MODERN RESEARCH METHODS OF PHYSICOCHEMICAL AND ELECTRO-CHEMICAL PROPERTIES OF ELECTROLYTES FOR Li-ION BATTERIES AND HYBRID SUPERCAPACITIES

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In review examinei base properties of modern non-aqueous electrolytes for Li-ion batteries and hybrid supercapacitors taking part in the formation of power density, electrochemical and thermal stability. Discussed such aspects as the electrolytes functions in electrochemical power sources, physicochemical and electrochemical properties of electrolytes for supercapacitors, the physicochemical and electrochemical properties of electrolytes for primary and secondary batteries, and methods of electrolytes research. As the base methodi for electrolytes studies considered: electrochemical impedance spectroscopy, voltammetry, amperometry, viscosimetry, and combined Ramman spectroscopy.

Key words: electrolyte, non-aqueous solvent, operating life, impedance, voltammetry, viscosity, conductivity.

INTRODUCTION. Modern electrolytes are complex physico-chemical systems which properties are formed by all components of these systems. Hence, receiving new knowledge about interactions between components of electrolytes could give the ability to move the properties of electrolytes according to their application. Today, we have a rather limited amount of methods to study the physicochemical and electrochemical properties of modern electrolytes. These are classical methods of density measurement [1–4], scanning calorimetry [5–8], thermal gravimetric analysis (TGA) [9–11], and electrochemical methods: conductivity measurement [12–14], cyclic voltamme-try [15–16], and electrochemical impedance spectroscopy [17–18]. The study of electrolyte systems in – situ is a more difficult task because it needs non-destructive physicochemical and electrochemical control methods [19–20] and is closely connected with the functions of electrolytes in electrochemical power sources and energy storages. In dependences of these functions, the research methods could be changed. For a better understanding of the ability of methods, it is necessary to know the differences in these functions according to various types of energy storage/power sources. Also, the great interest performs impact of solvent or mixture of solvents on ending properties of such

electrochemical systems. So, the main aim of this review is to combine specific tasks for the control of working parameters of batteries or capacitors with properties of electrolytes.

The electrolytes functions in electrochemical power sources (EPS). The charge transfer is the base function of electrolytes in chemical power sources. The conductivity y of electrolyte forms by the ion transfer component. The component with an electron transfer function contributing to the self-discharge of the element. The basic requirements for the electrolytes in all cases are:

– high ionic conductivity;

– electrochemical stability window of at least 4.5 V on a platinum electrode

– temperature range of the electrochemical window in the liquid state from - 60 °C to + 60 °C;

– no corrosion activity happening to structural materials (aluminum and copper current collectors, steel housing, etc.) [21].

Some particular requirements exist only for supercapacitors. Their electrochemical capacity depends on the number of charges, so very concentrated electrolytes and the use of ionic liquid lead to better performance. The region of electrochemical stability on the electrolyte plate narrows down from 4.5 V to 2.5 V, when the working material is replaced with porous carbon. Therefore, for the electrolyte used in the supercapacitor, the following characteristics decrease: the electrochemical stability window is not less than 2.5 V by solubility - 0.9 M and more [22–23].

Physiochemical and electrochemical properties of electrolytes for supercapacitors. Often, for the preparation of the electrolyte, conventional solvents such as acetonitrile, propylene carbonate, and other carbonate solvents and their mixtures are used [23–24]. Last year, the

solutions of tetrafluoroborate tetraethylammonium in acetonitrile are implemented in batteries manufacturing and the researcher domain. The last is charged up to the capacity of 2.5 V [23–28]. This salt has high electrochemical (~ 2.8 V on carbon) [26] and thermal stability (320 °C) [27]. But it is expensive to produce and highly toxic at the same time. Also, the hydrolysis with traces of water and fluorine-containing anion results in HF, which can lead to corrosion of the hull and the current collector. Therefore, the search for cheap, easy to manufacture, and environmentally friendly analogs of this salt is highly relevant.

Other types of known electrolytes are based on ionic liquids [29, 30, 31] and polymer electrolytes [22–24, 29]. They create a low vapor pressure, simplifying the assembly stage of the power source and providing fire safety.

The physicochemical and electrochemical properties of electrolytes for primary and secondary batteries. The properties of an electrolyte flow in the batteries are of great importance since it is the main way to transport the reagents to the electrodes. Thus, it affects the operational reliability of the entire electrochemical system. The requirements for electrolytes are simplified and do not change during the last decades for the primary power sources in the presence of irreversible chemical reactions [32]. In contrast to primary, the secondary power sources can cycle. The secondary power sources need a higher electrochemical (operating potential range) and thermal (operating temperature range) resistance to ensure high operating life. Modern electrolytes have sufficiently high values of the potentials operating range (3.5–5.1 V) [33–40]. Salt components have significant thermal stability (100–400 °C) (Table 1) [33–40].

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Table 1

Composition, operating temperature range, and potentials operating range of commercial and laboratory electrolytes for secondary power sources.

Salt component	T, °C	Electrochemical stability (solvent in which it was measured)	Literature cited
$LiClO_4$	400 °C	5.1 V (propylene carbonat	[33, 34],
$LiAsF_6$	340 °C	4,5 B propylene carbonate	[33, 35]
$LiBF_4$	293 °C	5.0 V (propylene carbonate)	[33, 35]
$LiPF_6$	30 °C – 117 °C	4.5 V (propylene carbonate)	[41, 36, 35, 33]
Lithium triflate	300 °C	5,1 B (sulpholane)	[33], [37], [38 p. 318],
propylene carbonate	360 °C	5,0 V (propylene carbonate)	[42], [37], [38 p. 318], [39]
Lithium Methanide	340 °C	4.0 V (tetrahydrofuran)	[39]
$LiSO_3F$	360 °C	4.9 V (γ-butyrolactone)	[40]

Table 2

Electroconductivity of the lithium salts in aprotic solvents.

σ, mCm*Cm^{-1}	$LiBF_4$	$LiPF_6$	$LiAsF_6$	$LClO_4$	$LiCF_3SO_3$	$LiN(SO_2CF_3)_2$	Literature cited
(1.0 M 25 °C) in ПК	3.4	5.8	5.7	5.6	1.7	5.1	[33], [35]
(1.0 M 25 °C) in EK/DMK	4.9	10.7	11.1	8.4		9.0	[33], [35]
(1,0 M 25 °C) in PC / DME	9.46	15.3	14.8	13.5	6.12	12.6	[35]

Nowadays, the industry samples contained mainly lithium compounds that have some operational problems. For example, $LiClO_4$ solutions in organic solvents can explode during exploitation [33]. $LiAsF_6$ and its decomposition products are toxic. $LiAsF_6$ and $LiBF_4$, $LiPF_6$ are sensitive to hydrolysis since their products - PF_5, BF_3, and AsF_5 initiate solvents polymerization. In addition, these reactions result in lithium fluoride, which stimulates the creation of a blocking film with cyclic carbonate on the electrodes [43, 37]. The other disadvantages typical for these fluorinated salts are high cost, limited use with cathode materials based on manganese spinel, and environmental hazards. But, despite the pointed problems, LiPF6 remains today the most common salt for liquid electrolytes in lithium-ion batteries with

different cathode and anode materials [43]. Although LiPF$_6$ begins to decompose by temperatures above 30 °C, even being in an electrolyte [41, 36, 35, 33].

Also, LiSO$_3$F does not dissolve in solvents which have proved to be efficient for lithium EPS. The lithium triflate solutions in non-aqueous solvents are inferior to other systems in terms of electrical conductivity. Lithium methanide and imide lead to corrosion of aluminum current collector [33, 37, 44].

Methods of electrolytes research. Analysis of the electrolytes features gives grounds to assert that CEI and CVA are the most informative methods for the study of electrochemical properties of electrolytes. For the determination of the ion's transportability of electrolyte, the density measurements are also actual.

Electrochemical impedance of lithium-ion battery. Spectroscopy of electrochemical impedance (SEI) has been promoted in recent years, and the number of objects under study is constantly growing. Many studies are used to understanding the processes into chemical power sources and their components. The electrochemical impedance spectroscopy could be used to study the battery as a whole [18, 4750, 54] or its parts (electrode or electrolyte) [20, 52, 5558]. Modeling allows us to understand the mechanisms of formation conductivity in liquid [55], solid and polymer electrolytes [57], colloidal solutions [52], and other heterogeneous systems. When modeling an electrolyte system and determining its elements, additional physical and chemical values such as the relaxation time of the system [18,56], and the diffusion coefficient (via calculating the Warburg impedance) should be identified. A very important aspect in research of lithium and sodium secondary power sources is to in-

vestigate the properties, formation, and functioning conditions of a solid protective film formed on cathode and anode materials after the first cycle due to the destruction of some electrolyte part [45-48, 50-51, 54]. The only possible way to carry out the study of this film without opening the battery is to construct an electrochemical model of the system, which will allow us to interpret the data obtained by electrochemical impedance spectroscopy and calculate the values of interest [47]. Most of the equivalent schemes constructed to explain the impedance of a lithium-ion battery follow one of the three examples (Fig.1) [17, 47]:
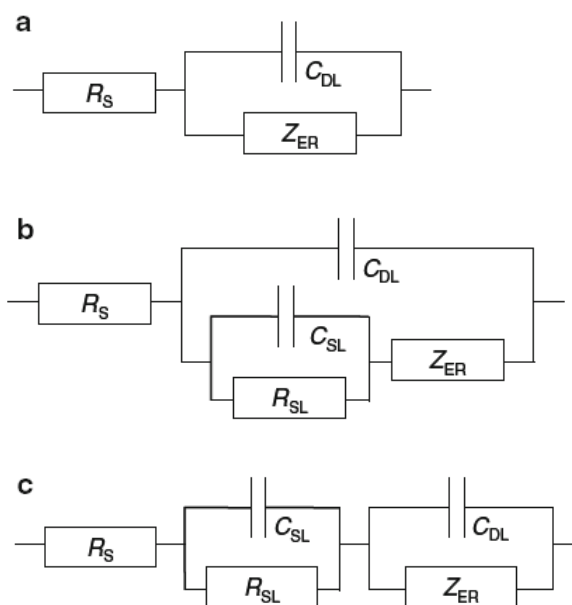

Fig. 1. Basic equivalent schemes of a lithium-ion battery: a unit model – without the solid passivation film on the surface of the electrode (a); 2 models – with the solid passivation film on the surface of the electrode materials (b, c). SL – indicates elements of the scheme associated with a solid passivation film, R_s – resistance of solution, C_{SL} – capacity of the passivation film, R_{SL} – resistance of the passivation film, C_{DL} – capacity of the double electric layer, Z_{ER} – boundary impedance.

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As a rule, we have to consider the formation of a passivation film on the metal surface of the current collector (or often oxide corrosive film) and the formation of a solid electrolyte film on the surface of the cathode and anode material, as well as the formation of a double electric layer [47]. Models of this type are given in Fig. 2.

According to [46], model equivalent circuit diagrams of the battery before discharge and after may differ significantly (Fig. 3)
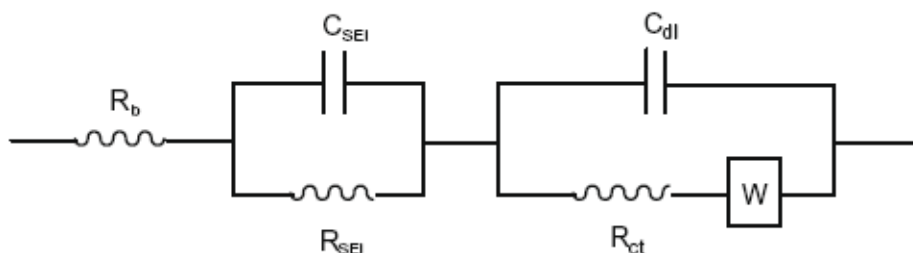

Fig. 2. Equivalent circuit diagram of the battery, considering the corrosion film on the surface of the current collector and the solid electrolyte film on the surface of the electrode material [45]. W – the Warburg element, Rb – resistance of the electrolyte, R_{SEI} – resistance of the passivation film, Rct – resistance of cathode, C_{SEI} – capacity of the passivation film, C_{dl} – capacity of the double electric layer.
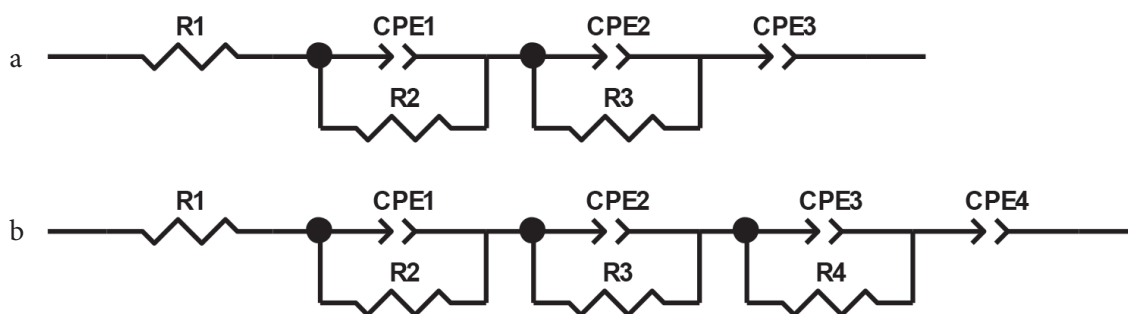

Fig. 3. Model equivalent circuits of the battery before discharge (a) and after discharge (b) [46].

This model has more than two constant phase elements connected with "capacitance dispersion" due to electrode porosity, surface roughness, and heterogeneities [19]. Also, such interpretation partially corresponds to the Voight's model for rubber-like materials (impedance at the local contact area between flexible surface film and electrode) [17, 59]. More reasonable is a model that takes into account the simultaneous transport of electrons and ions in the counterflow (Figure 4) [47]. More reasonable is a model, that takes into account the simultaneous transport of electrons and ions in the counterflow (Figure 4), [47]. Among all the mentioned examples, R_{SOL} elements and the double layer capacity of CSL / SOL could be attributed to the electrolyte component of the batteries because the electrolyte is directly involved in the formation of a solid surface film and ionic conductivity.
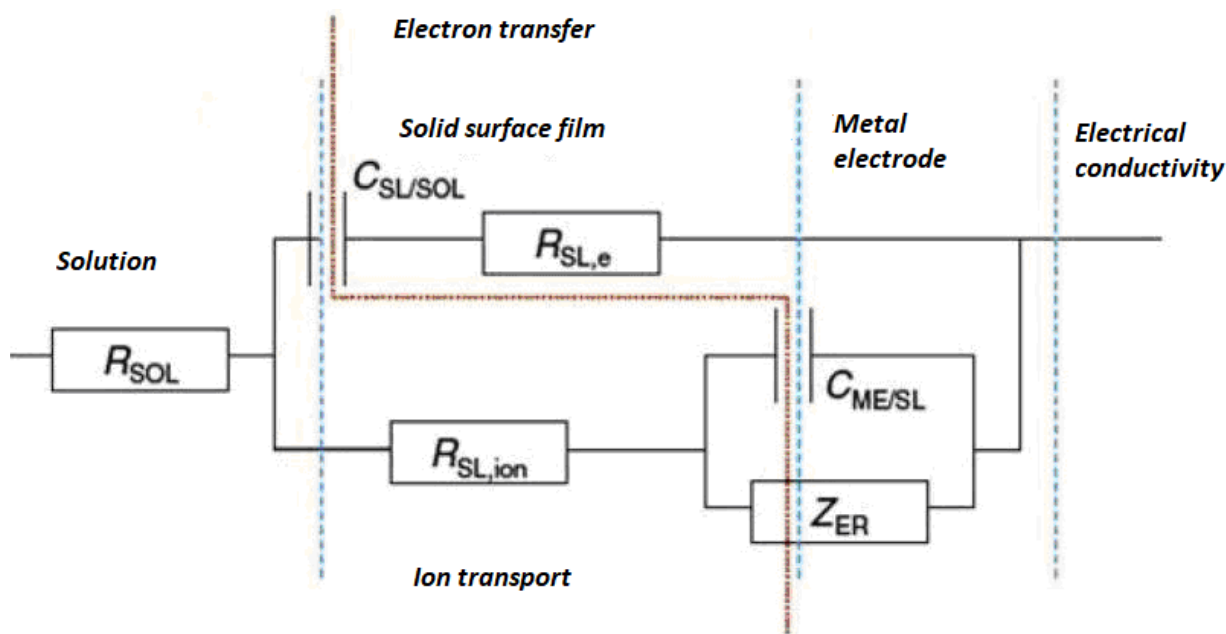
Fig. 4. Model equivalent circuit scheme of lithium-ion battery [47].

The conception of polymer electrolytes (PEs) is a highly specialized and multidisciplinary field that covers the disciplines of electrochemistry, polymer science, organic and inorganic chemistry. The good mechanical strength, ease of thin film fabrication with desirable shapes and the ability of forming good electrode/electrolyte contact are the main advantages of dry SPEs. The electrolyte scheme [17, 57–59] of a polymer electrolyte composed in a cell following the order Li | Polymer | Li is simpler (Fig. 5.). This equivalent circuit consists of two shunted CPE elements and closely connects with electrode porosity [19].
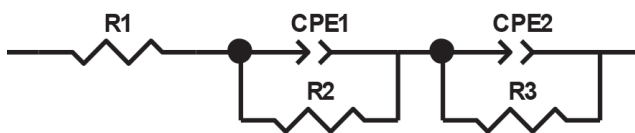

Fig. 5. Equivalent circuit of polymer electrolyte [58].

Attempts to construct equivalent models of primary power sources (lithium), sodium-ion battery, lead, Nickel-cadmium, Nickel-metal hydride batteries, and their electrodes are also reviewed [60]. All the described models need to be revised and refined.

Thus, the modeling of electrolyte systems is carried out periodically, in general, use the universal model [17]. We find this approach fundamentally wrong, as it does not consider the relationship between conductivity mechanism and the electrolyte aggregate state, as well as the dissolved salt-solvent interaction. However, these relationships form the prerequisites for changing the conductivity mechanisms.

Another method, often used in addition to modeling equivalent circuit diagrams, is the direct measurement of the active impedance component. However, the imaginary part of the impedance also has a significant effect due to thermal stress. It depends not only on the

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capacity of the double electric layer on the electrode surface but also on the change in its structure after chemical transformations. It is formed due to the diffusion of ions, which is increasingly fixed in the low-frequency range. Therefore, the high-frequency range is not always advisable, since at a frequency above 103 Hz the diffusion of the ions will be blocked [61].

So, EIS could be used to study electrolytes properties *in-situ* without the destruction of batteries and separately to detect their properties during contact with the electrode surface.

Voltammetry of electrolytes. The voltammetry method allows for the investigation of the overall electrochemical stability of the electrolyte and defines the so-called «electrochemical stability window» (the potentials interval where electrochemical processes are impossible), as well as the electrochemical reactions where the individual electrolyte components participate. Reference voltammetric studies are done on platinum electrodes, but the electrodes and current collectors used in real systems are made from copper, aluminum, and carbon. Therefore, voltammetric studies are carried out on noble metals – silver and gold, as well as on aluminum, copper, and glassy carbon [62]. The peaks of all these electrodes are associated with extraneous processes, such as oxygen reduction, reduction of the surface oxide film, reduction/oxidation of surface groups, etc [62]. The characteristic window of electrochemical stability of different classes of organic solvents with tetraalkylammonium (a) and a lithium background salt (b) are shown in Fig.6 [63]:
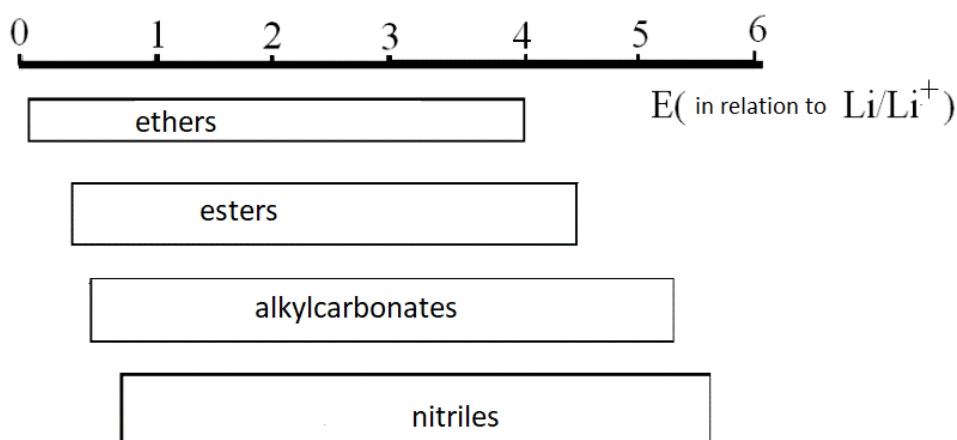

Fig. 6. The electrochemical stability of solvents.

Using voltammetry detected that many modern electrolytes have a low range of electrochemical stability. Their decomposition takes place at the potential range from 0,5–2 V. The typical products of solvent decomposition and the most popular in studies of background salts $LiClO_4$ and $LiPF_6$ are presented in Table 3. Moreover, it was shown the impact of salt anion on the electrochemical and temperature stability of electrolytes by voltammetry. In the case of the salicyl borate anion - the coordinate covalent bond in the aromatic nucleus has shifted the recovery peak to higher potentials (Table 4).
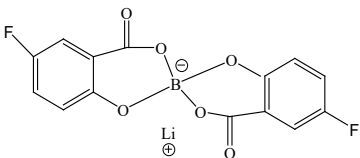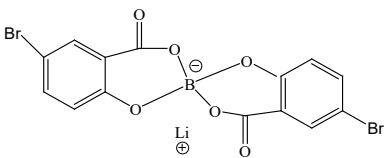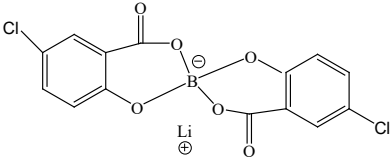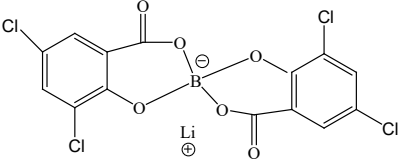
Table 3

The products of electrolyte decomposition [63].

Solvent and other components	Possible reduction products	Potential limit relative to Li/Li+
O_2	LiO_2, Li_2O_2	1,5 – 2 V
H_2O	LiOH	1,5 – 1,2 V
HF PF$_5$	LiF, Li_xPF_y	1.8 and below
Eters	ROLi	Below 0,5 V
esters	ROCOOLi (carboxylates)	Below 1,2 V
alkylcarbonates	ROCOOLi, ROLi	Below 1,5 V
ethylene carbonate	$CH_2(OCOOLi)$, $CH_2=CH_2$	Below 1,5 V
propylene carbonate	$CH_3CH(OCOOLi)$, $CH_2OCOOLi$, $CH_3CH=CH_2$	Below 0,5 V
dimethyl carbonate	$CH_3OCOOLi$, CH_3OLi	Below 1.2 V
$LiClO_4$	LiCl, $LiClO_x$	Below 1 V
$LiPF_6$	LiF, Li_xPF_y	Below 1 V
$LiN(SO_2CF_3)_2$	LiF, $LiCF_3$, $LiSO_2CF_3$, $Li_2NSO_2CF_3$	Below 1 V

Table 4

Reduction in the first cycle of lithium bis(Saltillo)borate substitution in the aromatic nucleus to Galogen atom [64].

The salt components of the electrolyte	Recovery potential at the first cycle relative to Li/Li+, V	The salt components of the electrolyte	Recovery potential at the first cycle relative to Li/Li+, V
	0.75 1.12 1.45		1.3
	1.3 1.65		1.35

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Measurements of densitometry and amperometry to evaluate the electrical conductivity of electrolytes. Known, that in non-aqueous solvents, the autoionization of the solvent, if protic, will be different to water, meaning that the ionization of these functional polymers will be different. In aprotic solvents, there will not be autoionizable protons, so solvent-solute proton transfer is not possible. The formation and stabilization of charges in non-polar low dielectric solvents is known to be challenging, and so it is not surprising that identifying ionic species in electrolytes is challenging. At another hand, introducing insulating phases into non-aqueous salt solution leads to remarkable conductivity enhancements, an effect ascribed to the breaking up of ion pairs. This new class of electrolytes combines the high ionic conductivities of liquids and the beneficial mechanical properties of soft matter [65].

Electrolyte viscosity is a macroscopic property, although its foundation lies on molecular-scale interactions between solvent and ionic species. A comprehensive understanding of viscosity behavior with respect to solvent composition, salt concentration and temperature is only possible with correct interpretations of molecular interactions and related quantities. For this purpose, the use of a combination of methods gives more corrective and informational results.

So, the following methods are widely used to study the physicochemical properties and conductivity of non-aqueous electrolytes: dielectrometry, differential scanning calorimetry, densitometry, viscometry and combined Ramman spectroscopy [66]. Such studies found the ability to form solvat complexes of metal cations with solvent components. Analyzing these calculations could determine the nature of ion solvation and the mechanism of charge carrier growth depending on the salt concentration. The difference between the conductivity nature of the systems based on lithium and sodium was established. It depends upon the structure and charge of the metal complex. In systems based on Li+ electrolytes form a complex $[Li(TFSI)_2]^-$, whereas, in sodium systems, the dominant form is $[Na(TFSI)_3]^{2-}$ complexes. It directly relates to the density change and electrolytes conductivity, depending on the metal salt concentration.
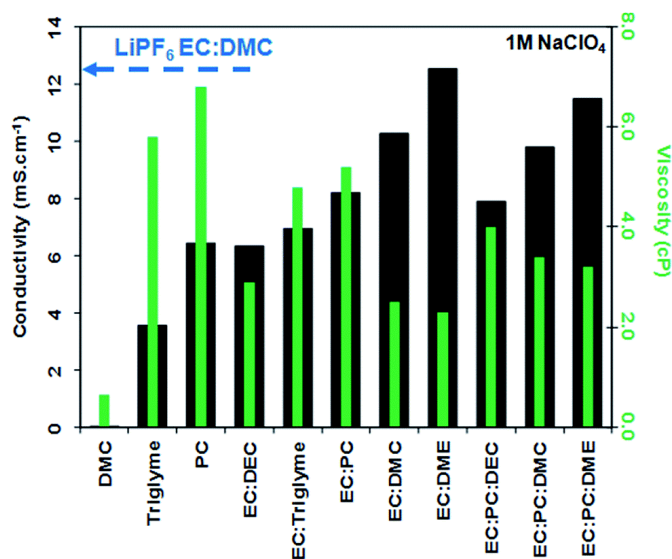

Fig. 7. Conductivity effect (black bands and axes of the left side of the axis) on the viscosity (green bands and the right side of the y axis) of electrolytes consisting fom 1 M $NaClO_4$ dissolved in various solvents and solvent mixtures [67].

The most informative is one hour study of the electrolyte's thermal behavior, ionic conductivity, and viscosity using inert and «real» electrodes. This approach allows optimizing the working electrolyte mixtures (salt and

solvent, to stabilize the film on the electrode surface, reduce polarization and achieve full power at a low potential plateau. For example, the relationship between conductivity, viscosity, and composition of the electrolyte system $LiPF_6$, on reference samples were investigated in various solvents. Results of measurements are shown in Fig. 7. There are no linear dependences in such systems, but the correlation between the optimal range of viscosity and maximum conductivity could be observed

Thus, the study of the temperature dependence of the conductivity on the salt concentration and electrolyte viscosity, dielectric properties of solvents and their mixtures can be a tool to select the optimal composition of electrolytes with high power in a wide range of potentials and a stable film on the electrode - electrolyte interface.

CONCLUSIONS. Spectroscopy of electrochemical impedance, voltammetry, amperometry with viscosimetry, and combined Ramman spectroscopy have been successfully used for the study properties of electrolytes necessary in the manufacturing of modern batteries and hybrid supercapacitors. They permit the analysis of properties that are difficult or even impossible to study by only one of these methods separately. EIS could be used to study electrolytes properties in-situ without the destruction of batteries and separately to detect their properties during contact with the electrode surface. The voltammetry method allows for the investigation of the overall electrochemical stability of the electrolyte and defines the so-called «electrochemical stability window» (the potentials interval where electrochemical processes are impossible), as well as the electrochemical reactions where the individual electrolyte components partici-

pate. The study of the temperature dependence of the conductivity on the salt concentration and electrolyte viscosity, dielectric properties of solvents and their mixtures can be a tool to select the optimal composition of electrolytes with high power in a wide range of potentials and a stable film on the electrode - electrolyte interface.

СУЧАСНІ МЕТОДИ ДОСЛІДЖЕННЯ ФІЗИКО-ХІМІЧНИХ І ЕЛЕКТРОХІМІЧНИХ ВЛАСТИВОСТЕЙ ЕЛЕКТРОЛІТІВ У ЛІТІЙ-ЙОННИХ АКУМУЛЯТОРАХ ТА ГІБРИДНИХ СУПЕРКОНДЕНСАТОРАХ

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В огляді надано базові властивості сучасних неводних електролітів для літій-іонних акумуляторів та гібридних суперконденсаторів, які беруть участь у формуванні потужності, електрохімічної та

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термічної стабільності. Обговорено такі аспекти, як функції електролітів в електрохімічних джерелах живлення, фізико-хімічні та електрохімічні властивості електролітів для суперконденсаторів, фізико-хімічні та електрохімічні властивості електролітів для первинних та вторинних батарей та методи дослідження електролітів. Як базові методи досліджень електролітів наведено: електрохімічну імпедансну спектроскопію, вольтамперометрію, амперометрію, віскозиметрію та комбіновану спектроскопію Рамана. Використання цих методів дозволяє аналізувати властивості, які важко або навіть неможливо вивчити за допомогою лише одного з цих методів. EIC можна використовувати для вивчення властивостей електролітів in-situ без руйнування батарей та окремо для виявлення їхніх властивостей під час контакту з поверхнею електрода. Метод вольтамперометрії дозволяє досліджувати загальну електрохімічну стабільність електроліту і визначає т. зв. «вікно електрохімічної стійкості» (інтервал потенціалів, де електрохімічні процеси неможливі), а також електрохімічні реакції, в яких беруть участь окремі компоненти електроліту. Вивчення температурної залежності провідності від концентрації солі та в'язкості електролітів, діелектричних властивостей розчинників та їхніх сумішей може бути інструментом для вибору оптимального складу електролітів із великою потужністю в широкому діапазоні потенціалів та стабільною плівкою на інтерфейс електрод – електроліт.

Ключові слова: електроліт, неводний розчинник, термін служби, імпеданс, вольтамперометрія, в'язкість, провідність.

REFERENCES

1. Millero F. J. Molal volumes of electrolytes. *Chemical Reviews*. 1971. **71**(2): 147–176.

2. Laliberte M., Cooper W. E. Model for calculating the density of aqueous electrolyte solutions. *Journal of Chemical & Engineering Data*. 2004. **49**(5): 1141–1151.

3. Li M., Wang C., Chen Z., Xu K., Lu J. New concepts in electrolytes. *Chemical reviews*. 2020. **120**(14): 6783–6819.

4. Lukatskaya M. R., Feldblyum J. I., Mackanic D. G., Lissel F., Michels D. L., Cui Y., Bao Z. Concentrated mixed cation acetate "water-in-salt" solutions as green and low-cost high voltage electrolytes for aqueous batteries. *Energy & Environmental Science*. 2018. **11**(10): 2876–2883.

5. Dalmazzone D., Clausse D., Dalmazzone C., Herzhaft B. The stability of methane hydrates in highly concentrated electrolyte solutions by differential scanning calorimetry and theoretical computation. *American Mineralogist*. 2004. **89**(8–9): 1183–1191.

6. Pehlivan İ. B., Marsal R., Niklasson G. A., Granqvist C. G., Georén P. PEI–LiTFSI electrolytes for electrochromic devices: Characterization by differential scanning calorimetry and viscosity measurements. *Solar energy materials and solar cells*. 2010. **94**(12): 2399–2404.

7. Zhang Z., Fouchard D., Rea J. R. Differential scanning calorimetry material studies: implications for the safety of lithium-ion cells. *Journal of power sources*. 1998. **70**(1): 16–20.

8. Sundaramahalingam K., Muthuvinayagam M., Nallamuthu N., Vanitha D.,

Vahini M. Investigations on lithium acetate-doped PVA/PVP solid polymer blend electrolytes. *Polymer Bulletin*. 2019. **76**(11): 5577–5602.

9. Nakajima H., Ohno H. Preparation of thermally stable polymer electrolytes from imidazolium-type ionic liquid derivatives. *Polymer*. 2005. **46**(25): 11499–11504.

10. Wilken S., Johansson P., Jacobsson P. Infrared spectroscopy of instantaneous decomposition products of $LiPF_6$-based lithium battery electrolytes. *Solid State Ionics*. 2012. **225**: 608–610.

11. Enotiadis A., Fernandes N. J., Becerra N. A., Zammarano M., Giannelis E. P. Nanocomposite electrolytes for lithium batteries with reduced flammability. *Electrochimica Acta*. 2018. **269**: 76–82.

12. Bešter-Rogač, M., & Habe, D. Modern advances in electrical conductivity measurements of solutions. *Acta chimica slovenica*. 2006. *53*(3).

13. Chintapalli M., Timachova K., Olson K. R., Mecham S. J., Devaux D., DeSimone J. M., Balsara N. P. Relationship between conductivity, ion diffusion, and transference number in perfluoropolyether electrolytes. *Macromolecules*. 2016. **49**(9): 3508–3515.

14. Valøen L. O., Reimers J. N. Transport properties of LiPF6-based Li-ion battery electrolytes. *Journal of The Electrochemical Society*. 2005.**152**(5): A882.

15. Muchakayala R., Song S., Wang J., Fan Y., Bengeppagari M., Chen J., Tan M. Development and supercapacitor application of ionic liquid-incorporated gel polymer electrolyte films. *Journal of industrial and engineering chemistry*. 2018. **59**: 79–89.

16. Li W., Zhang F., Xiang X., Zhang X. 2017. High-efficiency Na-storage performance of a nickel-based ferricyanide cathode in high-concentration electrolytes for aqueous sodium-ion batteries. *ElectroChem*. **4**(11): 2870–2876.

17. Impedance Spectroscopy. Theory, Experiment and Applications. /Ed. E. Barsoukov, J. Ross Macdonald. N.Y., Wiley. 2005. 616.

18. Riabokin O. L., Boichuk A. V., Pershina K. D. Control of the State of Primary Alkaline $Zn–MnO_2$ Cells Using the Electrochemical Impedance Spectroscopy Method. *Surface Engineering and Applied Electrochemistry*. 2018. **54**(6): 614–622.

19. Jean-Baptiste Jorcin, Mark E. Orazem, Nadine Pébère and Bernard Tribollet. CPE analysis by local electrochemical impedance spectroscopy. *Electrochimica Acta*. 2006. **51**(8–9): 1473–1479.

20. Pershina E.D., Burda V.E., Kazdobin K.A. *et al*. Identification of the sugars content in the production of champagne by the electrochemical impedance spectroscopy method. *Surf. Engin. Appl.Electrochem.* 2013. **49**: 348–354.

21. Etacheri, V., Marom, R., Elazari, R., Salitra, G., & Aurbach, D. Challenges in the development of advanced Li-ion batteries: a review. *Energy & Environmental Science*. 2011. **4**(9): 3243–3262.

22. Zhong, C., Deng, Y., Hu, W., Qiao, J., Zhang, L., & Zhang, J. A review of electrolyte materials and compositions for electrochemical supercapacitors. *Chemical Society Reviews*. 2015. **44**(21): 7484–7539.

23. Gao, H., & Lian, K. Proton-conducting polymer electrolytes and their applications in solid supercapacitors: a review. *RSC advances*. 2014. **4**(62): 33091–33113.

24. Sharma, K., Arora, A., & Tripathi, S. K. Re-

PHYSICAL CHEMISTRY

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ELECTROLYTES FOR Li-ION BATTERIES AND HYBRID SUPERCAPACITIES

view of supercapacitors: Materials and devices. *Journal of Energy Storage*. 2019. **21**: 801–825.

25. Kieran M., Dunens O., Harris A. A review of carbon nanotube purification by microwave assisted acid digestion. *Separation and purification Technology*. 2009. **66**(2): 209–222.

26. Waldvogel S., Malkowsky I., Griesbach U., Pötter H. Novel fluorine-free electrolyte system for supercapacitors. *Electrochemistry Communications*. 2009. **11**(6): 1237–1241.

27. Nanbu N., Ebina T., Uno H., Ishizawa S. Physical and electrochemical properties of quaternary ammonium bis(oxalato) borates and their application to electric double-layer capacitors. *Electrochimica Acta*. 2006. **52**(4): 1763–1770.

28. Diamant V.A., Pershina E.D., Trachevsky V.V. *et al.* Physicochemical properties of tetramethylammonium bis(salicylo)borate. *Russ J Appl Chem*. 2015. **88**: 901–907.

29. Diamant V. A., Malovanyy S. M., Pershina K. D., Kazdobin K. A. Electrochemical properties of Sodium bis [salicylato (2-)]-borate-γ-butyrolactone Electrolytes in Sodium Battery. *Materials Today: Proceedings*. 2019. **6**: 86–94.

30. Kirchner B. Ionic Liquids Volume Editor. *Heidelberg: Springer*. 2009: 354.

31. House L., Hill J. Ionic Liquids Physicochemical Properties. *Amsterdam: Elsevier*. 2009. 478.

32. Gilliam R.J., Graydon J.W., Kirk D.W., Thorpe S.J. A review of specific conductivities of potassium hydroxide solutions for various concentrations and temperatures. *Int. J. Hydrogen Energy*. 2007. **32**(3): 359–364.

33. Xu K. Nonaqueous Liquid Electrolytes for Lithium-Based Rechargeable Batteries. *Chemical Reviews*. 2004. **104**(10): 4303–4417.

34. Nikolsky B.P. Handbook of the chemist. *Leningrad: Chemistry*. 1971. 1169 p. [*in Russian*].

35. Dudley J., Wilkinson D., Thomas G., LeVae R. Conductivity of electrolites for rehargeble lithium batteris. Journal of Poweer Sources. 1991. **35**(1): 59–82.

36. Yang H., Zhuang G., Ross P. Thermal Stability of LiPF6 Salt and Li-ion Battery Electrolytes Containing $LiPF_6$. Journal of Power Sources. 2006. **161**(1): 573–79.

37. Webber A. Conductivity and Viscosity of Solutions of LiCF3SO3, $Li(CF_3SO_2)_2N$, and Their Mixtures. Journal of The Electrochemical Society. 1991. **138**(9): 2586–2590.

38. Schaltkwijk W. Advances in Lithium-ion Batheries. *New York: Kluwer Academic*. 2002. 507 .

39. Dominey L., Koch V., Blakley T. Thermally stable lithium salts for polymer electrolytes. *Electrochimical Acta*. 1992. **37**(9): 1551–1554.

40. Diamant V. A., Trachevskii V. V., Pershina K. D., Ogenko V. M., Donchu Chen, Huawen Hu, Min Chen, Xiaowen Wang, Menglei Chang. Specialties of the structure and conductivity of the non-aqueous electrolytes based on alkali metal bis(salicyl) borates and bis (oxalato) borates. *Ukr. Chem. Journal*. 2019. **85**(3): 47–57.

41. Diamant V. A., Pershina K. D., Trachevskii V. V., Kazdobin K. A. Synthesis of Alkali Metal Bis(salicilato)borates by Microwave Method. *Surface Engineering & Applied Electrochemistry*. 2016. **52**(2): 212–216.

42. Borup R., Meyers J., Pivovar B., Kim Y. S., Mukundan R., Garland N., Zelenay P. Scientific aspects of polymer electrolyte fuel cell durability and degradation. *Chemical reviews*. 2007. **107**(10): 3904–3951.

43. Ivanov-Shits A. K., Demyanets L. N. Materials of the Ionic of a Solid. *Priroda*. 2003. **12**: 35–43.

44. Gromadsky D.G. High-capacity super-capacitors based on porous carbon materials with optimized electrode constituents. *PhD thesis: Kyiv*. 2012. 166 p. [*in Ukrainian*].

45. Sun X., Angell C. A. Doped sulfone electrolytes for high voltage Li-ion cell applications. *Electrochemistry Communications*. 2009. **11**(7): 1418–1421.

46. Świętosławski M., Molenda M., Grabowska M., Wach A., Kuśtrowski P., & Dziembaj R. Electrochemical impedance spectroscopy study of C/Li_2MnSiO_4 composite cathode material at different states of charge. *Solid State Ionics*. 2014. **263**: 99–102.

47. Péter, L. A systematic approach to the impedance of surface layers with mixed conductivity forming on electrodes. *Journal of Solid State Electrochemistry*. 2013. **17**(12): 3075–3081.

48. Zhang L., Huang J., Youssef K., Redfern P. C., Curtiss L. A., Amine K., Zhang Z. Molecular engineering toward stabilized interface: an electrolyte additive for high-performance Li-ion battery. *Journal of The Electrochemical Society*. 2014. **161**(14): A2262–A2267.

49. Kazdobin K. A., Pershina K. D., Kokhanenko V. V., Maslyuk L. N., Zapol'skii A. K. Nature of the conductivity of kaolin under hydration and mechanochemical activation. *Surface Engineering and Applied Electrochemistry*. 2014. **50**(1): 95–100.

50. Cecchetto L., Salomon M., Scrosati B., Croce F. Study of a Li–air battery having an electrolyte solution formed by a mixture of an ether-based aprotic solvent and an ionic liquid. *Journal of Power Sources*. 2012. **213**: 233–238.

51. Ran L., Liu X., Tang Q., Zhu K., Tian J., Du J., Shan Z. Grinding aid-assisted preparation of high-performance carbon-$LiMnPO_4$. *Electrochimica Acta*. 2013. **114**: 14–20.

52. Pershina, E.D., Kokhanenko, V.V., Maslyuk, L.N. *et al.* Conductivity of aqueous suspensions of alumosilicates. *Surf. Engin. Appl.Electroche.* 2011. **47**:441–445.

53. Wu Q., Ha S., Prakash J., Dees D. W., Lu W. Investigations on high energy lithium-ion batteries with aqueous binder. *Electrochimica Acta*. 2013. **114**: 1–6.

54. Seh Z. W., Sun J., Sun Y., Cui Y. A highly reversible room-temperature sodium metal anode. *ACS central science*. 2015. **1**(8): 449–455.

55. Manivel A., Velayutham D., Noel M. Electrochemical behaviour of tetra-n-butylammonium nonaflate as an ionic liquid and as a supporting electrolyte in aprotic solvents: A comparative study. *Journal of electroanalytical chemistry*. 2011. **655**(1): 79–86.

56. Bisquert J., Randriamahazaka H., Garcia-Belmonte G. Inductive behaviour by charge-transfer and relaxation in solid-state electrochemistry. *Electrochimica Acta*. 2005. **51**(4): 627–640.

57. Hiller M. M., Joost M., Gores H. J., Passerini S., Wiemhöfer H. D. The influence of interface polarization on the determination of lithium transference numbers of salt

PHYSICAL CHEMISTRY

MODERN RESEARCH METHODS OF PHYSICOCHEMICAL AND ELECTROCHEMICAL PROPERTIES OF
ELECTROLYTES FOR Li-ION BATTERIES AND HYBRID SUPERCAPACITIES

in polyethylene oxide electrolytes. *Electrochimica Acta*. 2013. **114**: 21–29.

58. S.B. Aziz, T.J. Woo, M.F.Z. Kadir, H.M. Ahmed A conceptual review on polymer electrolytes and ion transport models. *Journal of Science: Advanced Materials and Devices*. 2018. 3(1):1–17.

59. K. D. Pershina, K. O. Kazdobin. Impedance spectroscopy of electrolytic materials. *Kyiv: Osvita Ukraine*. 2012. 223 p. [*In Ukrainian*].

60. Shih, Hong, and Tai-Chin Lo. Electrochemical impedance spectroscopy for battery research and development. *Cortech Corporation. CA, Tech. Rep*. 1996. **31**. 9–11.

61. Bisquert J., Compte A. Theory of the electrochemical impedance of anomalous diffusion. *Journal of Electroanalytical Chemistry*. 2001. **499**(1): 112–120.

62. Schweiger H.-G. Entwicklung und Erprobung neuer Messgeräte und Methoden für die rationelle Optimierung von neuen Elektrolyten für Lithium-Ionen-Batterien. *PhD thesis: Regensburg*. 2006.

63. Etacheri V., Marom R., Elazari R., Salitra G., Aurbach D. Challenges in the development of advanced Li-ion batteries: a review. *Energy & Environmental Science*. 2011. **4**(9): 3243–3262.

64. Kaymaksiz S., Wilhelm F., Wachtler M., Wohlfahrt-Mehrens M., Hartnig C., Tschernych I., Wietelmann U. Electrochemical stability of lithium salicylato-borates as electrolyte additives in Li-ion batteries. *Journal of Power Sources*. 2013. **239**: 659–669.

65. Bhattacharyya, A. J., & Maier, J. Second Phase Effects on the Conductivity of Non-Aqueous Salt Solutions:"Soggy Sand Electrolytes". *Advanced Materials*. 2004. **16**(9–10): 811–814.

66. Monti D., Jónsson E., Palacín M. R., Johansson P. Ionic liquid based electrolytes for sodium-ion batteries: Na$^+$ solvation and ionic conductivity. *Journal of Power Sources*. 2014. **245**: 630–636.

67. Ponrouch A., Monti D., Boschin A., Steen B., Johansson P., Palacin M. R. Nonaqueous electrolytes for sodium-ion batteries. *Journal of Materials Chemistry A*. 2015. **3**(1): 22.