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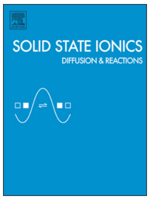

Thermodynamic stability of sulfide electrolyte/oxide electrode interface in solid-state lithium batteries

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ABSTRACT

Thermodynamic analyses were made on the sulfide electrolyte–oxide electrode interfaces in all solid-state lithium batteries using chemical potential diagrams, constructed under the local thermodynamic equilibrium approximation. The chemical potential diagrams were first made for the Li–S–O system and the Li–Co–O system, to show that the stable region for the Li_2S phase and the combined region of $LiCoO_2/CoO_2$ phases do not have a common overlap area in the same $\log a(\mathrm{Li})$ vs. $\log p(\mathrm{O_2})$ plot. Three dimensional diagrams of the Li–Co–S–O system and the Li–Co–P–S–O system were constructed by fixing $\log a(\mathrm{Li})$ at selected values. Based on the constructed diagrams, the chemical nature of the sulfide electrolyte–oxide electrode interface could be considered from both the high temperature electrochemical and chemical points of view. This aided the interpretation of recently reported microscopic analyses on the interfaces. The causes of the "high resistive layer" and cobalt diffusion can be reasonably interpreted as chemical processes, caused by the high Li potential during charging. The results present in this paper are also compared to recent results from theoretical calculations on the energetics of interface structure. The possible applications of the here presented chemical diagrams are discussed in terms of the stoichiometric numbers and energies of the local interface atomic arrangement.

1. Introduction

Solid-state lithium batteries [1–4] have recently attracted significant attentions due to the rapidly growing interest in using all solid-state batteries in automotive applications. Sulfide based electrolytes have been intensively investigated in the hunt for new high Li-conductivity compounds [5–11]. There have been investigations on the interface stability between sulfide electrolytes and oxide electrodes such as $LiCoO_2$. To overcome this issue, experimental investigations were made on elemental distributions across the interface [12–14]. Detailed analyses lead to some considerations of the chemical processes which take place across the interfaces. Meanwhile, theoretical investigations were also made to clarify the origin of high resistivity at the interfaces, leading to the proposal of a new mechanism that would explain the high resistivity in terms of the Space-Charge Layer at the sulfide–oxide interface [15–20]. Many attempts at coating the oxide electrodes have been made with some success at reducing interface resistance [16, 21–24]. However, further understanding of such issues is vital to the development of a solid-state lithium battery which can be utilized in many applications and fields. With this goal in mind, it seems interesting to clarify the chemical/electrochemical nature of the sulfide electrolyte–oxide electrode interfaces from a high-temperature electrochemical point of view. This is a well-established fundamental approach when analyzing solid oxide fuel cells and other high temperature electrochemical devices [25–28].

The chemical potential approach is quite important when examining room-temperature electrochemistry and the Pourbaix diagrams are widely used for aqueous-solution electrochemistry. However, there are several points to be careful of when using chemical potential diagrams [29]. Among those compounds which are treated at room temperature is not always in the most stable state. The metastable compounds exist without any transformation to the most stable state due to a kinetic hindering of nucleation. Another point to be considered is that the diffusion of atoms in solid states is often kinetically hindered. This suggests that the solid state reactions accompanied with solid-state diffusion should be similarly hindered. Despite such limitations, the local equilibrium should be established when determining the electrode potential because the equilibrium electrode potential is determined by the local equilibrium among Li^+, e^- and Li. Consequently, chemical potential diagrams were applied to discuss a determining factor of the positive electrode potential [30]. This discerned the trend in lithium potential in a series of transition metals. As described above, recent investigations reveal that chemical processes may occur at the sulfide electrolyte–oxide electrode interfaces and also theoretical investigations have already clarified that some atomistic rearrangement can be taken place in a scale of a few atomic layers at interfaces. This provides a good opportunity for examining the applicability of the chemical potential diagrams to such interface chemistry. Usually, the chemical potential diagrams are constructed for crystalline phases and therefore

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are not applied to systems having coherent interfaces or phases to be present at interfaces alone. Even so, rearrangement of atoms at interfaces without diffusion is very similar to the initial step of diffusion couple at high temperatures. Furthermore, the chemical potential diagrams are constructed on the basis of the equations characterized in terms of the stoichiometric numbers and Gibbs energy of respective phases. Chemical nature of systems such as redox properties or acid–base relation is represented by this set of stoichiometric numbers and Gibbs energy. Thus, the chemical potential diagram approach was applied to discuss whether the sulfide electrolyte–oxide electrode interface is thermodynamically stable, and to see what kinds of compounds form as a function of lithium potential at the interfaces. Then results are compared with the observed results on the elemental distributions and with the theoretical results as well. Even though the compounds predicted in the diagram are not actually observed, this comparison will make clear what kind of chemical processes can take place at interfaces during the electrochemical processes characterized in terms of the chemical potential of Li.

2. Methods

2.1. Chemical potential diagrams for the investigation of electrolyte–electrode interactions in high-temperature electrochemical devices

High-temperature-type chemical potential diagrams [27] have been successfully constructed to investigate the high temperature electrochemical cells [28,31] such as solid oxide fuel cells. An advantage; both the electrochemically active species and other elements can be considered simultaneously, because other elements are also important when considering interdiffusion across interfaces or chemical reactions at interfaces which may change the electrochemical characteristics of interfaces. This provides a basis of understanding performance degradation and durability.

2.2. Application to room temperature electrochemical devices

The same algorithm can construct diagrams for room temperature systems; considerations should be made on how to utilize the chemical potential diagrams and what information should be derived from the analyses with diagrams.

In typical Pourbaix diagrams, phase relations can be interpreted in terms of equilibrium between chemical media and substances surrounded by such media. Appropriate thermodynamic variables are adopted as diagram axes to identify the chemical nature of the media. For example, pH ($-\log c[\mathrm{H}^+]$) can be used for an aqueous solution. In the diagram, the stable chemical state of the target element is displayed. This corresponds to the situation where mass transfer associated with changes in the stable state is made only through this chemical media. In addition to this, special treatments are adopted in Pourbaix diagrams to broaden its applicability;

1) Treatment of metastable phases. In many cases, the nucleation of new phases is kinetically hindered at room temperature. Even so, many metastable phases actually contribute to the electrochemical processes. Thus, the most stable phases and metastable phases are included in Pourbaix diagrams. Usually different diagrams are constructed for respective the most stable and metastable phases. This avoids complexity. For example, metal oxides would be the focus of one diagram, the other metal hydroxide.
2) Implicit treatment of non-mobile elements of species. Since in many room temperature electrochemical devices, diffusion of cations or metallic elements will not be considered so that the chemical potentials of metallic elements are not displayed explicitly in diagrams.

2.3. Electrolyte–electrode interactions in solid-state lithium battery

In lithium batteries, lithium ions are the electrochemically active charge carrier, so the chemical potential of lithium becomes crucial to determining the electrical potential through the following electrochemical reaction:

$$\mathrm{Li}^+(\text{in electrolyte}) + \mathrm{e}^-(\text{in positive electrode}) = \mathrm{Li}(\text{in positive electrode}) \quad (1)$$

$$\mathrm{Li}(\text{in negative electrode}) = \mathrm{Li}^+(\text{in electrolyte}) + e^-(\text{in negative electrode}). \quad (2)$$

The electromotive force can be given as follows;

$$nFE = \mu(\text{Li in positive electrode}) - \mu(\text{Li in negative electrode}). \quad (3)$$

For the oxide positive electrode, $\mathrm{LiCoO_2}$, the Li potential is derived from the following electrode reaction:

$$\mathrm{Li}(\text{in positive electrode}) + \mathrm{CoO_2}(\text{in positive electrode}) = \mathrm{LiCoO_2}(\text{in positive electrode}) \quad (4)$$

$$\mu(\text{Li in positive electrode}) = \mu(\mathrm{LiCoO_2}) - \mu(\mathrm{CoO_2}). \quad (5)$$

Since these equilibria should be always established, even during the electrochemical charging or discharging processes, the chemical potential of Li at interfaces may change depending on these processes. During charging/discharging, Li or Li ions move across the interfaces. This is accompanied by a flow of Li ion in the electrolyte and Li diffusion in electrodes depending on the current density.

Since chemical reactions at interfaces happen simultaneously with interdiffusion across interfaces during charging/discharging processes, it becomes necessary to consider the movement of elements other than Li. In this sense, the high-temperature-type chemical potential diagrams become useful. The local thermodynamic equilibrium approximation suggests that electrochemical potential gradients for Li ions or electrons, or the chemical potential gradient of Li may cause the corresponding gradient of other species. This can be expressed as follows; e.g., for the oxide electrode,

$$\mathrm{Li(s)} + \mathrm{Co(s)} + 2\mathrm{O(s)} = \mathrm{LiCoO_2(s)} \quad (6)$$

$$\mu(\mathrm{Li}) + \mu(\mathrm{Co}) + 2\mu(\mathrm{O}) = \mu(\mathrm{LiCoO_2}) \quad (7)$$

$$\mathrm{d}\mu(\mathrm{Li}) + \mathrm{d}\mu(\mathrm{Co}) + 2\ \mathrm{d}\mu(\mathrm{O}) = 0. \quad (8)$$

For electrolyte,

$$3\mathrm{Li(s)} + \mathrm{P(s)} + 4\mathrm{S(s)} = \mathrm{Li_3PS_4(s)} \quad (9)$$

$$3\mu(\mathrm{Li}) + \mu(\mathrm{P}) + 4\mu(\mathrm{S}) = \mu(\mathrm{Li_3PS_4}) \quad (10)$$

$$3\mathrm{d}\mu(\mathrm{Li}) + \mathrm{d}\mu(\mathrm{P}) + 4\ \mathrm{d}\mu(\mathrm{S}) = 0. \quad (11)$$

The local chemical potential values of elements in a substance (e.g. $\mathrm{LiCoO_2}$) are obeyed to the above relation that is given in terms of its local composition (stoichiometric numbers), (1,1,2) for (Li,Co,O), and its energy, $\mu(\mathrm{LiCoO_2})$. Even so, only one equation is given for several chemical potentials, so gradients of $\mathrm{d}\mu(\mathrm{Co})$ and $\mathrm{d}\mu(\mathrm{O})$ are not determined separately to $\mathrm{d}\mu(\mathrm{Li})$. At high temperatures, these values can be determined by the diffusion properties of Co and O in the target substances [26].

The local thermodynamic equilibrium approximation suggests an important feature; in electrolyte and electrodes, the chemical potentials of elements should be continuously changed to obey the relations derived from the flows of all mobile species; the distribution of the

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