the safety, power capability, morphology of lithium deposits, shelf life, and cycle life of the battery.<sup>5-8</sup> For high performance of the lithium battery, the SEI must be an electronic resistor in order to avoid SEI thickening leading to high internal resistance, self-discharge and low faradaic efficiency ( $\epsilon_f$ ). To eliminate concentration polarization and to facilitate the lithium dissolution-deposition processes, the cation transport number should be close to unity. To reduce overvoltage, the SEI should be highly ion-conductive. In the case of the rechargeable lithium battery, it is very important that there be uniform morphology and chemical composition in order to ensure homogeneous current distribution. The SEI must be both mechanically stable and flexible. Good adhesion to the anode is important as well. As emphasized above, practical primary or secondary alkaline or alkaline-earth batteries can be made only if the dissolution or corrosion of the anode can be stopped. Therefore, the electrolyte must be designed to contain at least one material that reacts rapidly with lithium (or with the alkali-metal anode) to form an insoluble solid-electrolyte interphase — the SEI.

The importance of the SEI is well recognized in the scientific community; special sessions are devoted to it in battery-related meetings such as the International Meetings on Li Batteries (IMLB), International Symposium on Polymer Electrolytes (ISPE), and in other meetings, including the Electrochemical Society (ECS) Battery Symposium in Japan and the Materials Research Society (MRS). Hundreds of papers dealing with the SEI study have been published (most of them in the last twenty years) and it is impossible to summarize all of them here.

New techniques such as X-ray Photoelectron Spectroscopy (XPS), SEM, X-ray Diffraction (XRD), Surface-Enhanced Raman Spectroscopy (SERS), Scanning Tunneling Microscopy (STM), Energy-Dispersive X-ray Spectroscopy (EDS), FTIR, NMR, EPR, Calorimetry, DSC, TGA, Quartz-Crystal Microbalance (QCMB), Atomic-Force microscopy (AFM) and *in situ*

Neutron Radiography have been recently adapted to the study of the electrode surface and the chemical and physical properties of the SEI.

This chapter addresses several issues dealing with the mechanism of SEI formation on inert substrates, lithium, carbonaceous materials and tin-based alloys. Attention is currently focused on the correlation between the composition and morphology of the solid-electrolyte interphase forming on the different planes of highly ordered pyrolytic graphite (HOPG) and different types of disordered carbon electrodes in lithium-ion cells.

## 2 SEI Formation Processes and Morphology

### 2.1 The Main Principles and Routes of SEI Formation

The deposition-dissolution process of an electrode covered by an SEI involves three consecutive steps, which are described schematically as follows:

Electron transfer at the metal/SEI interface



Migration of cations from one interface to the other when  $t_M^+ = 1$  (or migration of anions when  $t_x^- = 1$ )



Ion transfer at the solid-electrolyte interphase/solution (SEI/sol). For  $t_M^+ = 1$



In principle, any one of these could be the rate-determining step (r.d.s.). However, it was found, by the use of a variety of experimental techniques, that ionic migration through the SEI is the rate-determining step for many systems. In addition, it was found that the rate of nucleation of the metal deposit is affected by the interfacial resistance.<sup>5,6</sup> This transport process is a key factor in the operation of non-aqueous SEI batteries.

The standard reduction potential of lithium is more negative than that of the solvated-electron system (at least in highly purified ammonia, amines and ethers). This results in the formation of the well known blue solutions of solvated electrons ( $e^-_{sol}$ ).<sup>9,10</sup> In rechargeable batteries under prolonged dissolution, a process of breakdown and repair may take place. Mechanical breakdown can be caused by both local preferential dissolution of the anode and by stresses in the SEI due to uneven retreat of the anode. The new anode surface, exposed to the electrolyte, immediately reacts with it to form a fresh