

SEMICONDUCTIVITY AND SOLID ELECTROLYTE CHARACTERISTICS OF SURFACE FILMS FORMED ON ACTIVE METALS OF INTEREST IN HIGH ENERGY DENSITY BATTERIES

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Summary

Active metals such as Li and Mg, of interest in battery systems, tend to be covered by surface films. Approaches available to estimate the electronic and ionic conductivity of these films are outlined. The role of these films in the anodic dissolution of the metal electrodes is described, and their relevance to the battery reactions is discussed.

It is shown that attempts to achieve high energy density by increasing the anodic half-cell potential tend to be thwarted by the corresponding increases in the resistance of the surface films. This arises because high values of the electrode potential for the M/M^{z+} reaction tend to herald high band-gap of the corresponding reaction film, M_mX_n , formed on the electrode surface.

Introduction

Active metals such as Li and Mg, which are of great interest in high energy density batteries, are readily covered with surface films formed by the reaction of the metal with the electrolyte. The electrochemical behaviour of these electrodes is then largely determined by the electronic and ionic conductivity of these films, although other factors such as the integrity (*e.g.*, adhesion, micro-fissures) and the defect structure also play an important role. In a recent excellent article [1], a number of salient characteristics of these films were discussed, somewhat inadequate attention was paid, however, to the semiconductivity of these films and especially to the procedures available to estimate this property as, for example, from thermodynamic data [2]. The purpose of the present paper is to elaborate upon this matter by drawing upon our previous work on the subject [3] which, it would seem, was inadvertently not included in this otherwise comprehensive paper [1]. In these respects, the present paper is a brief review of our previous work and complements the information contained in the recent review article by Kedrinsky *et al* [1].

The semiconductivity of surface films: qualitative aspects

In general, an active metal, M , in contact with an electrolyte that can act as a source of an anionic species, X , exhibits a reaction such as



where M_mX_n is the reaction film formed on the metal electrode surface and of interest in the present context. The anionic species X can also originate from a complex anion. The film M_mX_n may represent a metal oxide, -fluoride, -chloride, -bromide, -sulfide, etc., depending on the nature of the electrolyte solution. The focus here is to estimate the semiconductivity of such films and to relate it, wherever possible, to some electrochemical considerations of interest in high energy-density batteries.

Qualitatively, a poreless, compact film of a few layers is formed first on the metal which, in turn, is covered by a thicker film of various degrees of porosity depending on the electrode-electrolyte combination. The attention here is on the compact film that, more or less, covers the electrode completely.

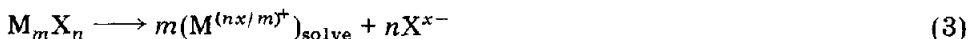
When reaction (1) is highly exothermic (*e.g.*, between lithium and fluoride), very high negative values of heats of formation per equivalent, $-\Delta H_e$, for the electrodic film M_mX_n are observed, and the film tends to be highly insulating. This is because the bandgap, E_g , of a binary solid (including the solid reaction film) is related to its heat of formation per equivalent, ΔH_e , by the equation [2]

$$E_g = 2(-\Delta H_e) \quad (2)$$

The ΔH_e values can be obtained from standard thermodynamic tables, as described previously [2].

Such a highly insulating film allows little electronic conductivity. If there is an appreciable difference in the electronegativity values of M and X of M_mX_n , the film is highly ionic and tends to allow ionic conductivity, *i.e.*, it behaves as a solid electrolyte as, for example, is the case of all compounds (especially fluorides) of alkali and alkaline earth metals, *e.g.*, Li , Na , Mg , Ca , etc. If, on the other hand, the surface film is highly covalent (*e.g.*, SiO_2 layer on Si) it allows little ionic conductivity (except, perhaps, for the proton space charge) and behaves as a perfect insulator, such films do not allow the electrochemical reaction to continue on the film-covered surface. Most corrosion reaction films tend to display some ionic character, however, and thus allow some ionic conduction necessary for the battery reactions to continue.

In a battery anode, the metal M passes into solution via the dissolution of the film M_mX_n , *viz*



where $(M^{(nx/m)^+})_{\text{solve}}$ is the solvated metal cation of valency (nx/m) . In other words, the metal M must first be converted to the film M_mX_n as in

eqn. (1) and then, via the dissolution of this film, furnish the solvated cations in the electrolyte

The semiconductivity of surface films: some quantitative aspects

For semiconducting materials, including surface films, the intrinsic electronic conductivity, σ , is given by [4]

$$\sigma = \sigma_0 \exp(-E_g/2kT) \quad (4)$$

where k denotes the Boltzmann constant and T is the absolute temperature. By combining eqn (4) with eqn (2) and by taking the logarithms of quantities in eqn. (4), one gets

$$\log \sigma = \log \sigma_0 + \frac{\Delta H_e}{2 \cdot 303 kT} \quad (5)$$

Equation (5) predicts a linear relationship between $\log \sigma$ and $1/T$ for a given semiconducting compound. For a series of related classes of materials, *e g*, oxides, chlorides, bromides, sulphides, etc for which $\log \sigma_0$ values fall within a narrow range, a rough correlation between $\log \sigma$ and ΔH_e values, at constant T , would be expected, with a slope equal to $1/2 \cdot 303 k$. This is verified here (Fig 1) for the case of oxides, based on our previous work [5]. The experimentally measured σ values were obtained from the literature, as mentioned previously [5], and ΔH_e values are from standard thermodynamic tables, noted previously [2].

One would expect a similar correlation for other classes of materials of interest in battery systems, *e g*, fluorides, chlorides, etc. In short, eqn. (2) provides an estimate of the bandgap of the reaction film and, through eqn.

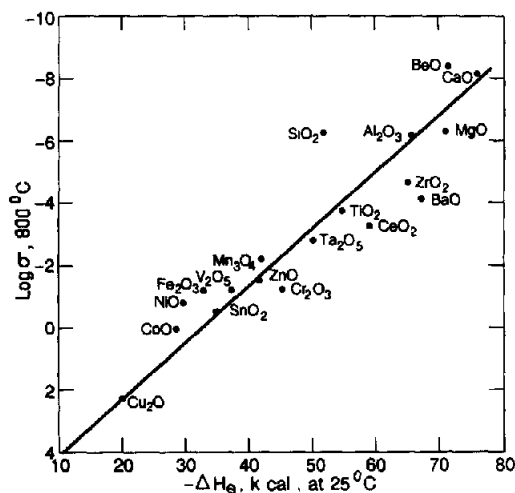


Fig 1 Correlation between "intrinsic" electronic conductivity, σ , and heats of formation per equivalent, ΔH_e , for various oxides [4]

(5) wherever data are available, some idea of the electronic semiconductivity of the surface films formed on active metals of interest in batteries or in the field of corrosion and oxidation of metals. Since intrinsic electronic conductivity had to be assumed in these simple estimates, the presence of impurities would tend to modify somewhat the estimated values.

It is believed that a simple procedure providing an estimate of the ionic conductivity of the surface films (*e.g.*, through some common thermodynamic data as for *electronic* conductivity in eqn (2)) is not available. In principle, one may calculate the ionic conduction in a highly ionic compound or a surface film by the relation [6]

$$\sigma_{\text{ion}} = \frac{Nq^2}{kT} D \quad (6)$$

where N is the number of ions (of a particular sign) per cubic centimeter of the solid, q is the electronic charge, k is the Boltzmann constant, T is the absolute temperature, and D is the diffusion coefficient or diffusivity of the ion.

Although estimates of ionic conduction cannot be readily obtained, a property of considerable interest for surface films, and yet accessible, is the total rate of their anodic dissolution (*viz.*, eqn (3)), *provided* that the film is predominantly ionic, *e.g.*, a fluoride. For the case of fluoride-covered metals dissolving in anhydrous hydrogen fluoride (AHF), it was deduced that [7]

$$\log v \approx K \frac{\Delta H_e}{2.3 kT} \quad (7)$$

where v is the total rate of anodic dissolution of the film, ΔH_e is its heat of formation per equivalent and K is a constant. For the case of anodic dissolution of metals in anhydrous hydrogen fluoride proceeding via a surface fluoride film [8], the dependence of the dissolution rates on the ΔH_e of the corresponding fluorides is indeed observed (Fig 2).

Electrode potentials of battery electrodes and bandgaps of the reaction product films

In high energy density batteries, the aim is to have a low equivalent weight of the active materials and a high half-cell potential for the anodic reaction



It is found [3], however, that the higher potential of the anode half-cell in eqn (8) tends to herald higher bandgap of the reaction product film (*e.g.*, oxide, fluoride, chloride, bromide, iodide, sulphide, etc) formed on the electrode surface. Thus highly insulating films (possessing high bandgap values) tend to arise in the choicest anode half-cells selected on the basis of

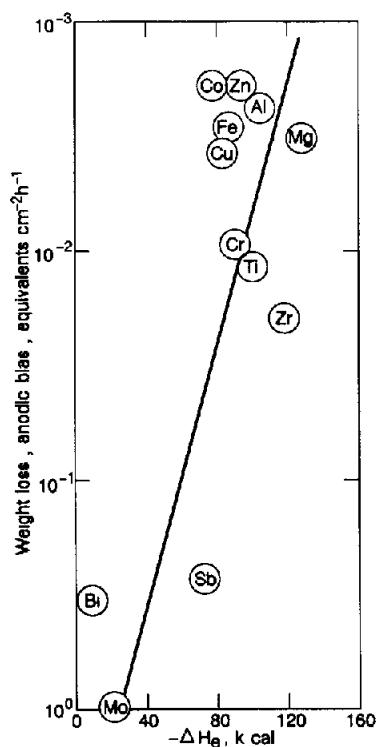


Fig 2 A plot of heats of formation per equivalent of the most stable metal fluorides *vs* the anodic dissolution rates of the corresponding metals in AHF [8]

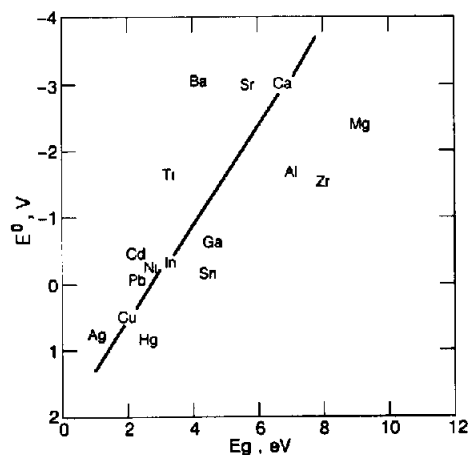


Fig 3 A plot of the E^0 , the standard electrode potential for the M/M^{z+} reaction, of the shown metals *vs* band gaps of their oxides [3]

higher electrode potentials (and low equivalent weights), and generally based on alkali and alkaline earth metal. This can be easily verified for the case of assorted metals with formed oxides (Fig. 3), bromides (Fig. 4), and sulphides

(Fig 5), for example, on the electrode surface, following our earlier work [3] High E° values of the M/M^{2+} couples tend to be related to the high bandgap values of the corresponding M_mX_n films (Figs 3 - 5) These films will tend to choke the energy-producing reaction in eqn (8) and increase the internal resistance of the battery In some fortuitous cases, the use of highly complexing non-aqueous solvent-solute systems might dissolve the insulating surface film (or at least a great deal of it) but the problem is inherently fundamental

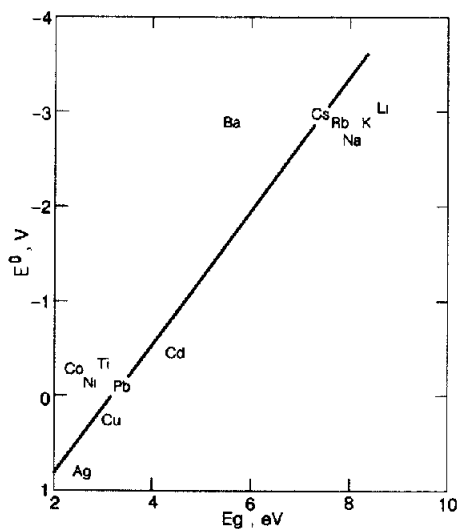


Fig 4 A plot of the E° of the shown metals vs band gaps of the corresponding metal bromides [3]

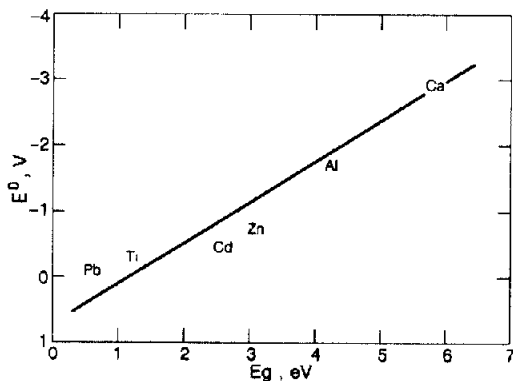


Fig 5 A plot of the E° of the shown metals vs band gaps of the corresponding metal sulphides [3]

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