The Role Of Surface Films on Electrodes in Li-Ion Batteries

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1.0 INTRODUCTION

1.1 Passivation Phenomena in Electrochemistry

Surface film formation on electrodes is a very common phenomenon in electrochemical systems. Most metal electrodes in both aqueous and nonaqueous solutions are covered at a certain range of potentials with surface films that control their electrochemical behavior [1]. Most of the commonly used metals in electrochemical studies, as well as electrochemical devices, are naturally covered by oxide layers that may be formed spontaneously during their casting, due to the reaction of the bare metal with air oxygen [2]. Hydration of oxide films forms an outer layer of hydroxide, while reactions of oxides with air CO₂ form an outer layer of carbonates. Surface films formed on metals comprised of oxides, hydroxides, and carbonates are electronically insulating, as they reach a certain thickness, but may be able to conduct ions: oxygen anions, protons and/or metal cations [3]. In spite of the huge diversity in the properties of metals, we can find a similarity in some properties of surface films formed on metals in terms of mechanisms and kinetics of growth, as well as transport phenomena and kinetics of ion migration through surface films.

When a fresh active metal is exposed to a polar solution whose components may be reduced on the active surface to form insoluble metal salts, a surface film grows via a corrosion process. The driving force for this process is the difference between the redox potentials of the active metal and the solution species $\Delta V_{M-S}$. As a first approximation, we can assume a homogeneous surface film and Ohm's law, connecting the corrosion current density $i_{corr}$ and $\Delta V_{M-S}$. Hence

$$i_{corr} = \frac{\Delta V_{M-S}}{(\rho f i (t))}$$

(1)
where \( \rho(\text{film}) \) is the surface film's resistivity for electron tunneling (assuming homogeneous condition), and \( l(t) \) is its thickness (which grows in time). Assuming that all the reduction products precipitate on the active metal surface, then

\[
\frac{dl}{dt} = K \cdot i_{\text{corr}}
\]

(2)

\( K \) is the proportionality constant that depends on the molecular size of the surface species and their density of packing on the surface. Combining Equations 1 and 2, and integrating them with the boundary condition \( t \to 0, l = 0 \) yields:

\[
l = \left( \frac{2KAV_{M-S}}{\rho(\text{film})} t \right)^{1/2}
\]

(3)

which is the well-known parabolic growth of the surface films \([4]\). When the active metal exposed to solution is already covered by initial surface films, and hence at \( t = 0, l = l_o \), then:

\[
l = \left( l_o^2 + \frac{2KAV_{M-S}}{\rho(\text{film})} t \right)^{1/2}
\]

(4)

We can assume that as the surface films formed on active surfaces in solutions reach a certain thickness, they become electronic insulators. Hence, any possible electrical conductance can be due to ionic migration through the films under the electrical field. The active surfaces are thus covered with a solid electrolyte interphase (the SEI model \([5]\)), which can be either anionic or cationic conducting, or both.

For a classical SEI electrode, the surface films formed on it in polar solutions conduct the electrode's metal ions, with a transference number \( (t_+) \) close to unity. In most cases, the surface films on active metals are reduction products of atmospheric and solution species by the active metal. Hence, these layers comprise ionic species that are inorganic and/or organic salts of the active metal. Conducting mechanisms in solid ionics have been dealt with thoroughly in the past \([6-10]\). Conductance in solid ionics is based on defects in the medium's lattice. Two common defects in ionic lattices are usually dealt with: interstitial (Frenkel-type) defects \([7]\), and hole (Schottky-type) defects \([8]\).

In the former case, the ions migrate among the interstitial defects, which may be relevant only to small metal ions. This leads to a transference number close to unity for the cation migration. In the other case, the lattice contains both anionic and cationic holes, and the ions migrate