Scientific paper

Space Charge Layer Effect in Solid State Ion Conductors and Lithium Batteries: Principle and Perspective

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This paper is dedicated to Prof. Dr. Janko Jamnik, who was my enthusiastic and helpful MPI colleague as well as with high academic level and reputation in science community.

Abstract

The space charge layer (SCL) effects were initially developed to explain the anomalous conductivity enhancement in composite ionic conductors. They were further extended to qualitatively as well as quantitatively understand the interfacial phenomena in many other ionic-conducting systems. Especially in nanometre-scale systems, the SCL effects could be used to manipulate the conductivity and construct artificial conductors. Recently, existence of such effects either at the electrolyte/cathode interface or at the interfaces inside the composite electrode in all solid state lithium batteries (ASSLB) has attracted attention. Therefore, in this article, the principle of SCL on basis of defect chemistry is first presented. The SCL effects on the carrier transport and storage in typical conducting systems are reviewed. For ASSLB, the relevant effects reported so far are also reviewed. Finally, the perspective of interface engineer related to SCL in ASSLB is addressed.

Keywords: Space charge layer, Defect chemistry, Interfacial resistance, All solid state lithium battery

1. Introduction

Space charge layer (SCL) effects correspond to carrier redistribution at space charge regions near a two-phase contact. This concept was first used by Carl Wagner to explain conductivity effects at the interface of two semiconductors. It was tentatively developed to explain the interfacial phenomena in ionic conductor systems by T. Jow and J. B. Wagner. Later on, J. Maier made fruitful achievement on understanding of SCL effects at various boundary problems, based on quantitatively derived profiles of defect concentrations through consideration of local thermodynamic and electrostatic relationships.³ From then on, SCL effects proved to be of great importance for ion conduction in solids, especially if the interfacial spacing is on the nanometre scale. In the last decades, a large number of instances for space charge effects on the ionic transport in solids have been provided. Variation of not only the magnitude but also the type of conductivity were verified in composites, grain boundaries in polycrystalline materials and epitaxial heterostructures.^{4–21} Conductivities of various functional materials might be manipulated for fundamental research as well as application. Introduction of interfaces not only led to strong variations in conductivity, but also induced qualitatively change of the type of conductivity.

In recent years, all solid state lithium batteries (ASSLB) have attracted a great deal of attention, since they may provide solution to the safety issue as well as enhancement of energy density compared to the currently commercial rechargeable lithium batteries. The key materials for ASSLB are the solid-state electrolytes and the critical problems are the relevant solid-solid interfaces between the electrolyte and the cathode or inside the composited electrolytes. Though there have already been some discussions on SCL at the sulphide-electrolyte-based batteries, ²² understanding of such effect is still in its infancy. In particular for oxide-electrolyte-based batteries, clarification as well as manipulation of SCL at the interfaces of composited electrolytes or electrolyte/cathode is highly demanded.

Therefore, in Section 2, we will address basic knowledge of the SCL effect according to defect redistribution near a two-phase contact. In Section 3, we will present typical examples of SCL effects occurred at various boundaries of functional materials. In Section 4, we will focus on the SCL effects in solid state batteries. The conclusion and outlook will be given finally.

2. Defect Chemistry at Space Charge Layers Near the Two-phase Boundary

At the boundary between the two materials, carrier redistribution in the space charge region is required from the thermodynamical point of view (uniformity of electrochemical potential).²³ The following discussion seems more closely related to a lateral two-phase contact, the basic knowledge is also applied to the interface in the systems including polycrystalline or composited materials.

In the core-space charge model, $^{2\bar{4},25}$ there are several assumptions: dilute defects on a continuum level, no structural changes up to the interface (x=0), and the same mobility of defects in SCL as in the bulk $(x=\infty)$. In the case of mobile carrier j, its concentration enrichment ζ in equilibrium is

$$\zeta_{j}^{1/z_{j}}(x) = \left[\frac{c_{j}(x)}{c_{j,\infty}}\right]^{1/z_{j}} = \exp{-\frac{e[\phi(x) - \phi_{\infty}]}{k_{B}T}}$$
(1)

where c is the carrier concentration of the defect, and ϕ the electrical potential which is determined by the Poisson equation

$$\nabla^2 \phi = -\rho / \varepsilon \, \varepsilon_0 \tag{2}$$

 ρ represents the charge density equal to $\sum_k z_k e c_k$. In the above expressions, ε and ε_0 are the relative permittivity and the dielectric constant of free space, k_B and T are the Boltzmann's constant and the temperature, e is the absolute value of the electronic charge, z_k is the charge number of the defect k.

If all the carriers are mobile in equilibrium, their electrochemical potentials are constant. Then combination of Eq. (1) and (2) leads to the Poisson-Bolzmann relationship in the direction perpendicular to the interface

$$\frac{\partial^2}{\partial x^2} \left[\phi(x) - \phi_{\infty} \right] = -\frac{e}{\varepsilon \varepsilon_0} \sum_{k} c_{k,\infty} z_k \exp \left[- \left[z_k e \frac{\phi(x) - \phi_{\infty}}{k_B T} \right] \right]$$
(3)

Note that in this case the excess charge is directly given by the species that determine the conductivity. The solution of Eq. (3) for semi-infinite boundary conditions comes to the Gouy-Chapman profile, ^{24,26,27} which can be written as

$$\zeta_{\pm}(x) = \frac{c_{\pm}(x)}{c_{+\infty}} = \left(\frac{1 + \theta_{\pm} \exp(-x/\lambda)}{1 - \theta_{+} \exp(-x/\lambda)}\right)^{2} \tag{4}$$

where $c_{+\infty} = c_{-\infty} \equiv c_{\infty}$ because of the electroneutrality in bulk and x being the distance from the interface. As a result, x = 0 and $x = \infty$ refer to the interface and the bulk, respectively. λ is the Debye length,

$$\lambda = \left(\frac{\varepsilon \varepsilon_0 k_B T}{2z^2 e^2 c_\infty}\right)^{1/2} \tag{5}$$

The parameter ϑ (dependent on ζ_0 and hence on c_0 is defined as follows

$$\theta_{\pm} = \frac{\zeta_{\pm 0}^{1/2} - 1}{\zeta_{\pm 0}^{1/2} + 1} = -\theta_{\mp} \tag{6}$$

and represents the degree of influence. For $\vartheta_{\pm}=0$, i.e. $\zeta_{\pm 0}=1$, the defect chemistry in the space charge region is the same as in the bulk. It approaches +1 for maximum enrichment $(\zeta_{\pm 0}>>1)$ and -1 for maximum depletion $(\zeta_{\pm 0}\leq 1)$. Such profiles are shown in Figure 1a.

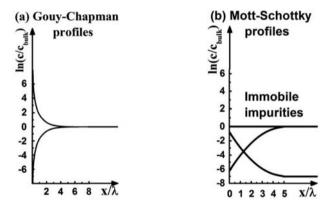


Fig.1. Typical defect profiles in the case of (a) Gouy-Chapman and (b) Mott-Schottky.

While Gouy-Chapman profiles serve as a natural picture for accumulation layers, enrichment effects can also be found in Mott-Schottky situations. Then the conductivity determining carrier has to be a minority carrier with a high mobility in order to surpass the bulk value of the majority carrier significantly. Now, we refer to an extrinsic situation in which the mobile majority species are impurity compensated in the bulk but depleted close to the interfaces. Ideally the impurity profile is assumed to be flat everywhere as shown in Figure 1b. The impurity then is considered to be incorporated during preparation but frozen under operation. In such cases, Eq. (1) is only valid for the mobile carriers. As to Eq. (2), the invariant quantity $c_{\mathit{imp},\infty}$ dominates the space charge density and hence Poisson's equation reads approximately

$$\frac{\partial^2}{\partial x^2}\phi(x) = \begin{cases} -\frac{z_{imp}ec_{imp,\infty}}{\varepsilon\varepsilon_0} = const & \text{for } 0 < x \le \lambda^* \\ 0 & \text{for } x \ge \lambda^* \end{cases}$$
(7)

Eq. (7) can be easily integrated with the boundary

conditions:
$$\frac{\partial \phi}{\partial x}\Big|_{x=x^*} = 0$$
 and $\phi(x=0) = \phi_0$ denoting the

define value from the potential in the electroneutral bulk by ϕ_{∞} , resulting in a quadratic potential profile, ^{28,29}

$$\phi(x) = \frac{-z_{imp}ec_{imp,\infty}}{2\varepsilon\varepsilon_0} \left(x - \lambda^*\right)^2$$
 (8)

Where λ^* is the effective space charge thickness:

$$\lambda^* = \sqrt{\frac{2\varepsilon\varepsilon_0}{z_{imp}ec_{imp,\infty}}} (\phi_{\infty} - \phi_0)$$
 (9)

that exceeds λ by the factor $\sqrt{\frac{4z_{\rm imp}e}{k_{\scriptscriptstyle B}T}\left(\phi_{\scriptscriptstyle \infty}-\phi_{\scriptscriptstyle 0}\right)}$.

Since the typical potential difference is on the order of several 100 mV, this equation indicates that the space charge region in the Mott-Schottky case can be significantly more extended than in the Gouy-Chapman case.

At the point $x = \lambda^*$, ζ_j , becomes unity, i.e. the concentration of the mobile carrier reaches the bulk value. When $x \le \lambda^*$, according to Eq. (1), the defect concentration can be expressed as

$$\zeta_{j}^{1/z_{j}}(x) = \left[\frac{c_{j}(x)}{c_{j,\infty}}\right]^{1/z_{j}} = \exp\left(\frac{x - \lambda^{*}}{2\lambda}\right)^{2}$$
 (10)

In the overlap situation (i.e. $\ell < 2\lambda^*$), the electroneutral bulk does not exist and thus $\phi(\ell/2) \neq \phi_{\infty}$. Rather in

this case, the preferred boundary conditions are $\frac{\partial \phi}{\partial x}\Big|_{x=\ell/2} = 0$ and $\phi(0) = \phi_0$. Hence, the integration of Eq. (7) yields a potential profile

$$\phi(x) = \frac{-z_{imp}ec_{imp,\infty}}{2\varepsilon\varepsilon_0} \left[\left(x - \frac{\ell}{2} \right)^2 - \left(\frac{\ell}{2} \right)^2 \right] + \phi_0$$
 (11)

and the defect concentration profile becomes

$$\zeta_{j}^{1/z_{j}}(x) = \left[\frac{c_{j}(x)}{c_{j,\infty}}\right]^{1/z_{j}} = \\
= \exp\left\{\frac{z_{imp}}{4\lambda^{2}}\left[\left(x - \frac{\ell}{2}\right)^{2} - \left(\frac{\ell}{2}\right)^{2}\right] - \frac{e}{k_{B}T}(\phi_{0} - \phi_{\infty})\right\} \tag{12}$$

As the mobile majority carrier is depleted, Mott-Schottky analysis mainly applies to resistive boundaries. If however a minority carriers of the same sign as the impurity has a very high mobility, it can well be conceived that its accumulation leads to a conductance increase even though the impurity level is not exceeded. As already pointed out, this demands a high ratio of $u_{\text{minority}}/u_{\text{majority}}$ (u, carrier mobility).

3. Space Charge Layer Effects on Conductivities at Various Boundaries

Based on the above discussed carrier redistribution at SCL, conductivity anomaly at various boundaries has been quantitatively studies. Briefly speaking, the SCL concept has quantitatively accounted for the composites (Figure 2a), polycrystallines (Figure 2b) and heterostructural multilayers (Figure 2c), the typical examples which are respectively addressed in the following.

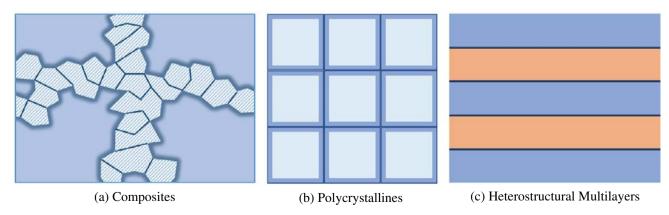


Fig. 2. Typical space charge layer situations of (a) composites; (b) polycrystallines; (c) heterostructural multilayers.

The earliest attractive composite known as "composite electrolytes" or "heterogeneous electrolytes" was the two-phase system LiI-Al₂O₂, reported by Liang et al. with the ionic conductivity 50 times greater than that of the pure LiI.³⁰ Concerning that the Al₂O₂ particles are insulating, the conductivity enhancement is attributed to the boundary layer phenomena, which can be perfectly explained by the SCL effects. Besides Al₂O₃ similar oxides including SiO₂, CeO₂, ZrO₂ and BaTiO₃ were found to be also effective. Since there were a lot of papers on this respect, readers can refer to the literature in Ref. [3]. Further with mesoporous Al₂O₃ as the insulating phase, the enhancement of conductivity can be more effective, which is satisfactorily explained in the framework of the ideal space-charge model.³¹ Here, it is worthwhile mentioning "Soggy Sand Electrolytes". 32,33 The total conductivities are highly increased by virtue of the very high conductivities at the edge of the space charge profiles. This work is of significance owing to evidence of heterogeneous doping mechanism as well as improvement of mechanical behaviour for the polymer electrolytes in the field of solid-state lithium batteries.

Besides composite electrolytes, composite electrodes are also worth noting. A novel interfacial storage mechanism for lithium in the nanocrystalline boundaries was elucidated by J. Jamnik and J. Maier.³⁴ Later on, many works both in experiment and theory demonstrated valid of the interfacial storage. Li et al. found the Li storage in TiF₃ and VF₃, which was attributed to the interfacial effect since neither LiF nor Ti and V could store the Li.¹² Yu et al. prepared LiF, Ti and LiF/Ti composite thin films in the same thickness using pulsed laser deposition. Discharge and charge tests revealed that the LiF and Ti films had negligible capacities, while the LiF/Ti composite film showed significant Li storage capacity, which increased with increasing thickness. These results clearly indicate existence of interfacial storage. 35,36 In theory, the first principle calculation proved the reasonability of interface storage from the view point of thermodynamics.⁵ Such mechanism is beneficial not only to increase the storage capacity at low potential but also to improve the rate performance.

For polycrystalline systems, there have been many good examples demonstrating the SCL effects at grain boundaries in micrometer scale. The details will not be presented here. Readers can refer to previous reports on ZrO₂, CeO₂ and SrTiO₃.⁹⁻¹¹ With respect to the mesoscopic scale, the nanocrystalline SrTiO₃ gives direct and unambiguous evidence of space charge overlap as characteristic size effect. Owing to the significant extension of depletion zones for the holes, the bulk impedance signal disappears at about 100 nm grain boundary spacing.⁸

Heterojunctions in two-phase systems are particularly advantageous on study of the SCL effects at crystal-line interfaces owing to the controllable spacing between the two boundaries. CaF₂/BaF₂ heterolayers prepared by molecular beam epitaxy serve as a nice demonstration of the potential of nanoionics. They show that ion conducti-

vities both parallel and perpendicular to the interfaces increase with decrease in interfacial spacing. This size effect is attributed to the thermodynamically necessary redistribution of the mobile fluoride ions. 15,37 On this basis, the striking phenomenon of an upward bending in the effective parallel conductivity as a function of inverse interfacial spacing for low temperatures has been satisfactorily explained by application of a modified Mott-Schottky model for BaF₂. 38 This model was further confirmed by measurements perpendicular to the interfaces that offer complementary information on the more resistive parts. This successful comprehensive modeling of parallel and perpendicular conductivities for the whole parameter range gives a nice picture of ion redistribution at the interfaces and the boundary zones overlap as well as the predicted mesoscopic size effect. This mechanism allows achievement of artificial ionically conducting material with anomalous transport properties.^{37–41}

4. Space charge Layer Effects in All Solid State Lithium Batteries

The SCL effects in ASSLB have been intensively studied by Takada et al. with Li₄GeS₄-Li₃PS₄ (thio-LISICON) as electrolytes and LiCoO₂ as cathodes. 42-49 Concerning the difference in chemical potential between the sulphide and the oxide, the SCL may forms at the twophase boundary according to requirement of thermodynamic equilibrium. Further concerning that the oxide is more absorptive with Li than the sulphide, the Li ion may transfer from the sulphide to the oxide, as schematically shown in Figure 3a. Electrons of the mix-conducting oxide will eliminate the concentration of Li interstitials near the boundary, extending thickness of SCL at the oxide side. The defect chemistry situation is depicted in Figure 3b. Since the transport property of the interface is determined by the Li interstitial movement, such carrier redistribution may enlarge the interfacial resistance, increasing the polarization and worsening the rate capability. This phenomenon was indeed proved in experiment as well as in theory.²²

To overcome the shortcomings brought by the SCL as mentioned above, an intermediate layer (IL) with sole ionic-conducting property was supposed to be effective. As shown in Figure 3c, with introduction of such a layer between the two phases, the potential difference between the oxide and the sulphide can be greatly eliminated, leading to reduced Li transfer from the oxide side. With negligible electron concentration in the intermediate layer, the depletion region of Li is also reduced, as shown in Figure 3d. Consequently, the interfacial resistance decreases and the rate capability is enhanced. In experiment, Li₄Ti₅O₁₂, Li-NdO₃, LiTaO₃, Li₂SiO₃ thin layers have been used as the intermediate layer between the sulphide and the oxide, and shown effects to reduce the interfacial resistance and in-

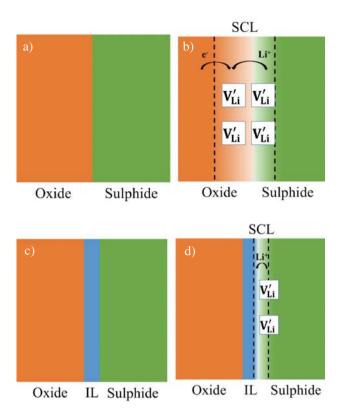


Fig. 3. (a) The two-phase boundary of oxide and sulphide; (b) The defect chemistry situation after the formation of SCL; (c) Introduction of ionic-conducting intermediate layer (IL) between the two phases; (d) The defect chemistry situation after the introduction of the IL.

crease the power density of the ASSLB.^{48–51} Interestingly, the Al-enriched domains formed at the LiAl_yCo_{1-y}O₂ surfaces perform the same functionality as the aforementioned intermediate oxide layers, while with more effective influence on reduction of the interfacial resistance and improvement of rate capability.⁵² These results are in agreement with the relevant theoretical calculation.²²

Although not many, discussions on the SCL effect at interfaces between oxides were also reported. Yamada et al, demonstrated that the nonsintered grain boundary resistance of a highly conducting solid electrolyte (Li_{1.3}Al_{0.3}Ti_{1.7}(PO₄)₃) could be suppressed by being coated with poorly conducting solid electrolyte (Li₂SiO₃).⁵³ In addition, Yamada et al. found that at interfaces of solid oxide electrolytes and active materials, lithium-ion transfer across the interfaces occurred, dependent on the potential of the active materials. The Li⁺ transfer caused change in the ionic conductivity at the interface and, in some cases, changed in the crystal structure. The Li⁺ transfer would be more critical for batteries with high Li⁺ conducting solid electrolytes, because the main charge carriers of them are not lithium vacancies but lithium interstitials. The Li⁺ transfer from such solid oxide electrolytes to cathodes with high electrode potential leads to depletion of the charge carriers in the solid electrolytes at the interface and thus increases in the interfacial resistance.^{54,55} With reduction of SCL effect at the grain boundaries, the total conductivity could be increased. Hitosugi et al. reported the surprisingly low electrolyte/electrode interface resistance in thin-film batteries, which is an order of magnitude smaller than that presented in previous reports on ASSLB as well as smaller than that found in liquid electrolyte-based batteries. Such low interface resistance was attributed to the fact that the negative SCL effects at the Li₃PO_{4-x}N_x/LiCoO₂ interface were negligible.⁵⁶

5. Conclusion and Perspective on All Solid State Lithium Batteries

The SCL effects at the interfaces relate to the carrier redistribution near the two-phase boundary, which is led by the SCL potential derived from the requirement of thermodynamic equilibrium at the contact between the two phases. From early experimental phenomena, to qualitative and quantitative understanding, and to interfacial design for manipulation of conductivity by nano technique, many systems including composites, polycrystallines, heterolayer structures have proven important role of the SCL effects in the carrier transport and storage. Especially in research of ASSLB that has attracted much attention recently, the SCL shows the key influence on the interfacial resistance and thus on the rate capability. Though the SCL at the interface between the sulphide electrolyte and the oxide electrode has been deeply discussed, more relevant effects at the interfaces between the oxide electrolyte and the oxide electrode, between the polymer electrolyte and the oxide electrolyte, and between the polymer electrolyte and the oxide electrode are still in infancy. Existence of such effect either at the electrolyte/cathode interface or at the interfaces inside the composites is one of the key issues for ASSLB, which is currently deemed to be a solution to safety as well as enhancement of energy density in the field of rechargeable lithium battery. Therefore, it is clear that study of SCL related to the ASSLB is significant. More researches in this direction can be expected.

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Povzetek

Efekt prostorsko nabite plasti (SCL) so prvotno razvili za razlago anomalnega zvišanja prevodnosti v kompozitih ionskih prevodnikov. V nadaljevanju so model razširili na razumevanje kvalitativnega in kvantitativnega medfaznega fenomena v drugih ionsko prevodnih sistemih. SCL efekt lahko uporabimo za manipulacijo prevodnosti na sistemih nanometerskih dimenzij, kjer lahko konstruiramo umetne prevodnike. V zadnjem času je obstoj takih efektov na medfazi elektrolit-katoda oz. na medfazah znotraj kompozita v litijevih baterijah s trdnim elektrolitom (ASSLB) pritegnil veliko pozornosti. V zvezi s tem, ta pregledni članek predstavlja prvi pregled SCL principa in njegov vpliv na transport in shranjevanje v tipičnih prevodniških sistemih. Predstavljamo tudi pregled relevantnih efektov za ASSLB baterije. V zaključku obravnavamo še inženirski vidik vezan na SCL in ASSLB sisteme.