

The use of neutron reflectometry methods for the study of nanometer-scale electrochemical systems: a review

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A method of optimizing a model electrochemical cell for conducting a neutron reflectometry experiment to study the processes of formation and evolution of a critically important solid electrolyte interphase layer on the electrode is proposed. During the optimization of the model cell, its optimal parameters are set. The conducted experiment proved the possibility of using neutron reflectometry on an optimized model experimental cell for the study of the solid electrolyte interphase layers with a thickness of more than 1 nm.

Keywords: neutron reflectometry, X-Ray reflectometry, Li-ion batteries, solid electrolyte interphase, experimental electrochemical cell.

Використання методів нейтронної рефлектометрії для дослідження електрохімічних систем нанометрового масштабу: огляд. *Є.Косіячкін*

Запропоновано метод оптимізації модельної електрохімічної комірки для проведення експерименту з нейтронної рефлектометрії по дослідженню процесів формування на електроді критично важливого міжфазного твердого шару електроліту та його еволюції. Під час проведення оптимізації модельної комірки встановлено її оптимальні параметри. Проведений експеримент засвідчив можливість застосування нейтронної рефлектометрії на оптимізованій модельній експериментальній комірці для дослідження шарів міжфазного твердого електроліту товщиною більше 1 нм.

1. Introduction

The modern development of portable electronic devices from telephones to electric cars [1, 2] and "green" technologies of electricity production [3, 4] proves the importance of the development of batteries.

To date, lithium-ion batteries remain the leaders of the commercial market of power carriers, which is due to their advantages: high values of operating voltage and specific capacity, and low self-discharge rate [5]. One of the problems with using such chemical current sources is the reduction of the life cycle. This happens due to the formation of "dead lithium", which is the cause of the loss of charge carriers [6, 7] and also due to the degradation of the elec-

trode surface [8, 9]. Another problem is the non-zero probability of an internal short circuit, which can lead to an explosion. The reason for this is the uncontrolled deposition of lithium on the electrode, which leads to the growth of lithium dendrites [6, 7]. The main cause of the problems is considered the insufficient formation of the near-surface solid electrolyte interphase layer, which is thought to be a passivating element that protects the electrode from the chemically aggressive environment of the electrolyte and affects the uniform deposition of lithium on the electrode [6–9].

It is the interest in the study of the processes of the formation of the solid electrolyte interphase layer and the evolution of its parameters during the cyclic operation

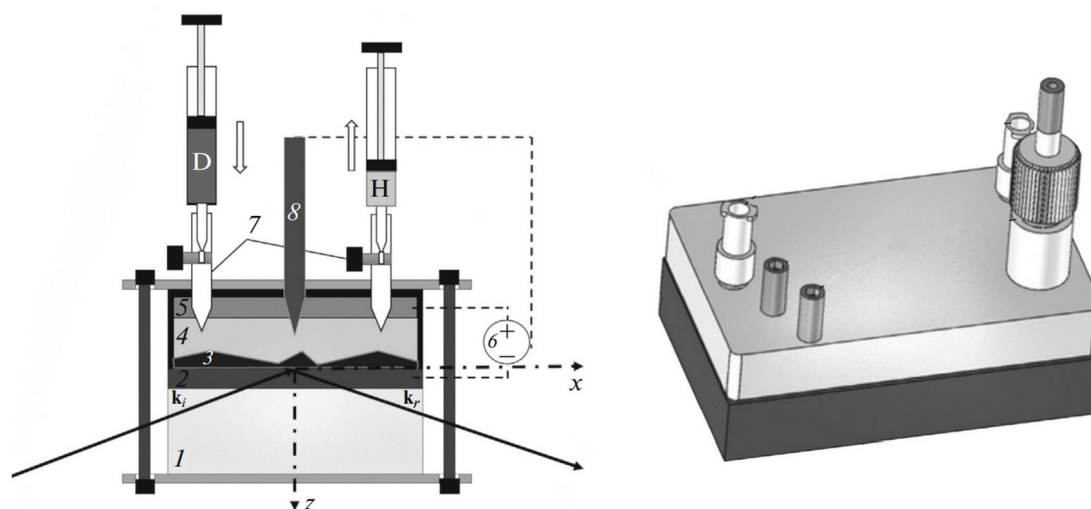


Fig. 1. Schematic (left) and model (right) representation of a model electrochemical cell for a neutron reflectometry experiment (with the option of varying the neutron scattering length density of the liquid electrolyte phase). Components of the cell: 1 — silicon substrate, 2 — metal electrode, 3 — solid electrolyte interphase layer, which is formed or evolves during the experiment, 4 — liquid electrolyte, 5 — opposite electrode, 6 — potentiostat, 7 — the system for realisation of variation of neutron scattering length density in the liquid phase, 8 — control electrode [13].

of lithium-ion batteries that prompts the application of new experimental methods for the study of near-surface layers at the boundary of phase separation. One of the few such methods is neutron reflectometry, which allows the investigation of parameters of the layers of an electrochemical cell at the subnanometer level [10]. Note that the electrochemical cell is a complex multi-component system. Due to that to increase the sensitivity of the experimental method regarding the appearance and evolution of near-surface layers, preliminary optimization of the model cell is necessary. In works [11–13], a procedure for optimizing an electrochemical cell and an example of its implementation [13] were proposed to increase the sensitivity of neutron reflectometry to the formation and evolution of the solid electrolyte interphase layer.

2. Experimental

A detailed description of the model electrochemical cell (Fig. 1) is given in [13]. The main components are: 1) a single-crystal silicon substrate (Holm GmbH, Germany) with a size of $8.5 \times 5 \times 1.5$ cm and a roughness of the working surface of 0.5 nm; 2) a metal electrode (thickness up to 100 nm), which was sputtered to the surface of the substrate by the method of magnetron sputtering with control of the thickness and roughness of the layer. At the same time, the material of the electrode and

its thickness could vary; 3) a custom bath-tub made of polyether ether ketone for creating a working volume of liquid electrolyte in the amount of 3.2 ml; 4) As a reference electrode, a Li/Li⁺ electrode was used; 5) As the counter electrode lithium foil on a nickel grid was used. 6) A 0.5 M solution of lithium perchlorate (LiClO₄, Sigma-Aldrich, USA) in protonated or deuterated propylene carbonate (PC, d-PC, Sigma-Aldrich, USA) was used as an electrolyte (with the possibility of varying the neutron scattering length density).

The method of optimizing the components of the electrochemical cell to increase the sensitivity of neutron reflectometry to the appearance and evolution of the near-surface solid electrolyte interphase layer is described in works [11, 12]. Its essence is to evaluate the change in the neutron reflection curves in the entire working range of scattering vectors, between the initial state of the system (without a solid electrolyte layer or before its evolution) and the final state of the system (after the appearance or evolution of the layer). An electrochemical cell with the maximum change in the reflection curve between the initial and final state is considered optimal, which is expressed by the formula [11, 12]:

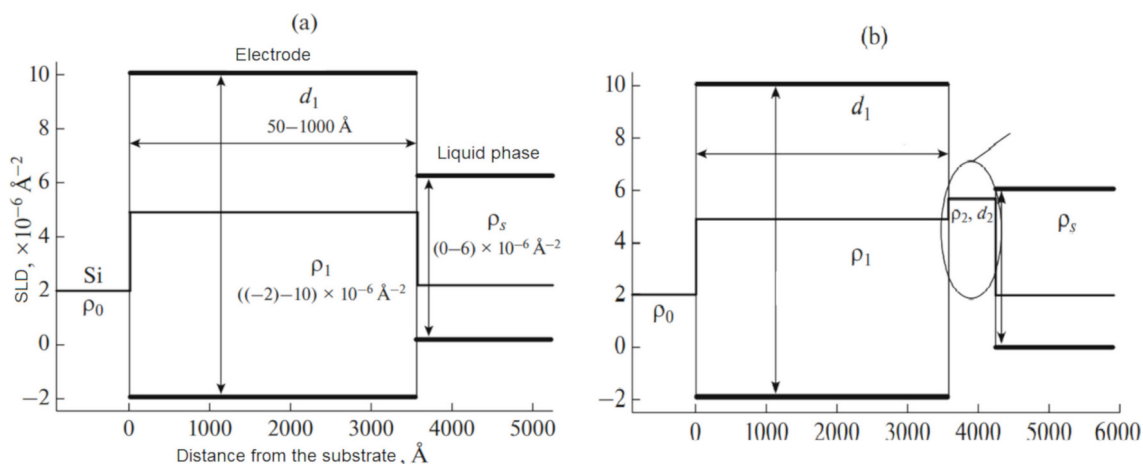


Fig. 2. Schematic representation of the initial (a) and final states (b) of the experiment. The main parameters of variation and their ranges of values: d_1 is the thickness of the electrode, which varies between 50 and 1000 Å; ρ_1 is the neutron scattering length density of the electrode, which varies within $(-2-10) \cdot 10^{-6} \text{ \AA}^{-2}$; ρ_s is the neutron scattering length density of the liquid phase of the electrolyte, which varies within $(0-6) \times 10^{-6} \text{ \AA}^{-2}$ [12].

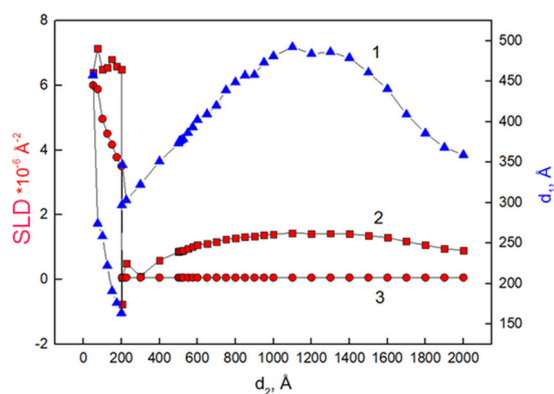


Fig. 3. Dependence of the optimal thickness of the electrode layer d_1 (1), the density of the neutron scattering length of the electrode layer ρ_1 (2) and the electrolyte ρ_s (3) on the thickness d_2 of the solid electrolyte interphase layer. At $d_2 = 200 \text{ \AA}$, there is a jump-like change in the values of the optimal parameters [12].

$$\chi^2 = \frac{\int dq_z [R_{in}(q_z, \rho_0, \rho_1, \rho_s, d_1) - R_{fin}(q_z, \rho_0, \rho_1, \rho_2, \rho_s, d_1, d_2)]^2}{\int dq_z [R_{in}(q_z, \rho_0, \rho_1, \rho_s, d_1) - bkg]^2} \quad (1)$$

where R_{in} is the neutron reflection curve from the system in the initial state; R_{fin} is the neutron reflection curve from the system in the final state; bkg is a background intensity; ρ_0 , ρ_1 , ρ_2 , ρ_s are values of the neutrons' scattering lengths densities for substrate, electrode, solid electrolyte interphase layer, and liquid electrolyte, respectively; d_1 , d_2 are thicknesses of the elec-

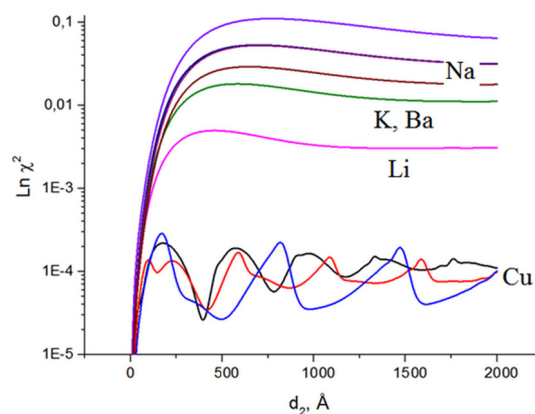


Fig. 4. Logarithmic dependence of the difference of the reflectometry curves between the initial and final states of the system on the thickness of the solid electrolyte interphase layer. Possible metals for use as an electrode are represented by symbols [12].

trode and solid electrolyte interphase, respectively.

The search for the optimal cell parameters was carried out by varying the parameters of the electrode, namely its thickness and its material (the value of the neutron scattering length density), and the liquid electrolyte — the relative composition of the protonated and deuterated components of the solvent. The physical and electrochemical limits of parameter variation are highlighted in [12] and shown in Fig. 2. The method described above is implemented in Matlab software by using Parrat's recursion [14].

Table 1. Values of optimal parameters of model cells with different electrode materials. ρ_0 , ρ_1 , ρ_s are the values of the neutron scattering length density of the silicon substrate, metal electrode, and electrolyte, respectively. d_1 is the thickness of the electrode. χ^2 is the value of different reflectometric curves from the initial and final states [12]

No.	Si	Electrode		Electrolyte	χ^2
	$\rho_0, \times 10^{-6} \text{ \AA}^{-2}$	$d_1, \text{ \AA}$	$\rho_1, \times 10^{-6} \text{ \AA}^{-2}$	$\rho_s, \times 10^{-6} \text{ \AA}^{-2}$	$\times 10^{-3}$
1	2.07	457.73	6.388	6.003	6.3439
2	2.07	258.66	6.486	4.966	10.8953
3	2.07	176.14	6.591	3.784	12.4126
4	2.07	297.23	-0.768	0.065	11.8009
5	2.07	351.12	0.595	0.067	26.3756
6	2.07	420.22	1.169	0.066	32.5676
7	2.07	483.98	1.417	0.066	26.2973
8	2.07	409.01	1.177	0.066	19.9617
9	2.07	359.26	0.897	0.066	19.0530

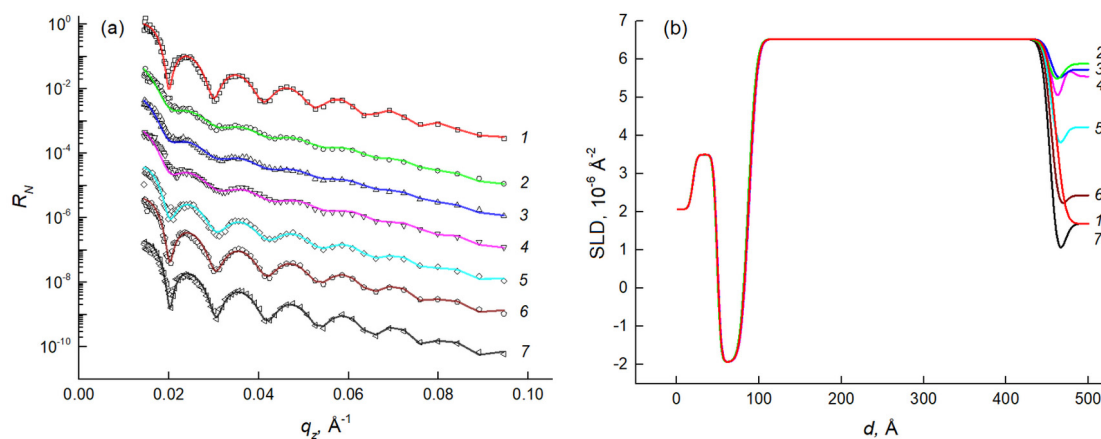


Fig. 5. Reflectometry curves (a) and corresponding neutron scattering length density profiles (b) in the experiment with a variation of the scattering length density of the liquid phase of the electrolyte. The numbering of the curves corresponds to the concentration of the deuterated component: 1 — initial configuration with a fully protonated electrolyte, 2 — deposition of the initial solid electrolyte layer, 3–7 — concentration of the deuterated component 20 %, 40 %, 60 %, 80 %, 90 % (by volume), respectively [13].

3. Results and discussion

When studying the change in neutron specular reflection curves (formula 1), depending on the variation of the parameters of the electrochemical cell (Fig. 2) and the thickness of the solid electrolyte layer, two optimal regimes were established (Fig. 3), which are determined by the thickness of the solid electrolyte interphase layer (less and more than 20 nm) and have a jump-like change in optimal parameters at the transition point [12].

In Fig. 4 the logarithmic dependence of the difference of the reflectometric curves on the thickness of the deposited solid electrolyte interphase layer is shown. The dependencies are represented by different values of the neutron scattering length density of the electrode [12]. The parameters of such systems are shown in Table 1. The value of the difference of the reflectometric curves for the copper electrode is several orders of magnitude smaller than others due to the presence of a plateau of total

external reflection of neutrons at the initial values of the scattering angles, which is important for intensity normalization when using neutron reflectometry.

Based on the optimization results, a model electrochemical cell (Fig. 1) was created. With the help of the optimized model cell, an experiment on neutron reflectometry (Fig. 5) was carried out with a variation of the contrast of the neutron scattering length density of the liquid phase of the electrolyte [13]. The purpose of the experiment is to identify the minimum values of the thickness of the solid electrolyte interphase layer (which are 1 nm), which can be investigated by the method of neutron reflectometry, due to the use of the proposed method of optimization of the experimental model cell.

4. Conclusions

Thus, in the series of papers [11–13], a method for optimizing the parameters of a model electrochemical cell was proposed to increase the sensitivity of the neutron reflectometry method regarding the appearance and evolution of the solid electrolyte interphase layer at the electrode-electrolyte boundary. The authors draw attention to the universality of the method of use and the possibility of its adaptation to other investigated systems. An example of the creation of an electrochemical cell according to such an algorithm is given, and the value of the minimum detection thickness of the solid electrolyte interphase layer when studied by neutron reflectometry with this con-

figuration of the experimental cell is experimentally determined.

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References

1. Z.P.Cano et al., *Nat. Energy*, **3**, 279 (2018).
2. V.Etacheri, R.Marom, R.Elazari et al., *Energy Environ. Sci.*, **4**, 3243 (2011).
3. P.A.Owusu, S.Asumadu-Sarkodie, *Cogent Engineering*, **3**, 1167990 (2016).
4. D.Gielen, F.Boshell, D.Saygin et al., *Energy Strategy Reviews*, **24**, 38 (2019).
5. Y.Shao et al., *Adv.Funct.Mater.*, **23**, 987 (2013).
6. M.Arakawa, S.Tobishima, Y.Nemoto et al., *Journal of Power Sources*, **43**, 27 (1993).
7. J.Yamaki, S.Tobishima, K.Hayashi et al., *Journal of Power Sources*, **74**, 219 (1998).
8. E.Peled, S.Menkin, *J. Electrochem. Soc.*, **164**, A1703 (2017).
9. A.Funabiki, M.Inaba, T.Abe, Z.Ogumi, *J. Electrochem. Soc.*, 146 (443).
10. J.E.Owejan, J.P.Owejan, S.C.DeCaluwe, J.A.Dura, *Chem. Mater.*, **24**, 2133 (2012).
11. V.I.Petrenko, Ye.N.Kosiachkin, L.A.Bulavin, M.V.Avdeev, *J. Synch. Investig.*, **12**, 651 (2018).
12. V.I.Petrenko, Y.N.Kosiachkin, L.A.Bulavin, M.V.Avdeev, *Journal of Surface Investigation*, **14**, 215 (2020).
13. Ye.N.Kosiachkin et al., *Journal of Surface Investigation: X-ray, Synchrotron and Neutron Techniques*, **15**, 87 (2021).
14. L.G.Parratt, *Physical Review*, **95**, 359 (1954).