Space-charge model of the SEI conduction in the Li/SOCl$_2$ system

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Introduction

The SEI model for the passive layer formed on Li in SOCl$_2$, proposed by Peled [1], has been generally accepted. The passive layer has been regarded as a conductor for Li ions (vacancies) and, practically, as an insulator for electrons. This assumption excellently explains the performance of Li batteries. The ionic conduction itself was supposed to be controlled by the transport of ions across the bulk region of SEI, whereas the influence of both interfaces involved was neglected (Fig. 1). The following characteristics of the SEI model have been found:

● In general, the layer consists of at least two microstructurally and electrically-different sublayers (Fig. 2(a), i.e., the primary (compact) and the secondary (porous) sublayer
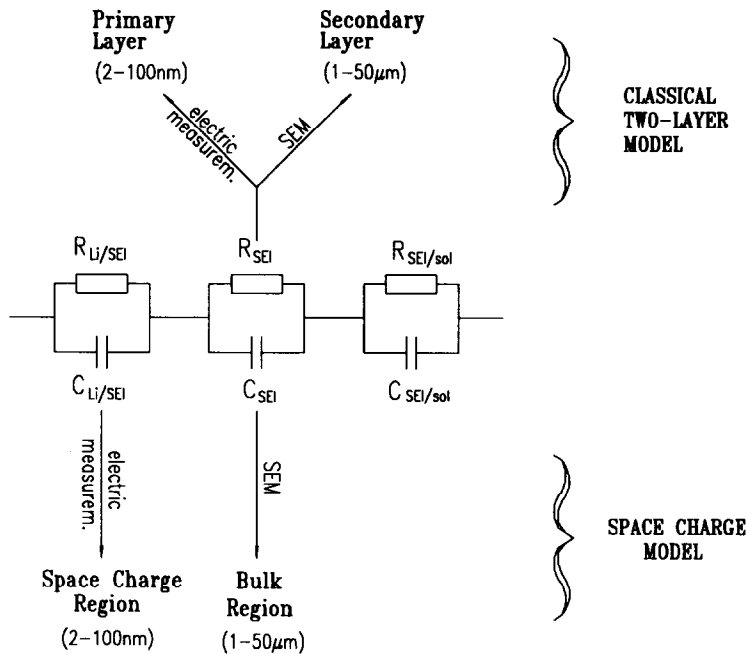

Fig. 1. Relation between the general equivalent circuit for the Li/passive layer/electrolyte system and the two models discussed, i.e. the classical two-layer model and the space-charge model of the SEI conduction.
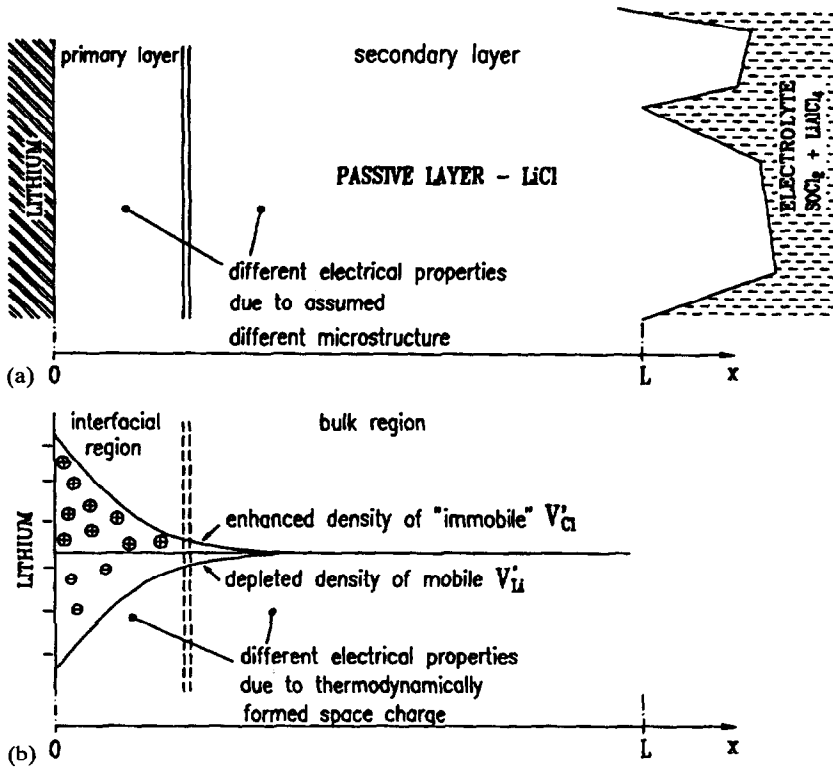
Fig. 2. Comparison of the electrical properties of the (a) two-layer model and the (b) space-charge model.

● Evaluation of the electrical parameters of the compact sublayer is possible by applying the eqn. of Young [2], especially its simplified form at very high electrical fields, i.e., a Tafel-like expression [1]

● The unusual passive layer behaviour at galvanostatic or potentiostatic discharge measurements (e.g., the delay effect) has been explained by the so-called breakdown and repair mechanism, i.e., mechanical cracking and regrowth of the compact sublayer

In the present paper we try to show that an essentially different, but not less consistent, picture of electric processes in this (and perhaps in some other) passive layer arises if one assumes that the rate-controlling process is the charge transfer across the Li/passive layer interface rather than the conduction across the bulk of the compact sublayer. Although some recent experiments [3, 4] do support this approach, one should regard the space-charge model, presented here, merely as an attempt to introduce, into the field of power sources, certain ideas that have been intensively studied in several similar systems, e.g., in ionic conductors such as LiI, AgCl, AgBr [5–9].

Space-charge model of the SEI conduction

As SEI is a rather thin solid-ionic conductor (order of 1–10 μm) one might expect that the influence of both interfaces, represented by the outer RC terms in Fig. 1,

on ionic transport could be quite significant, if not crucial. For example, from Table 1 it can be seen that in various thin solid-ionic conductors the influence of the interface (expressed as the Debye length) may extend over distances comparable with the thickness of the primary layer, or even further. Basing on this comparison and on some experimental results [3, 4] we have proposed that what is usually referred to as the primary layer might be in fact nothing else than the space-charge region at the Li/passive layer interface (Fig. 2). The high resistance of this region results then from the sum of two contributions: the charge-transfer resistance and the resistance due to the depletion of mobile charge carriers (Li vacancies) within the space-charge region. The corresponding differential capacitance is due to the space-charge region and is approximately determined by the magnitude of the Debye length. On the other hand, the resistance of the bulk region and that of the right interface is practically negligible, i.e., about or less than 1% of the resistance of the Li/passive layer interface.

Consequences of the space-charge model

If classical electrical measurements (impedance, delay effect) of the passive layer are explained by the space-charge model, then the following conclusions arise [3, 4]:
• At impedance spectroscopy the arc in the range 65000–1 Hz pertains to the Li/passive layer interface. The response below 1 Hz appears only when more than just one type of charge carriers (i.e. Li vacancies) is mobile
• Thicknesses calculated from the high frequency arc are determined by the magnitude of the space-charge region (the Debye length) at the Li/passive layer interface. It is thus reasonable that electrical measurements will always give thicknesses smaller than optical methods by which only the total layer thicknesses (bulk + two interfaces) may be observed
• Estimated bulk conductivity is much higher (10^{-4}–10^{-5} Ω^{-1} cm^{-1}) than usually reported (10^{-7}–10^{-8} Ω^{-1} cm^{-1}). This, however, need not be regarded as a surprising result. Namely, the passive layer is polycrystalline and presumably doped with Al^{3+}. As seen from Table 2, both the polycrystallinity and impurities essentially increase the conductivity of certain ionic conductors so that quite high conductivity values may arise when both effects are present simultaneously (e.g. in our case)
• Modification of electrical parameters (resistance, capacitance) under nonlinear excitation is due to the accomodation of the space-charge region to new conditions. Figure 3 shows schematically what happens if whether the Li electrode is anodically biased or the temperature is abruptly increased. The time needed for establishing a new steady-state shape is determined by the transport of the slowly mobile defect

TABLE 1
Debye length value in selected ionic conductors

Material	Substrate	T (°C)	Total thickness (nm)	Debye length (nm)	Reference
LiCl	sapphire	25	5–300	30	5
AgCl	KCl	127	200–1000	55	6
AgCl	sapphire	25	50–1000	180	7
AgCl	(emulsion)	25	~1000	1000	8
AgBr	mica	25	100–5000	140–950	9

TABLE 2
Influence of polycrystallinity and impurities on the bulk conductivity of certain ionic conductors

| Material	Substrate	Microstructure	T (°C)	Dopant	Bulk conductivity (Ω^{-1} cm^{-1})	Reference
AgBr		single crystal	35		2.2×10^{-8}	12
AgBr	mica, NaCl	epitaxial film	25		$\sim10^{-8}$	9
AgBr	(emulsion)	microcrystals	34		2.6×10^{-6}	13
AgCl		single crystal	20.9		2.89×10^{-9}	10
AgCl		single crystal	20.9	Cd^{2+} (0.6 mol%)	1.6×10^{-6}	10[a]
AgCl	sapphire	polycrystalline film	25		10^{-5}–1×10^{-6}	7
LiCl		single crystal	25		3.7×10^{-19}	11[a]
LiCl		single crystal	25	MgCl$_2$ (0.036 mol%)	6.32×10^{-8}	11[a]
LiCl		single crystal	25	MgCl$_2$ (0.77 mol%)	1.35×10^{-6}	11[a]
LiCl	Lithium	polycrystalline film	25	Al^{3+} (? mol%)	10^{-4}–10^{-5}	3, 4

[a]Extrapolated from published data.
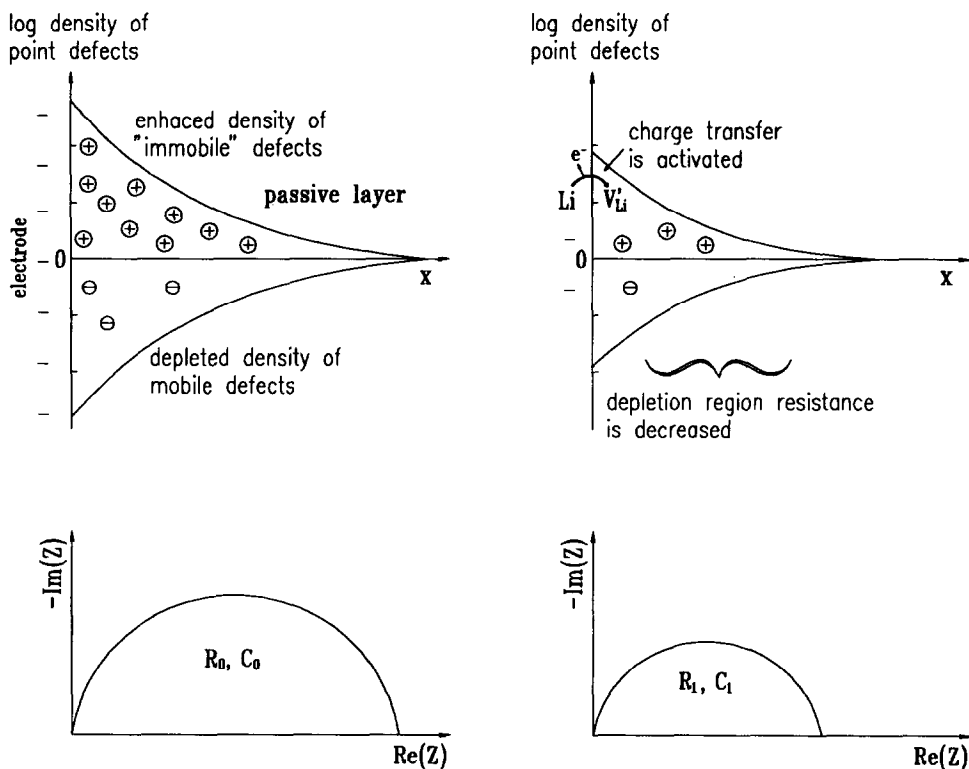
Fig. 3. The influence of external excitation of the Li/passive layer interfacial region.

type (e.g., chlorine vacancy in the undoped case). In essence, this explains the so-called delay effect by merely referring to the intrinsic electrical properties of the system which means that the problematic assumption of mechanical cracking, etc., becomes unnecessary.

We have made several attempts [4] to perform a series of electrochemical measurements that would unambiguously confirm or refute our approach. However, it seems that the regarded system is too complex to draw a final conclusion on the basis of relatively simple experiments. On the contrary, a comprehensive analysis of the data already published should be done and the results compared with the data obtained by some new carefully-designed experiments, involving perhaps also new experimental techniques [14]. The work in this direction is in progress.

Although the actual significance of the space-charge model has not been established as yet, one already may anticipate its principal advantage over the classical approach — namely, the space-charge model requires a smaller number of assumptions to explain various phenomena. For example, the space-charge model does not require the existence of the passive-layer porosity to explain the discrepancy between optical and electrical measurements although it allows its presence. Furthermore, it is able to explain the delay effect without introducing a mechanical or a dielectrical breakdown of the layer. It easily explains the temperature dependence of the capacitance while the classical model should in this case assume temperature dependence of the dielectric constant which is a very rare case if no phase transition is involved.

Conclusions

When thin solid-ionic conductors are in contact with other conductive materials then the space region formed at the interfaces may play an important if not crucial role as regards the electric transport across the system. The passive layer formed on Li in $SOCl_2$ might be an example of such a system. We have shown that some typical results of electrical measurements on the $Li/SOCl_2$ system may be explained consistently if one assumes that the electric transport is controlled by the Li/passive layer interface; in the classical SEI the space-charge region at this interface has been referred to as the primary (compact) sublayer.

Acknowledgement

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