

Chemical interactions in the cathode half-cell of lithium-ion batteries Part I. Thermodynamic simulation

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Abstract

The method of thermodynamic simulation was used to study chemical interactions in the cathode half-cell of lithium-ion battery, which contained LiCoO₂ as cathode active material and a LiPF₆ solution as the electrolyte. It was shown that in the temperature range 298–400 K in thermodynamic equilibrium state a layer of solid products of chemical reaction formed on the cathode/electrolyte interface. The layer predominantly consisted of LiF and LiPO₃ in the molar ratio about 2:1 (corresponding to the volume ratio 2:3). In equilibrium state also some soluble interaction products formed, namely: CoF₂ (considerable quantity), POF₃ and PF₅. The concentration of the later two substances was small, but it increased with increase of the temperature. Furthermore, in equilibrium state oxygen gas formed as a product of chemical interactions in cathode half-cell.

Thermodynamic characteristics of Co₂O₃ and LiCoO₂ compounds were determined using a set of calculation methods.

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1. Introduction

The study of processes concerned with the degradation of lithium-ion batteries is one of the main research topics in the field of chemical power sources. In spite of the fact that the characteristics of the cells produced by different manufacturers vary within broad range, there are several common problems for Li-ion batteries (hereafter LIB), namely: capacity fading, aging, acceleration of these processes with increase of the temperature, and considerable gassing under heating [1–5].

Various aspects of degradation phenomena in LIB have been considered in a number of papers and the relevant results have been summarized in reviews [6–8]. Special attention was paid to

the analysis of electrode surface layers. Most of the studies deal with the formation of anode surface layers (see, e.g. [9–12]), while the cathode/electrolyte interface was much less studied [13–15].

The present study is dedicated to chemical interactions in the cathode half-cell of LIB and to the processes concerned with these interactions and leading to degradation of the cells in the course of long-term storage. The study was carried out using the cells produced by Samsung SDI on a mass scale, which contain LiCoO₂ as cathode active material and 1.15 M LiPF₆ solution in mixture of alkyl carbonates as the electrolyte. The Part I of the series of papers reports results of a thermodynamic simulation of the interactions on the cathode/electrolyte interface. The Part II is concerned with the experimental study of chemical processes taking place in the cathode half-cell. X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and electrochemical impedance spectroscopy (EIS) were used.

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2. Method of thermodynamic simulation

Theoretical principles of the thermodynamic analysis of complex reagent systems were formulated in the classical thermodynamics by Gibbs. Lewis and Randall [16] bridged the theory and the practice. One of the pioneering algorithms for computer-aided calculation of the equilibrium composition was proposed by Brinkley and Kandiner [17,18]. Another algorithm, which is based on the minimization of Gibbs energy, was developed later [19]. The first software kit, which was designed for mass calculations of the equilibrium composition and had a database of thermodynamic properties of individual substances, was elaborated by Zeleznik, Gordon and McBride [20,21]. The methods of thermodynamic simulation proved to be incredibly fruitful for the analysis of metallurgical processes. This promotes further improvement of the simulation methods [22–24]. By now, several hundreds of algorithms and software kits have been developed to calculate the equilibrium composition of multi-component systems. The most popular algorithms are comprehensively reviewed in [25–28].

The method of thermodynamic simulation (TS) essentially consists in a comprehensive thermodynamic analysis of the equilibrium state of the *system as a whole*. Modern algorithms are based on the variation principles of the thermodynamics developed by Dorn [29]. It is assumed that the thermodynamic system is closed and isolated, that the system obeys the laws of statistical physics (it is true, if the number of atoms in the system is over 10^5), that the system is isotropic and not influenced by magnetic, electric and gravitational fields. A full thermodynamic analysis of the equilibrium state of a model system allows one not to take into account individual chemical reactions. The final result of the simulation is the quantitative determination of *equilibrium interaction products* in a given model system. Since the aim of this study is to determine the degradation mechanism of LIB during a long-term storage one can assume that the system under the study is close to equilibrium state. The comparison between calculated and experimental data makes the interpretation of experimental data much easier since only the products of interaction, which are thermodynamically allowed and therefore should form according to modeling, could be taken into account.

All modeling calculations were done using ASTRA 4 software kit with the ASTRA.BAS database [30]. In the frame of the model used the criterion of the equilibrium state was the maximum of the entropy of the system. The following thermodynamic values of the studied compounds were used for the simulation: standard formation enthalpy ($\Delta_f H_{298}^\circ$), stan-

dard entropy (S_{298}°), heat capacity under standard conditions (c_p°), the incremental enthalpy ($H_{298}^\circ - H_0^\circ$), and the coefficients of the temperature dependence of the heat capacity in Mayer–Kelli's equation $c_p = a + bT - cT^{-2}$. Thermodynamic values of some compounds could be found in the literature and added to the database. Thermodynamic values of LiPF_6 were taken from [31,32]. Characteristics of LiCoO_2 and Co_2O_3 were calculated using empirical methods [33] and the method of thermodynamic simulation [34] adopting the model of ideal solutions of interaction products [35]. Reference characteristics necessary for calculation of thermodynamic properties were taken from [36,37] and ASTRA.BAS.

3. Results and discussion

3.1. Calculation of thermodynamic properties of the components of the system

3.1.1. Calculation of thermodynamic properties of Co_2O_3

Thermodynamic characteristics of LiCoO_2 , which are not yet reported in the literature, could be calculated using thermodynamic properties of cobalt (III) oxide. However, there exists no reliable literature data concerned with Co_2O_3 as well. Therefore, thermodynamic values of Co_2O_3 were calculated by the empirical method. The calculations were based on the analogy of thermodynamic properties between cobalt (CoO , Co_2O_3 and Co_3O_4) and iron (FeO , Fe_2O_3 and Fe_3O_4) oxides. The standard enthalpy of formation and standard entropy of Fe_3O_4 is larger than the corresponding total values of the mixture of $\text{FeO} + \text{Fe}_2\text{O}_3$ by 22 kJ mol^{-1} and $2 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively [34]. Assuming the same relationship between these values for cobalt oxides, we estimated the standard enthalpy of formation and standard entropy of Co_2O_3 using well-known thermodynamic characteristics of CoO and Co_3O_4 .

It is known that for some transition metals (including iron) c_p of metal oxide depends linearly versus index x in the oxide chemical formula MeO_x [38]. Assuming that this dependence is correct for cobalt oxides, we estimated the heat capacity of Co_2O_3 under standard conditions (dependence of the heat capacity versus index x in the formula CoO_x was linearly extrapolated to $x = 1.5$).

The enthalpy increment and the coefficients in Mayer–Kelli's equation (describing dependence of the heat capacity versus temperature) were calculated using empirical equations given in [39].

Calculated thermodynamic values of Co_2O_3 are given in Table 1.

Table 1
Calculated thermodynamic properties for Co_2O_3 and LiCoO_2

Compound	$\Delta_f H_{298}^\circ$ (kJ mol ⁻¹)	S_{298}° (J K ⁻¹ mol ⁻¹)	$c_p = a + bT - cT^{-2}$ (J K ⁻¹ mol ⁻¹)			$H_{298}^\circ - H_0^\circ$ (J mol ⁻¹)
			a	$b \times 10^3$	$c \times 10^{-5}$	
Co_2O_3	-631.6	62.3	113.3	4.5	46.46	16000
LiCoO_2	-738	84.4	90.64	0.47	24.0	9800

3.1.2. Calculation of thermodynamic properties of LiCoO₂

The standard enthalpy of formation ($\Delta_f H_{298}^\circ$), the standard entropy (S_{298}°) and the heat capacity under standard conditions (c_p°) of the lithium cobaltite were calculated by the method proposed by Moiseev and Vatolin [34]. The method is based on the model of ideal solutions of interaction products (which is a particular case of the model of ideal associated solutions proposed by Prigogine and Defay [40]) and includes TS. The method is described in details in [34,41]. This empirical method for calculation of thermodynamic characteristics was applied by Moiseev and Vatolin to several hundreds of complex oxides and was proved to give a good fit with experimental data [34].

To simulate the properties of LiCoO₂ we set the composition of the initial system as follows: 1 mol Li + 1 mol Co + 20 mol O₂. All condensed phases in the modeled system were assumed to be components of an ideal solution of interaction products. In other words, all known oxides in the systems Co–O and Li–O were considered as constituents of this solid solution. The ASTRA.4 software package and the ASTRA.BAS database were used for the thermodynamic simulation of the equilibrium composition of the system in the temperature range from 273 to 1500 K (with a step equal to 10 K) under total pressure 10⁵ Pa. For each given temperature T numbers of moles m_i of simple oxides, which form solution of interaction products, were calculated. The values obtained were used to calculate the oxygen index y of the solution:

$$y = \sum_i m_i x_i, \quad (1)$$

where x_i is the oxygen index of the i th simple oxide. The temperature dependence of the total oxygen index y for the system “1 mol Li + 1 mol Co + 20 mol O₂” is shown in Fig. 1. The variation of the total oxygen index y takes place thanks to change of the ratio between different lithium and cobalt oxides forming the solution (Li₂O, Li₂O₂, CoO, Co₂O₃ and CoO₂). As could be seen in Fig. 1, total oxygen index y of the solution of interaction products coincides with oxygen index of LiCoO₂ ($y=2$)

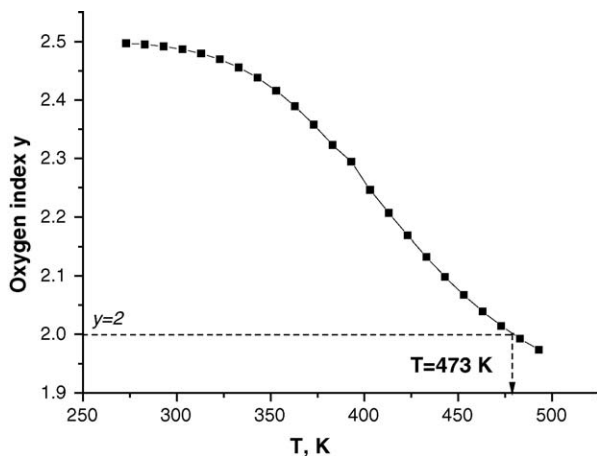


Fig. 1. Temperature dependence of total oxygen index y of an ideal solution of interaction products for “1 mol Li + 1 mol Co + 20 mol O₂” model system.

at 473 K. The numbers of moles m_i of the simple oxides forming the solution of interaction products at 473 K were used for the calculation of thermodynamic characteristics of LiCoO₂ as shown below.

The standard entropy of LiCoO₂ was calculated using the equation given in [34]:

$$S_{298}^\circ(\text{LiCoO}_2) (\text{J K}^{-1} \text{ mol}^{-1}) = \sum_i m_i S_{298}^\circ(i), \quad (2)$$

where m_i is the number of moles of i th simple oxide forming the solution of interaction products and $S_{298}^\circ(i)$ is the standard entropy of the i th simple oxide.

The heat capacity under standard conditions was calculated using the equation given in [34]:

$$c_{p,298}^\circ(\text{LiCoO}_2) (\text{J K}^{-1} \text{ mol}^{-1}) = \sum_i m_i c_{p,298}^\circ(i), \quad (3)$$

where $c_{p,298}^\circ(i)$ is the heat capacity under standard conditions of the i th simple oxide.

The standard enthalpy of formation of LiCoO₂ was calculated using the equation given in [34]:

$$\begin{aligned} \Delta_f H_{298}^\circ(\text{LiCoO}_2) (\text{J mol}^{-1}) \\ = \sum_i m_i \Delta_f H_{298}^\circ(i) + \sum_i m_i (\text{min}) \Delta_f H_{298}^\circ(i), \end{aligned} \quad (4)$$

where $m_i(\text{min})$ is the number of moles of i th simple oxide, except Li₂O and Co₂O₃ (which are basic for LiCoO₂) and $\Delta_f H_{298}^\circ(i)$ is the standard enthalpy of formation of the i th simple oxide.

The incremental enthalpy ($H_{298}^\circ - H_0^\circ$) and the coefficients of the temperature dependence of heat capacity in the equation $c_p = a + bT - cT^{-2}$ were calculated using empirical equations given in [39].

The calculated thermodynamic values of LiCoO₂ are given in Table 1.

3.2. The reaction zone model

The interaction between the cathode active material (LiCoO₂) and the electrolyte, which consists of the mixture of alkyl carbonates and LiPF₆ lithium salt, was simulated using the following model of the reaction zone. It was assumed that alkyl carbonates were chemically inert to the lithium cobaltite. It is known that all these compounds have a wide electrochemical window (>4.5 V) and they are stable with respect to cathode materials [13]. It was assumed therefore that all chemical processes in the cathode half-cell are concerned with interaction between LiCoO₂ and LiPF₆ only. The reaction zone of the model system is drawn schematically in Fig. 2. Also it was assumed that in the beginning of the chemical reaction there was a large excess of lithium cobaltite in the system and then the ratio between the components changed smoothly and LiPF₆ part increased until the entire LiCoO₂/electrolyte interface got covered with a monomolecular layer of the lithium salt. To calculate the composition of the model system quantitatively the LiCoO₂:LiPF₆ ratio was changed by 2–8 mol% steps. Thus, the first step of the simulation corresponded to the individual lithium

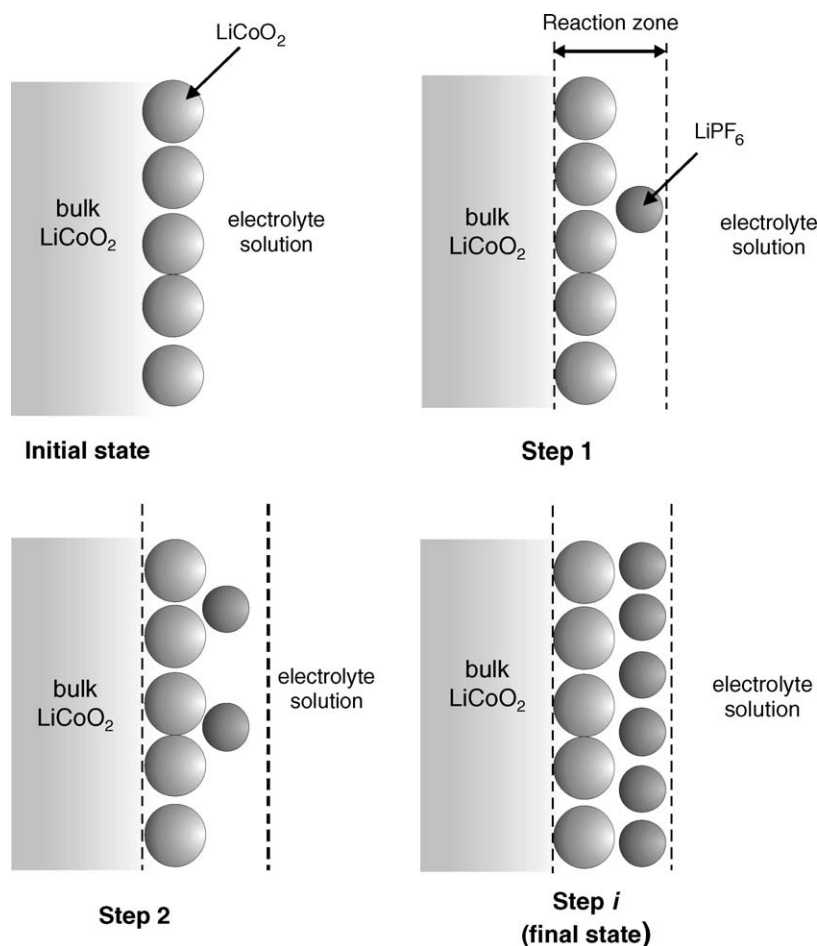


Fig. 2. Scheme of the reaction zone on the “LiCoO₂/electrolyte solution” interface.

cobaltite, while the last step corresponded to the interaction between a monomolecular LiPF₆ layer with a monomolecular LiCoO₂ layer counting per surface unit of the interface (Fig. 2).

Thickness of the monomolecular layer of the *i*th reagent, $\delta(i)$, was calculated using the equation given in [42,43]:

$$\delta(i) \text{ (cm)} = 2R(i)_T \approx 2 \left[\frac{V_{im}(T)}{2\pi A} \right]^{1/3}, \quad (5)$$

where $R(i)_T$ is the effective radius of the interaction (the Onsager radius) between molecules of the *i*th reagent at a temperature *T*; $V_{im}(T)$ the molar volume of the *i*th reagent at a temperature *T*; and *A* is the Avogadro constant.

Hence, the mass of the initial reagents LiCoO₂ and LiPF₆ per unit area of the reaction zone was determined using the following equation:

$$m(i) \text{ (g cm}^{-2}\text{)} = 2d(i) \left[\frac{V_{im}(T)}{2\pi A} \right]^{1/3}, \quad (6)$$

where $d(i)$ is the density of the *i*th reagent. The calculated molar fraction of LiCoO₂ at the last step of the simulation amounted 0.56.

3.3. Thermodynamic simulation of chemical interactions in the cathode half-cell

To perform thermodynamic simulation, we set the composition of the initial system as follows: LiCoO₂ + LiPF₆ + Ar. LiCoO₂:LiPF₆ ratio was varied in the range 0–0.56 mentioned above. The argon concentration in the model system was fixed to 1 mass%. The simulation was done for total pressure of 10⁵ Pa and temperatures range 298–400 K (with 10 K steps). Based on the preliminary estimations we assumed that traces of water in the electrolyte (50 ppm) made negligible influence on the equilibrium state of the system and therefore they were not taken into account.

The results of the simulation for the temperature 298 K are shown in Fig. 3. The increase of the temperature slightly effected equilibrium concentrations. The main effect was exclusively due to the decomposition of LiPF₆ at 348 K. In the temperature range 273–348 K the concentrations of PF₅ and POF₃ increased from 10⁻⁷ to 10⁻⁵ and from 10⁻⁵ to 10⁻³, respectively (mole fraction units).

The results obtained let us conclude that solid LiF and Co₂O₃ as well as small quantities of gaseous POF₃ and PF₅ products formed in equilibrium state on initial stage of the interaction (which corresponds to the excess of lithium cobaltite). The

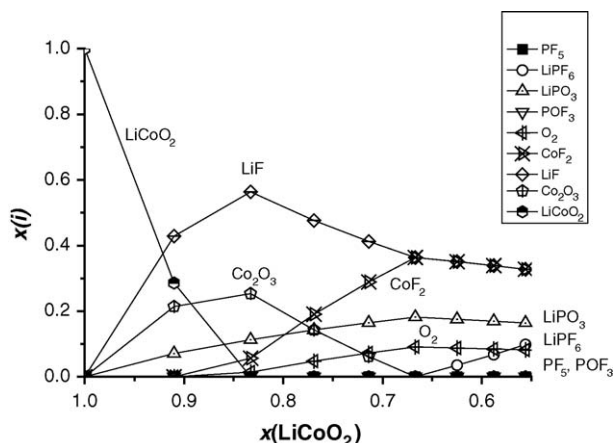


Fig. 3. The dependence of equilibrium concentrations of interaction products in “LiPF₆ + LiCoO₂ + Ar” model system at 298 K vs. the ratio of the reagents in the reaction zone (in mole fraction units).

increase of LiPF₆ concentration led to the formation of CoF₂, LiPO₃ and oxygen gas instead of the cobalt (III) oxide.

Let us analyze the simulation results. In thermodynamic equilibrium state the layer of solid interaction products formed on the cathode/electrolyte interface. The layer consisted predominantly of LiF and LiPO₃ in molar ratio about 2:1 (it corresponds to volume ratio 2:3). One can expect, that this layer can separate the reagents and inhibit further chemical interaction, but does not prevent the transport of lithium cations (LiPO₃ is a known lithium-conducting solid electrolyte [44]). However, along with passivating film on the surface of lithium cobaltite particles a soluble compound, namely CoF₂, forms. CoF₂ probably dissolves in electrolyte solution. Moreover, Lewis acids POF₃ and PF₅ form. The presence of these compounds in electrolyte solution even in small quantities can cause the decomposition of organic solvents and the formation of several liquid and gaseous products [45]. Finally in cathode half-cell gaseous oxygen forms, which can participate in the chemical interactions within the anode half-cell.

3.4. Comparison of calculation and experimental results

The results of the experimental study of the chemical processes taking place in the cathode half-cell of LIB containing LiCoO₂ as cathode active material and LiPF₆ solution as electrolyte are describe in details in Part II of this series of the papers. To compare TS and experimental results briefly, summary of XPS data is given below. As it was shown by the study of LiCoO₂ surface after contact with LiPF₆ solution the layer of the interaction products contained LiF, LiPO₃ and CoF₂. So, experimental data are in good agreement with the results of thermodynamic simulation of chemical interactions in cathode half-cell of lithium-ion battery.

4. Conclusion

The study of chemical interactions in the cathode half-cell of LIB by the method of thermodynamic simulation demonstrated

that LiCoO₂ and LiPF₆ are not chemically inert to each other. The data obtained lets one conclude that their interaction leads to the formation of the layer of interaction products on the surface of LiCoO₂ particles. The layer predominantly consists of LiF and LiPO₃. Considerable quantity of soluble CoF₂ and small amounts of Lewis acids POF₃ and PF₅ also form and dissolve in electrolyte solution. The gaseous oxygen can form in the cell as well. The increase of the temperature slightly effects the equilibrium composition of the interaction products, except POF₃ and PF₅, whose concentration rises considerably with increase of the temperature, but still remains not significant.

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