

# 1 Introduction

PETER G. BRUCE

*Department of Chemistry, University of St Andrews*

I formerly described a substance, sulphuret of silver, whose conducting power was increased by heat; and I have since then met with another as strongly affected in the same way: this is fluoride of lead. When a piece of that substance, which had been fused and cooled, was introduced into the circuit of a voltaic battery, it stopped the current. Being heated, it acquired conducting powers before it was visibly red-hot in daylight; and even sparks could be taken against it whilst still solid.

M. Faraday; *Philosophical Transactions of the Royal Society of London*  
(1838)

## 1.1 *A brief history of solid state electrochemistry*

Solid state electrochemistry may be divided into two broad topics.

- (a) Solid electrolytes, which conduct electricity by the motion of ions, and exhibit negligible electronic transport. Included in this group are crystalline and amorphous inorganic solids as well as ionically conducting polymers.
- (b) Intercalation electrodes, which conduct both ions and electrons. Again there are numerous examples based mainly on inorganic solids and polymers.

The field of solid state electrochemistry is not new. It has its origins, as does so much of electrochemistry, with Michael Faraday who discovered that  $\text{PbF}_2$  and  $\text{Ag}_2\text{S}$  were good conductors. He therefore established both the first solid electrolyte and the first intercalation electrode (Faraday, 1838). Faraday had the wisdom to appreciate the benefits of unifying science rather than compartmentalising it. Regrettably, in the years after Faraday's pioneering work on electrochemistry this wisdom was largely lost. The two subjects of solid and liquid electrochemistry grew apart and developed separately until recent times. The dominance

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of the latter was probably due to the ease with which a wide range of liquid electrolytes could be prepared and purified. Solid state electrochemistry developed steadily up to the late 1960s. Conducting polymers were, in that period, unknown; the subject dealt exclusively with inorganic solids and glasses. Warburg (1884) demonstrated that  $\text{Na}^+$  ions could be transported through glass and together with Tegetmeier (Warburg and Tegetmeier, 1888) carried out the first transference number measurement in solids. The dawn of the twentieth century saw the first technological application of ion transport in solids, when no less an electrochemist than Nernst (1900) proposed a new form of electric light, the 'Nernst glower'. He described how  $\text{ZrO}_2$  when doped with a small amount of  $\text{Y}_2\text{O}_3$  would emit a bright white light on the passage of a current at high temperature, due to its ability to conduct oxide ions. This remains one of the few non-electrochemical applications of solid electrolytes. Until the 1960s solid state ionics was confined largely to the study of oxide ion conductors such as doped  $\text{ZrO}_2$  and  $\text{Ag}^+$  ion conductors such as  $\text{AgI}$ , which above  $147^\circ\text{C}$  adopts a structure that sustains very high ionic conductivity. In fact Tubandt and Lorenz (1914) found that the conductivity of solid  $\text{AgI}$  is higher just below its melting point than that of the molten salt! Insertion electrodes were also under investigation in the early years, specifically  $\text{Ag}_2\text{S}$ . The theory of transport in such mixed ionic and electronic conductors owes much to the elegant work of Carl Wagner (1956) whose academic descendant, W. Weppner is a contributor to this book.

The latter half of the 1960s and the early years of the 1970s saw an explosion of interest in solid state electrochemistry. In 1966 Kummer and Weber at the Ford Motor Company announced the development of a new type of battery which would be light in weight and deliver significant power. The sodium/sulphur cell consists of a solid sodium ion conductor, known as sodium beta alumina, separating electrodes of molten sodium and sulphur. This battery relies on the unique aspect of a *solid* electrolyte separating *liquid* electrodes. The  $\text{Na}^+$  ion conductor sodium beta alumina, often referred to as  $\beta\text{-Al}_2\text{O}_3$ , was first discovered embedded in the linings of glass making furnaces. It had formed at high temperatures due to reaction between soda from the glass melt and the bricks of the furnace walls, which contained the common  $\alpha\text{-Al}_2\text{O}_3$  phase. The oil crisis of the early 1970s focused attention on the development of batteries and fuel cells (Steele, 1992) for electric traction, and other contenders joined sodium/sulphur; most relied on the use of either solid electrolytes or intercalation electrodes. The intensive search for, and study of, new

### 1.1 A brief history

intercalation electrodes led to an appreciation that the long-established battery technologies such as zinc/manganese dioxide and lead/lead dioxide also rely on the process of intercalation. In the 1990s powerful environmental concerns have, to some extent, replaced the oil crisis as a technological driving force in the field of solid state ionics, both from the point of view of batteries and gas sensors. Of no less importance is the development of compact low power batteries for portable electronic equipment, including heart pacemakers, mobile telephones, laptop computers, etc. and electrochromic devices such as SMART windows, which are electrochemical cells that can change their opacity by the passage of a small amount of charge. Many of these applications are discussed in Chapter 11.

The desire to realise technological goals has spurred the discovery of many new solid electrolytes and intercalation compounds based on crystalline and amorphous inorganic solids. In addition an entirely new class of ionic conductors has been discovered by P. V. Wright (1973) and M. B. Armand, J. M. Chabagno and M. Duclot (1978). These polymer electrolytes can be fabricated as soft films of only a few microns, and their flexibility permits interfaces with solid electrodes to be formed which remain intact when the cells are charged and discharged. This makes possible the development of *all-solid-state* electrochemical devices.

Along with the explosion of new electrochemical solids and the intense effort in the field of applications, there have been significant advances in our understanding of the fundamental physical principles of solid state electrochemistry since the 1960s. As is the case for other branches of electrochemistry, fundamental understanding and technological progress have frequently occurred together, often in the same laboratories. Electrochemistry in general is the richer for the synergy between theory and applications. In the 1990s solid and liquid electrochemistry are, after a separation of 150 years, growing together. Electronically conducting polymer electrodes provide the most obvious link. Much early work on these materials was carried out using the models of solution electrochemistry which were frequently inappropriate, when, in fact, polymer electrodes are much more akin to insertion electrodes based on inorganic solids (Chapter 8), where the concepts of charge transfer at the insertion electrode/solution interface and the coupled diffusion of dopant ions and electrons within the electrode, are well established. Conversely, polymer electrolytes are in many senses closer to aprotic liquid electrolytes than to inorganic solids, as acknowledged by the inclusion of polymer electrolytes in the latest general electrochemistry textbooks (e.g. Koryta, Dvořák

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and Kavan, 1993). There is also much that can be learned about the most fundamental aspects of electrochemistry in general by studying solid state systems. New insights into the nature of the electrical double layer and the mechanism by which electron transfer reactions are activated can be obtained since solid electrolytes do not possess freely rotating or librating dipoles. If this book can play a part in bringing solid and liquid phase electrochemistry together, as well as widening the access of solid state electrochemistry to scientists at large, it will have more than justified the effort in its production.

The authors of the succeeding chapters in this book have, in large measure, provided a sufficiently clear presentation of their topics that this introductory chapter can be much shorter than would otherwise have been necessary. However, for those new to the field, a concise overview of solid state electrochemistry may be of value and is presented in the following sections.

### 1.2 *Crystalline electrolytes* (Chapters 2 and 3)

These materials provide an essentially rigid framework with channels along which one of the ionic species of the solid can migrate. Ion transport involves hopping from site to site along these channels. Whereas all ionic solids conduct, only those with very specific structural features are capable of exhibiting conductivities comparable to liquid electrolytes. For example, one such solid electrolyte,  $\text{RbAg}_4\text{I}_5$ , possesses a conductivity of  $0.27 \text{ S cm}^{-1}$  at  $25^\circ\text{C}$  (Owens and Argue, 1970) comparable to many liquid electrolytes.

Crystalline solid electrolytes which conduct  $\text{Ag}^+$ ,  $\text{Cu}^+$ ,  $\text{Tl}^+$ ,  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{H}^+$ ,  $\text{O}^{2-}$  and  $\text{F}^-$  as well as many divalent and trivalent cations are all readily available. The most important applications are of oxide ion conductors for solid oxide fuel cells and oxygen gas sensors. The latter are already widely used to monitor vehicle exhaust gases in catalytic converters.

### 1.3 *Glass electrolytes* (Chapter 4)

Rather specific structural features appear to be necessary for high ionic conductivity in crystalline solids, and as a result it may seem surprising that glasses can support high ionic conductivity. For example, a  $\text{Li}^+$  conductivity of  $0.16 \text{ mS cm}^{-1}$  at  $25^\circ\text{C}$  for a glass with the composition

### 1.6 Interfaces

0.7 Li<sub>2</sub>S–0.3 P<sub>2</sub>S<sub>5</sub> has been reported, which compares favourably with the best crystalline Li<sup>+</sup> ion conductors at the same temperature. Again a hopping mechanism for ion transport is believed to operate, although there is still debate concerning the detailed mechanism (Chapter 4). Glasses capable of transporting Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Cs<sup>+</sup>, Rb<sup>+</sup>, Ag<sup>+</sup> and F<sup>-</sup> (Angell, 1989) have been prepared.

### 1.4 Polymer electrolytes (Chapters 5 and 6)

These materials are introduced in Chapter 5 and only brief mention of them is necessary here. It is important to appreciate that polymer electrolytes, which consist of salts, e.g. NaI, dissolved in solid cation coordinating polymers, e.g. (CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub>, conduct by quite a different mechanism from crystalline or glass electrolytes. Ion transport in polymers relies on the dynamics of the framework (i.e. the polymer chains) in contrast to hopping within a rigid framework. Intense efforts are being made to make use of these materials as electrolytes in all solid state lithium batteries for both microelectronic medical and vehicle traction applications.

### 1.5 Intercalation electrodes (Chapters 7, 8 and 9)

Intercalation is the process of inserting an atom (or ion with its charge compensating electrons) into a solid and removing the atom from the solid. The archetypal example is the insertion of Li between the layers of graphite. This particular insertion process has gained great technological interest as a replacement for lithium metal electrodes in rechargeable lithium batteries. Most of the work has concentrated on lithium intercalation because batteries with a high energy density may be fabricated. Li<sup>+</sup> or I<sup>-</sup> ions may be intercalated into  $\pi$ -conjugated polymers such as polyacetylene (CH)<sub>x</sub>, the ionic charge being balanced respectively by the addition or removal of electrons on the polymer chain. These polymer intercalation electrodes find application in batteries and electrochromic devices.

### 1.6 Interfaces (Chapter 10)

To date the greatest emphasis in solid state electrochemistry has been placed on ionics, i.e. the study of ion transport in the bulk phases. This

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situation is changing. All electrochemical devices rely on the performance of the interfaces between electrolytes and electrodes, at least as much as on the performance of the bulk phases. As a result interfacial studies are growing rapidly in importance. This has only served to emphasise how little is presently understood concerning the fundamental processes at such interfaces. The solid state interface in particular exhibits unique behaviour. Our present knowledge in this most important area is described by Armstrong and Todd.

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## 2 Crystalline solid electrolytes I: General considerations and the major materials

A. R. WEST

*Department of Chemistry, University of Aberdeen*

### 2.1 Introduction

High ionic conductivity in crystalline solids is a widely recognised, although still relatively rare, phenomenon. Most ionic solids are electrical insulators unless they exhibit electronic conductivity. They begin to show significant levels of ionic conductivity only at high temperatures, as the melting point is approached. Materials in the family of crystalline *solid electrolytes* (also called *superionic conductors*, *fast ion conductors* or *optimised ionic conductors*), however, exhibit high conductivity in one of their ionic sublattices – the *mobile ion sublattice* – at temperatures well below melting and often as low as room temperature.

The first half of this chapter concentrates on the mechanisms of ion conduction. A basic model of ion transport is presented which contains the essential features necessary to describe conduction in the different classes of solid electrolyte. The model is based on the isolated hopping of the mobile ions; in addition, brief mention is made of the influence of ion interactions between both the mobile ions and the immobile ions of the solid lattice (ion hopping) and between different mobile ions. The latter leads to either ion ordering or the formation of a more dynamic structure, the *ion atmosphere*. It is likely that in solid electrolytes, such ion interactions and cooperative ion movements are important and must be taken into account if a quantitative description of ionic conductivity is to be attempted. In this chapter, the emphasis is on presenting the basic elements of ion transport and comparing ionic conductivity in different classes of solid electrolyte which possess different gross structural features. Refinements of the basic model presented here are then described in Chapter 3.

The second half of this chapter deals with the most important solid electrolytes and also includes discussion of their structures and properties.

## 2 Crystalline solid electrolytes I

### 2.2 Conduction mechanisms

Ionic conductivity occurs by means of ions hopping from site to site through a crystal structure, therefore it is necessary to have partial occupancy of energetically equivalent or near-equivalent sites.† Two broad classes of *conduction mechanism* – *vacancy* and *interstitial migration* – may be distinguished. In vacancy migration, a number of sites that would be occupied in the ideal, defect-free structure are in fact, empty perhaps due to either a thermally generated *Schottky defect* (a cation and anion vacancy pair) formation or the presence of charged impurities. An ion adjacent to a vacancy may be able to hop into it leaving its own site vacant. This process is regarded as vacancy migration, although, of course, it is the ions and not the vacancies that hop. An example of vacancy migration in NaCl is shown schematically in Fig. 2.1(a).

Interstitial sites are defined as those that would usually be empty in an ideal structure. Occasionally in real structures, ions may be displaced from their lattice sites into interstitial sites (*Frenkel defect* formation). Once this happens, the ions in interstitial sites can often hop into adjacent interstitial sites. These hops may be one stage in a long range conduction process. A schematic example is shown in Fig. 2.1(b): a small number of Na<sup>+</sup> ions are displaced into the tetrahedral interstitial sites and can subsequently hop into adjacent tetrahedral sites. It should be noted, however, that while a small number of Frenkel defects may form in NaCl, conduction is primarily by means of vacancies whereas in some other structures, e.g. AgCl, Frenkel defects do predominate.

The above two mechanisms may be regarded as isolated ion hops. Sometimes, especially in solid electrolytes, *cooperative ion migration* occurs. An example is shown in Fig. 2.1(c) for the so-called *interstitialcy* or *knock-on* mechanism. A Na<sup>+</sup> ion, A, in an interstitial site in the ‘conduction plane’ of  $\beta$ -alumina (see later) cannot move unless it persuades one of the three surrounding Na<sup>+</sup> ions, B, C or D, to move first. Ion A is shown moving in direction 1 and, at the same time, ion B hops out of its lattice site in either of the directions, 2 or 2'. It is believed that interstitial Ag<sup>+</sup> ions in AgCl also migrate by an interstitialcy mechanism, rather than by a direct interstitial hop.

In crystalline electrolytes, *conduction pathways* for the mobile ions

† A particular site must clearly be either full (i.e. contain an ion) or empty. By partial occupancy, we mean that only some of the sites in a particular crystallographic set are occupied.



## 2.2 Conduction mechanisms

permeate the 'immobile ion sublattice' in one, two or three dimensions, depending on the structure of the material. Thus, in  $\beta$ -alumina, Fig. 2.1(c),  $\text{Na}^+$  ions can migrate only in two dimensions. The sites containing the mobile ions are not fully occupied and are connected, via open windows or *bottlenecks*, to adjacent sites that are also partially occupied or empty. In crystalline electrolytes, the sites for the mobile ions are clearly defined by the structure of the immobile sublattice (unlike melts, for instance, where there is no fixed set of sites). Ionic conduction occurs, therefore, by means of a series of definite hops between adjacent sites in the

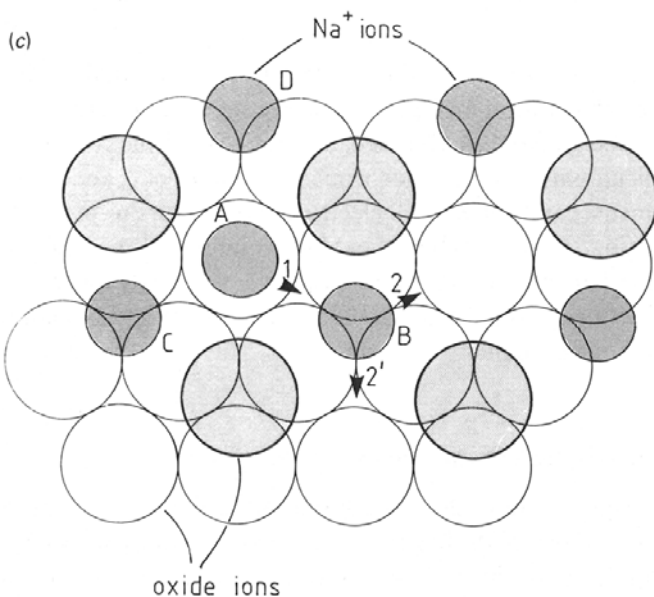
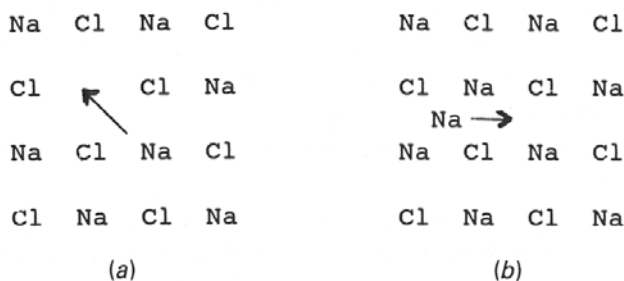


Fig. 2.1 (a) Vacancy, (b) interstitial and (c) interstitialcy conduction mechanisms. In (c),  $\text{Na}^+$  ion A can move only by first ejecting  $\text{Na}^+$  ion B from its site.

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conduction pathways. For most of the time, the 'mobile' ions are located in a particular site, where they undergo thermal vibrations within the site. Just occasionally, they escape from their site and hop quickly into an adjacent site where they may then reside for a considerable time before either moving on or hopping back into their original site.

This notion of occasional ion hops, apparently at random, forms the basis of *random walk theory* which is widely used to provide a semi-quantitative analysis or description of ionic conductivity (Goodenough, 1983; see Chapter 3 for a more detailed treatment of conduction). There is very little evidence in most solid electrolytes that the ions are instead able to move around without thermal activation in a true liquid-like motion. Nor is there much evidence of a free-ion state in which a particular ion can be activated to a state in which it is completely free to move, i.e. there appears to be no ionic equivalent of free or nearly free electron motion.

A simple yet valuable starting point for treating ionic conductivity,  $\sigma_i$ , is as the product of the concentration,  $c_i$ , of mobile species (interstitial ions or vacancies), their charge,  $q$  and their mobility,  $u_i$ :

$$\sigma_i = c_i q u_i. \quad (2.1)$$

This same equation is, of course, also used to rationalise the general electronic behaviour of metals, semiconductors and insulators. The quantitative application of Eqn (2.1) is handicapped for ionic conductors by the great difficulty in obtaining independent estimates of  $c_i$  and  $u_i$ . *Hall effect* measurements can be used with electronic conductors to provide a means of separating  $c_i$  and  $u_i$  but the Hall voltages associated with ionic conduction are at the nanovolt level and are generally too small to measure with any confidence. Furthermore, the validity of Hall measurements on hopping conductors is in doubt.

### 2.3 Mobile ion concentrations: doping effects

The parameter  $c_i$ , Eqn (2.1), is capable of variation by many orders of magnitude in ionic solids. In good solid electrolytes such as Na  $\beta''$ -alumina and RbAg<sub>4</sub>I<sub>5</sub>, all of the Na<sup>+</sup>/Ag<sup>+</sup> ions are potentially mobile and hence  $c$  is optimised. At the other extreme, in pure, stoichiometric salts such as NaCl, ionic conduction depends on the presence of crystal defects, whether