

THE KINETICS OF CHARGE-TRANSFER REACTIONS ON PASSIVE LITHIUM ELECTRODES

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Summary

Lithium anodes are covered by LiCl passive films in SOCl_2 solutions. At open-circuit, film growth is controlled by electronic processes within the film. Under discharge, solid-state ionic processes control the kinetic behavior of the electrode. These processes are not independent of each other. In this report, the interaction of electronic and ionic processes in LiCl passive films is reviewed. Special attention is directed to the role of lattice imperfections in establishing and controlling the mechanisms of electronic and ionic charge transport.

Introduction

Lithium anodes are covered by passive films in aprotic liquid electrolytes. The passive film inhibits the open-circuit corrosion of the lithium by imposing a potential barrier to electron conduction from the metal surface to the electrolytic solution. The film also inhibits the kinetic performance of the anode under discharge by imposing a physical barrier to the mass transport of lithium cations from the electrode surface. These electronic and ionic processes ultimately define the kinetic behavior of the lithium anode. The relationship between electronic and ionic processes for lithium anodes in neutral $\text{LiAlCl}_4\text{-SOCl}_2$ electrolytes is shown schematically in Fig. 1. For the most part, electronic processes are shown in parallel with ionic processes. Therefore, neither current pathway is independent. They are each directly coupled to the potential gradient within the passive film. It is not apparent from Fig. 1, however, that the electronic and ionic processes are also indirectly coupled by lattice imperfections such as structural disorder, point defects, and impurities within the passive film. In fact, the mechanisms of electronic and ionic charge transport are established by lattice imperfections.

In this report, the relationship between electronic transport, ionic transport, and lattice imperfections of the LiCl passive films will be reviewed. The control of these two, rate-limiting processes is expected to lead to significant improvements in the discharge characteristics and shelf lives of Li/SOCl_2

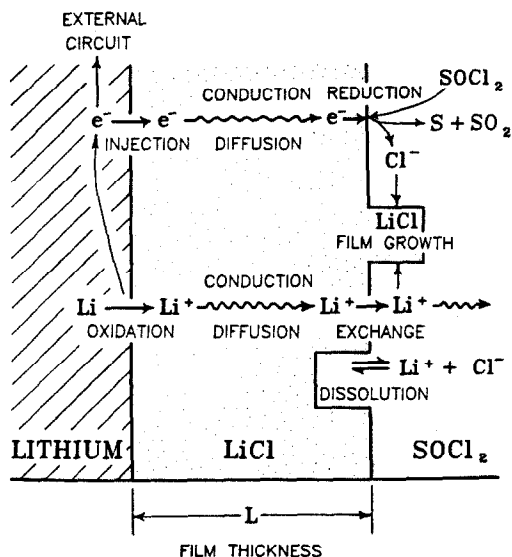


Fig. 1. Schematic representation of a passive lithium anode in SOCl_2 electrolyte. Intermediates in the SOCl_2 reduction reaction are not depicted.

batteries. Control of these two, rate-limiting processes will most likely be achieved through the control of LiCl lattice imperfections.

Background

Mechanisms of ionic transport in LiCl

In pure single crystals above 0 K, atomic defects arise from the spontaneous tendency of the crystal to increase its disorder (entropy). Free energy is required to create these defects, however, and the opposing tendency of the system to minimize free energy results in an equilibrium concentration of native defects in the crystal. In LiCl single crystals at elevated temperatures, the dominant atomic defects are Schottky defects [1, 2]. These defects consist of cation vacancies (V_{Li}) and anion vacancies (V_{Cl}) in the crystal lattice. The law of mass action implies that these vacancies equilibrate according to eqn. (1).

$$[V_{\text{Li}}][V_{\text{Cl}}] = K = A \exp\left(\frac{-E_s}{kT}\right) \quad (1)$$

In this equation, K is effectively a solubility product and E_s is the energy of formation of a Schottky defect pair. At temperatures above 300°C , Haven [2] measured the energy of formation of Schottky defects in single crystals of LiCl ($E_s = 2.12$ eV). Since the cation vacancy is mobile in LiCl , Haven [2] also measured the activation energy of cation vacancy conduction ($W = 0.41$ eV). In order to make these measurements, Haven doped the LiCl crystals

with Mg^{2+} cations to establish a known concentration of Li^+ cation vacancies by charge compensation. This was done because his low-temperature (300 °C - 450 °C) measurements of conductivity were dominated by impurity-induced, rather than thermally induced, Schottky defects. If one accepts Haven's interpretation of cation vacancy conduction in LiCl and extrapolates his data to room temperature, one finds that thermally induced Schottky defects yield a specific ionic conductivity of $\kappa \sim 10^{-18} \Omega^{-1} \text{cm}^{-1}$. His impurity-induced cation vacancies yield $\kappa \sim 10^{-8} \Omega^{-1} \text{cm}^{-1}$. This difference of ten orders of magnitude emphasizes the overwhelming control that impurities can have upon the ionic conductivity in LiCl crystals. Pertinent to this report, one must also mention that long-range lattice disorders can also control the nature and density of point defects, and therefore exert an influence on the specific ionic conductivity of LiCl. For example, edge dislocations may serve as sources (or sinks) for Frenkel defects (vacancy + interstitial) [3]. Finally, the high degree of disorder in grain boundaries suggests that these structures can serve as high conductivity pipelines for ionic transport, and thereby short circuit the bulk-phase ionic transport mechanisms.

Mechanisms of electronic transport in LiCl

Pure single crystals of LiCl are electronic insulators with band gap energies of 9.33 eV [4]. Thermal excitation of electrons from the valence band to the conduction band is therefore negligible. Any mobile electronic charge in LiCl must arise from impurities (donors or acceptors), or by injection at the crystal surfaces. The conduction band in LiCl results from 2s orbital overlap within the lithium cation sublattice. Electronic mobility in this band is very low. Therefore, in the presence of a sufficient density of deep localized states within the band gap, electronic injection into these lower energy states, and electronic transport through these states, takes place preferentially [5]. Electron mobility within these localized states, however, is determined by lattice-phonon interactions according to the hopping conduction mechanism [6, 7], and this mechanism does not yield ohmic behavior except under the restrictive conditions of very low electric fields [8]. Deep localized states can be established by structural disorder in the LiCl lattice or by point defects such as deep donors or deep acceptors.

The coupling of ionic and electronic processes through lattice imperfections in LiCl

In principle, specific lattice imperfections can influence either, neither, or both, mechanisms of charge-transport (ionic and electronic) in LiCl. When both charge-transport mechanisms are influenced by the same imperfection, then special consideration must be given to the interaction. In this section, specific imperfections are considered, and the controlling factors which distinguish the nature and extent of the interaction of the ionic and electronic processes will be discussed.

Li⁺ cation vacancy

The lithium cation vacancy is the majority charge carrier at elevated temperature [2] and is probably the majority charge carrier under most circumstances at room temperature. Due to the repulsive effect of the nearest neighbor anions, this cation vacancy site is a very shallow electron trap in LiCl [9], which probably remains thermally ionized at room temperature. Therefore, the mobile cation vacancy cannot simultaneously serve as an ionic charge carrier and as an electronic charge carrier, nor as a deep, mobile, localized state within the electronic band structure.

When LiCl is placed between two ionically blocking electrodes and a potential is applied, then the mobile cation vacancies will accumulate at the positive electrode/LiCl interface and establish a space-charge region consistent with Poisson's equation. The depletion of cation vacancies from the negative electrode/LiCl interface leaves uncompensated, immobile anion vacancies which establish a space-charge region at that interface. Space-charge redefines the local field at, and near, each interface, and thereby controls the bending of the electronic energy states within the interfacial regions. In the presence of sufficient space-charge, the electric field can be completely shielded from the interior of the LiCl crystals. In this respect, uncompensated ionic charge can control the mechanism of electronic charge injection at the interface [8] and establish the driving force for electronic charge transport (conduction in the potential gradient and diffusion in the concentration gradient) within the interior of the crystal.

Cl⁻ anion vacancy

The anion vacancy in LiCl cannot serve as an ionic charge carrier because it is immobile. However, the vacant anion lattice site does serve as a deep potential well for electrons. When occupied by an electron, this site is called an F-center (or color-center) with an optical absorption maximum at 3.1 eV [10]. Therefore, the Cl⁻ anion vacancy can serve as a localized state in the electronic structure of LiCl, and the electron can conduct through these states by the hopping conduction mechanism. From the optical adsorption spectrum of the F-center, one can conclude that the localized states reside at least 3.1 eV below the conduction band of the LiCl lattice. The Cl⁻ anion vacancy therefore couples the density of electronic states to the density of ionic charge carriers (V_{Li}) through the law of mass action, eqn. (1).

Cation impurities

When LiCl crystals are grown in the presence of foreign cations, these impurities are expected to associate with F-centers. In these cases, the octahedral symmetry of the F-center is reduced from O_h to C_{4v} and the threefold degeneracy of this state will be split [11]. This represents a redistribution of localized electronic levels which can affect the hopping conduction of the F-center electrons through the band gap of the LiCl crystal. In addition,

these foreign cations may themselves serve as localized electronic energy states in the band gap*.

Divalent and trivalent cations require charge compensation and thereby induce mobile cation vacancies in the LiCl lattice. The resulting dramatic change in ionic conductivity, and the electronic band bending which accompanies this change, has already been discussed above. These impurity-induced vacancies must also decrease the equilibrium concentration of anion vacancies in accordance with eqn. (1). Therefore, in addition to the splitting of the degeneracy of the F-center electrons, the cation vacancies (induced by the impurity) can dramatically reduce the density of F-centers in the crystal and thereby reduce the electronic conduction through these states.

Structural disorder

Lattice structural disorder such as edge dislocations and grain boundaries provide sources and sinks for vacancies and interstitials. These long-range structures exert a direct influence on the density of mobile ionic carriers. These structures also severely disrupt the periodicity of the LiCl lattice and induce a manifold of electronic states below the conduction band and above the valence band. Lattice disorder has the effect of smearing the band edges. Discrete localized levels within the band gap are also distributed by this disorder. All electronic transitions are distributed by lattice structural disorder.

Point defects, impurities, and lattice structural disorder all disrupt the normal modes of lattice vibrations. The interaction of these lattice phonons with electrons in deep localized states represents the essence of the hopping conduction mechanism of electronic charge transport [7]. A discussion of this indirect influence (through phonon interaction) on electronic charge transport is beyond the scope of this report.

Open-circuit film growth

When a lithium electrode is placed in a $\text{LiAlCl}_4/\text{SOCl}_2$ solution, the lithium is spontaneously oxidized by the SOCl_2 to form a LiCl passive film on the electrode surface. This oxidation-reduction reaction continues as electrons from the lithium oxidation reaction are transported through the film to be consumed by the SOCl_2 reduction reaction at the LiCl/ SOCl_2 interface. Cl^- which are formed by this reduction react immediately with Li^+ in solution to precipitate more LiCl at the LiCl/ SOCl_2 interface. Thus, the film grows thicker upon standing at open circuit. Ultimately, the rate of film growth is limited by the transport of electronic charge from the Li/LiCl interface to the LiCl/ SOCl_2 interface. This sequence of events is shown schematically in Fig. 1.

*The assignment of electronic levels to specific cations in LiCl is not known to this author. However, the electronic states assigned to divalent cations in KCl are extensively discussed by Kröger [3]. See also references therein.

It is very difficult to evaluate or control film growth on Li by electrochemical techniques because the mobile electrons are the minority charge carriers in LiCl. All polarizations from open-circuit are dominated by ionic processes. Characteristics of electronic transport must be deduced by indirect measurements such as the determination of film thickness by impedance (dielectric response) or by *ex situ* examinations.

It is possible to diminish the ionic processes by studying LiCl passivation on blocking electrodes such as Mo, W, and Ta. When SOCl_2 is potentiostatically reduced on these electrodes in LiAlCl_4 solutions, Cl^- anions are formed at the electrode surface as a reduction product. These Cl^- anions immediately precipitate with the Li^+ cations in solution to nucleate LiCl at the electrode surface. The resulting LiCl film passivates the electrode surface, and the film continues to grow as it does on Li electrodes.

All ionic processes cannot be eliminated at passive blocking electrodes, however, because the $\text{LiCl}/\text{SOCl}_2$ interface is non-blocking to ions. At this interface, the $\text{LiAlCl}_4\text{-SOCl}_2$ solution can inject mobile cation vacancies (see discussion below) into the passive film. Therefore, polarization of a passive blocking electrode will include a slow, transient response as the ionic space-charge re-equilibrates with the solution and redistributes within the film to accommodate this change in potential. At steady state, however, electronic processes will dominate on passive blocking electrodes.

Delnick *et al.* [8] utilized this concept of the re-equilibration of ionic space-charge to deduce the basic electronic structure of LiCl passive films on Mo electrodes in $\text{LiAlCl}_4\text{-SOCl}_2$ solutions. They concluded that film growth is first limited by the injection of electronic charge from the Fermi level of the Mo electrode to deep, localized electronic states within the film. Ultimately, however, as the ionic space-charge accumulates at the Mo/LiCl interface, the electric field is enhanced at this interface and shielded from the interior of the film. The interfacial injection of electrons is therefore enhanced and electronic conduction through the interior is reduced. Thus, a change in mechanism from interfacial injection control to bulk phase transport of electronic charge results [8].

Based upon the kinetic analysis of film growth, Delnick *et al.* [8] deduced that the deep, localized electronic states in LiCl must reside 3 - 4 eV below the conduction band. These states must correspond to either deep impurity acceptors or to the F-center states of the anion vacancies.

The basic electronic structure of LiCl films is expected to be the same on Li and on Mo substrates; however, two important distinctions must be recognized. First, the Mo electrode cannot annihilate cation vacancies or inject cation interstitials (the Li electrode can) and second, the Fermi level of the Li electrode resides ~ 2 eV above that of Mo. Therefore, the space-charge region at the Mo/LiCl interface will differ from that at the Li/LiCl interface. It follows that band bending of the electronic states will also differ for these two interfaces, and the rates and mechanisms of electron injection and transport may also differ.

In general, if the electric field is completely blocked from the interior of the LiCl film, then electronic transport will be limited by diffusion. If space-charge does not completely block the electric field, then charge transfer may be limited by conduction or injection. In limiting circumstances, these processes yield the same power-law expression for film growth [8, 12]:

$$L = \text{film thickness} = kt^\gamma \quad (2)$$

In this equation, the time exponent, γ , depends upon the mechanism which limits the film growth. It has been observed [12 - 14] that this power-law expression describes the kinetics of LiCl film growth on Li in SOCl_2 solutions; however, the measured time exponent, γ , does not unambiguously identify the limiting mechanism of film growth and the measurement of γ is complicated by irreproducibilities attributed to lattice imperfections [13]. The quantitative relationship between electronic structure and lattice imperfections has not been established for LiCl films on Li anodes.

Discharge of passive anodes

Regardless of the mechanism of film growth, the discharge of passive lithium anodes is controlled by ionic processes.

Steady-state discharge

Referring to Fig. 1, the discharge of the passive Li anode is represented by the reaction.



All other processes and reactions shown in Fig. 1 are significant only to the extent that they influence, or limit, the rate of the lithium oxidation reaction. This reaction is depicted as the solid-state injection of Li^+ cations into the LiCl passive film. In order for this injection to take place, however, space must be available in the film to accommodate the Li^+ cation. In general, the undistorted LiCl lattice will not accommodate an interstitial Li^+ cation (Schottky defect preferred over Frenkel defect). However, in the presence of significant structural disorder, interstitial injection may occur, with subsequent transport away from the interface through grain boundaries. A high electric field at the Li/LiCl interface may provide the energy needed for this injection process. On the other hand, if the structural disorder at the interface (and in the grain boundaries) predominantly accommodates cation vacancies, then Li^+ injection into these lower energy vacant sites will be preferred, and the transport of Li^+ cations from the Li/LiCl interface to the LiCl/ SOCl_2 interface is better represented as the transport of mobile cation vacancies (V_{Li}) from the LiCl/ SOCl_2 interface to the Li/LiCl interface, where they are annihilated by the lithium oxidation reaction (4).



In this equation, Li_i^+ represents a lithium cation which occupies a normal position in the cation sublattice of LiCl. When eqn. (4) describes lithium oxidation, then the Li^+ exchange reaction at the LiCl/SOCl₂ interface (see Fig. 1) is more appropriately represented as the injection of cation vacancies into the film, and the LiCl dissolution reaction should be represented as the simultaneous injection of cation vacancies and surface anion vacancies.

It has already been established [8, 12, 15] that under many conditions of discharge, the solid-state conduction of point defects in the passive film limits the lithium oxidation reaction according to the equation of Young [16]:

$$i = 4azFv[d] \exp\left(\frac{-W}{RT}\right) \sinh\left(\frac{azF\bar{E}}{RT}\right) \quad (5)$$

In this equation, $[d]$ represents the concentration of mobile point defects in the film, W is the activation energy of conduction, and \bar{E} is the electric field. Other symbols have their customary definitions.

Young's equation applies whether the mobile defects are interstitials or vacancies. Measurements [15, 17] of the activation energy of conduction in LiCl passive films at ambient temperature generally agree with Haven's measurements of the activation energy of cation vacancy conduction in single crystals of LiCl above 300 °C. This suggests that cation vacancy conduction is the dominant mechanism of charge transport in passive LiCl films. As pointed out earlier, however, structural disorders and impurities can exert very strong influences on the ionic conductivity of LiCl. Therefore, contributions from the higher energy interstitial mechanism should not be dismissed based on this limited information.

As lithium oxidation proceeds: (i) the film will thicken as the product (LiCl) builds up at the electrode surface, or (ii) the film will dissipate to a new, thinner barrier layer to accommodate a higher rate of discharge. This film dissipation controls the delayed response of the battery (voltage delay or current delay). Once the thinner barrier layer is established, the new steady-state current is also limited by the solid-state conduction of cation defects according to the equation of Young (5) [12].

Delayed response

Delayed response under discharge results when injected ionic charge carriers (interstitials at the Li/LiCl interface and/or cation vacancies at the LiCl/SOCl₂ interface) dominate the intrinsic mobile defects in the film. The intrinsic defects are established by structural disorder and/or impurities incorporated into the film during growth, and they are maintained within the film by the open-circuit chemical and electrochemical reactions at the opposing interfaces of the film [17].

Conclusions

Under most circumstances, the kinetic behavior of lithium anodes in SOCl_2 solutions is limited by either electronic or ionic transport through the LiCl passive film. These processes seldom take place independently of each other. They are coupled by the potential gradient within the film, and they are coupled by lattice imperfection in the LiCl .

Specific lattice imperfections such as long-range structural disorder, impurities, and point defects, establish the energies and distributions of electronic states within the band gap of the passive film. These imperfections also establish the density of mobile ionic charge carriers (primarily cation vacancies). These majority charge carriers establish space-charge regions at each interface, thereby bending the energy levels of the electronic states, and establishing the mechanism of electron charge injection and the driving force for electronic transport (conduction/diffusion). In this respect, the ionic charge carriers indirectly control open-circuit film growth. During discharge, however, the ionic charge carriers dominate the polarization characteristics of the passive lithium electrodes. In order to control passive lithium anodes, one must control the lattice imperfections in the passive film.

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