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Short communication

The solid electrolytes Li₂O–LiF–Li₂WO₄–B₂O₃ with enhanced ionic conductivity for lithium-ion battery



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Introduction

Nowadays, safety issue and high cost of the materials are essential criteria considering to seek and develop new lithiumbattery-systems in particular such as an alternative of battery systems with an aqueous electrolyte and all-solid-state battery with solid and/or ceramic materials compared to conventional lithium-ion battery systems (LIBs) [1–4]. Furthermore, selection of the electrolyte-containing system such as polymers, ionic liquids, and "water-in-salt" electrolytes, aqueous electrolyte solutions, solid electrolyte and ceramic materials for the new generation battery systems are pushed researchers to seek the electrolyte candidates with performance which will be meet criteria of high energy and power capability, and long cycle life and in combination with high safety, use of abundant and low-cost materials, environmental friendliness for further development of nextgeneration battery systems which can replace conventional LIBs for applications in various energy storage systems [5-7]. Therefore, among these alternatives of new batteries system could distinguish all-solid-state battery with solid and/or ceramic materials which following aforementioned criteria.

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ABSTRACT

In this study, it is obtained solid electrolytes $60Li_2O-10LiF-10Li_2WO_4-20B_2O_3$ with content of LiF is 10 mol% and Li_2WO_4 with 10 mol% exhibit high ionic conductivity of $1.7410^{-6} \text{ S cm}^{-1}$ compared to the solid electrolyte $50Li_2O-20Li_2WO_4-30B_2O_3$ without LiF is $2.510^{-7} \text{ S cm}^{-1}$ at room temperature. The obtained solid electrolyte is used as the surface agent of the active material LiCoO₂ which displays cycling stability and low electrode resistance via surface stabilization at a high potential of 4.4 V (vs. Li/Li⁺) at the 1C current density for 100 cycles compared to the pristine material.

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To development of all-solid-state batteries system with the solid and/or ceramic materials are required following criteria of high ionic and low electronic conductivities, chemical stability in a contact with the active materials, electrochemical stability window in wide operation potential range, and also combination of environmentally friendly and low-cost materials, and easy process [8–10]. It should be noted that among these materials for all-solid-state battery, the solid electrolytes are attractive from point of view of potential advantages. As is well-known that glassy solid electrolytes (non-crystalline) are caused to increase of scientific interest which finds wide application compared to the crystalline solid electrolyte thanks to isotropic ionic conduction, no grain boundaries and easy synthesis [11–13]. Furthermore, among solid electrolytes, the oxide solid electrolytes based on $Li_2O-P_2O_5$, and Li₂O–B₂O₃ systems are attractive for application in the battery system with these materials [12,14]. However, the Li₂O–P₂O₅ and $Li_2O-B_2O_3$ systems have lower ionic conductivity of 10^{-8} S cm⁻¹ that can be limited to their application [14]. Therefore, for increasing the ionic conductivity of these solid electrolytes use of the doping salts such as LiF, Li₂SO₄, Li₂WO₄ etc. [15-17]. It should be noted that lithium fluorides are attractive candidates for increasing the ionic conductivity thanks to strong ionic bonding with high ionic conductivity, chemical and electrochemical stability which can have the significant use in various batteries applications [18–20]. The other candidate for improvement of the ionic conductivity of the solid electrolytes is used Li₂WO₄ due to large ionic radius of W-ion into the structure of the solid electrolyte

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which leads to increasing the ionic conductivity. Moreover, large polyhedrons [WO₄] can lead to substantial increase of free volume of the solid electrolyte resulting to improvement of their ionic conductivity thanks to "loosening" of structure of the solid electrolyte consisting of groups [BO₃], [BO₄] and large polyhedrons [WO₄] [21]. Therefore, using combination of LiF and Li₂WO₄ to increasing the ionic conductivity of the solid electrolytes Li₂O- B_2O_3 can provide possibly application of such systems for the allsolid-state battery system. Furthermore, it should be emphasized that investigation of the solid electrolyte Li₂O-LiF-Li₂WO₄-B₂O₃ for the battery systems in particular in lithium-ion and all-solidstate battery systems is still rarely studied. Therefore, in this work, were the synthesized solid electrolytes Li₂O-LiF-Li₂WO₄-B₂O₃ which require responding of high ionic conductivity which can be applied in the various application of high-performance batteries with the solid electrolytes.

Experimental

To synthesis of the solid electrolytes $Li_2O-LiF-Li_2WO_4-B_2O_3$ was used following the reagent-grade chemicals (Aldrich) of Li_2CO_3 , LiF, H_3BO_3 , Li_2WO_4 as starting materials. The solid electrolytes were synthesized by a high-temperature solid-state reaction at 950 °C for 30 min in air.

The densities of the solid electrolyte samples were determined by an Archimedes technique with toluene as an immersion fluid at room temperature. While three samples of each solid electrolyte were used to determine the density.

The ionic conductivity of the solid electrolytes with thickness of 1 μ m (the solid electrolyte film before and after a bend test as shown in Fig. S1, supporting information) was measured between two symmetric ions blocking electrodes (platinum) which were deposited on both sides of samples (the solid electrolytes and the non-blocking electrodes of platinum were sputtered by the magnetron sputtering deposition method) by and AC impedance method (VoltaLab 40, PGZ 301) was used for determination the conductivity in the frequency range of 100 kHz–1 Hz with voltage amplitude of 10 mV at a temperature of 25 °C in a calorstat at kept set temperature for 1 h.

The surface of active electrode material $LiCoO_2$ was improved via the obtained solid electrolyte $Li_2O-LiF-Li_2WO_4-B_2O_3$ (composition of 60: 10: 10: 20, mol%, as shown in Table 1) and this material was obtained by a mechanochemical coating with the subsequent heat treatment at 700 °C for 2.5 h where fully description of this method as reported in the supporting information and also that was reported elsewhere [10].

The amorphous state of solid electrolytes and crystalline structures of the bare and coated LiCoO₂ materials were confirmed by the X-ray diffraction (XRD) using a Rigaku SmartLab diffractometer with Cu K α radiation (40 kV, 250 mA) in the 10°–80° and

 2θ range at a scan rate of 0.02° s⁻¹. The surface morphologies of obtained samples were observed using FE-SEM (JSM 7800F) and transmission electron micrographs (TEM, JEOL ARM-200F).

To evaluate electrochemical performance of the bare and coated LiCoO₂ materials as cathode were carried out with a 2025-type coin cell which were assembled in glove box with argon atmosphere using porous polyethylene membrane (Celgard 2400) as the separator and lithium electrode as anode in an organic electrolyte of 1 M LiPF₆ in EC-DMC (1:1 v/v) solution. Working electrodes were prepared by mixing 80:10:10 weight percent of the bare and coated samples, carbon black and PVdF binder, respectively, which were spread on the surface of Al foil as a current collector. Then the samples with a diameter of 12 mm and electrode mass of approximately 2 mg were dried at 120 °C for 12 h under vacuum. The repeated charge-discharge cycling was carried out at a current density of 1C rate (140 mAh g⁻¹) in a potential range of 3.5-4.4 V. The surface resistance of bare and coated samples was determined by electrochemical impedance spectroscopy (EIS) using a multichannel electrochemical workstation (ZIVELAB, MP1, WonATech) in a frequency range of 100 kHz-100 mHz at a voltage amplitude of 10 mV. To determine the Co ions concentration of bare and coated LiCoO₂ electrodes in an organic electrolyte after 100 cycles were measured by an inductively coupled plasma optical emission spectrometer (Thermo Scientific iCAP 7000 series ICP-OES).

Results and discussion

As it was noted above that use of the solid electrolytes Li₂O- B_2O_3 containing ions of large ionic radius such as WO₃ are attractive from the point of view of the application these materials for battery systems in particular for lithium-ion and all-solid-state batteries. Furthermore, it can be expected that at adding these ions into the structure results in increase of free volume because of "loosening" of the structure consisting of [BO₃], [BO₄] and [WO₄] groups and as consequence, lead to increase of the ionic conductivity. It should be mentioned that with increasing W⁶ ⁺-ions into the structure of the solid electrolyte Li₂O-LiF-Li₂WO₄- B_2O_3 with a Li₂O content of above 35 mol% leads to polymerization of tungsten groups of [WO₄] that confirming enhance of the ionic conductivity these solid electrolytes as shown in Table 1, where Fig. S2 (Supporting information) shows the typical Nyquist plots of the solid electrolytes Li₂O-LiF-Li₂WO₄-B₂O₃ at room temperature and Fig. S3 (Supporting Information) of the equivalent circuit which was used for determination of the ionic conductivities of the solid electrolytes. In addition, the density of solid electrolytes is observed to increase with an increase in the concentration of Li₂WO₄ due to replacement of lighter lithium and boron ions with heavier tungsten ions in the glass matrix that can lead to connectivity of the structure with further addition of the Li₂WO₄

Ionic conductivity and density of the solid electrolyte Li ₂ O-LiF-Li ₂ WO ₄ -B ₂ O ₃ at room temperature.

Composition	Composition of solid electrolytes, mol%				Ionic conductivity, $\sigma \times 10^{-6}$ S cm ⁻¹	Density, g cm ⁻³
	Li ₂ O	LiF	Li ₂ WO ₄	B ₂ O ₃		gem
1	40	10	20	30	0.97	3.11
2	40	20	20	20	0.12	3.04
3	45	10	15	30	0.10	2.91
4	50	10	10	30	0.48	2.84
5	50	10	15	25	1.26	2.95
6	50	0	20	30	0.25	3.13
7	50	10	20	20	0.79	3.17
8	55	10	10	25	1.07	2.93
9	55	10	20	15	1.34	2.82
10	60	10	10	20	1.74	2.74

content. While increase of the density can be related to composition of the solid electrolytes than to type of structural units. Therefore, according to a previous study [21], the W-ion into groups [WO₄]²⁻ exists only in strongly alkaline solutions, acidification of which leads to formation of polymers consisting of octahedra [WO₆]. As is well-known that solid electrolytes which can be called as supercooled liquids, therefore it can be assumed that in line with aqueous solutions into the solid electrolytes with Li₂O content above of 35 mol%, the tungsten cations can have coordination of groups [WO₄]. The amorphous state of these solid electrolytes can be related to increase of degree of polymerization their structural network that leads to substitution of the borate groups [BO₃] and [BO₄] into distorted tetrahedra [WO₄]. The groups [WO₄] have two shortened double bonds which can not have to participate in formation of continuous structural glass network as shown in Fig. 1a. While the groups $[WO_4]^{2-}$ which perform bridging function into the structure due to these two bonds which are a weak link. Therefore, the obtained solid electrolytes Li₂O-LiF-Li₂WO₄-B₂O₃ are characterized by increased crystallization ability with formation into the structure of lithium tungstates with various basicity (predominantly crystalline phase of Li₂WO₄; JCPDS 12-0760) as shown in Fig. 2.

It can be assumed that partial replacement of the lithium oxide on fluoride ions (lithium fluoride) into the structure of solid electrolyte $Li_2O-Li_2WO_4-B_2O_3$ can lead to formation of oxyfluoride polytungeston of $[WO_4]F_2^{4-}$ groups into the structure, similar formation occur to the solid electrolyte $Li_2O-LiF-P_2O_5$ [9]. In this case, localization of F-anions near W-cations can lead to change of coordination number from W⁴⁺ to W⁶⁺ as shown in Fig. 1b. While these groups do not have bonds, which can be connected to threedimensional spatial structural network that result to decrease of the crystallization ability and increase of free volume and ionic conductivity as shown in Fig. 2 and Table 1. Furthermore, we can



Fig. 2. XRD patterns of compositions of the solid electrolyte $Li_2O-Li_2WO_4-B_2O_3$ with content of LiF (a) 0 mol% (composition #6), (b) 10 mol% (composition #5), (c) 20 mol% (composition #2). Number of compositions are corresponded to the Table 1.

assume that solid electrolyte Li₂O–LiF–Li₂WO₄–B₂O₃ with low content of B₂O₃ have all boron cations in three-coordinated state. In this case, anionic skeleton of the solid electrolyte can be formed nonpolar structure groups as [BO₃] and [WO₄] with which Lications are bonded through the unbridged oxygen anions (the dissociated lithium cations). It is obvious that presence of the lithium cations into the structure of solid electrolyte is located in dissociated state that leads to increase of free volume and ionic conductivity (Table 1). In addition, it is confirmed by XRD analysis, as shown in Fig. 2, at adding fluoride ions into the structure of solid electrolyte Li₂O–LiF–Li₂WO₄–B₂O₃ results in decrease of free volume and that lead to enhance of the ionic conductivity of the



Fig. 1. The models of structural groups of (a) polytungeston of $[WO_4]^{2-}$ and (b) oxyfluoride polytungeston of $[WO_4]F_2^{4-}$ into the structure of the solid electrolyte, (c) structure of the solid electrolyte Li₂O-LiF-Li₂WO₄-B₂O₃.



Fig. 3. (a) XRD patterns and SEM images of (b) bare and (c) coated LiCoO₂ materials. Surface analysis of bare and coated LiCoO₂ materials by TEM analysis is inserted as an inset in Fig. 3a and b, respectively.

solid electrolyte Li₂O–LiF–Li₂WO₄–B₂O₃ compared to Li₂O–Li₂WO₄–B₂O₃ (Table 1). It is important to note that at same Li₂O content (58.3 mol%) and LiF content (10 mol%) results in increase of the ionic conductivity of 1.2610^{-6} , S cm⁻¹ (composition #5, Table 1) compared to the solid electrolyte without LiF (composition #6, Table 1).

Thus, on the basis of obtained experimental data, it can be concluded that increase of the ionic conductivity of the solid electrolytes $Li_2O-LiF-Li_2WO_4-B_2O_3$ related to adding LiF that leads to increasing of the free volume and decrease of crystallization ability. Furthermore, presence of the large ions of tungsten ions into the structure of solid electrolytes is beneficial to transport of Li-ions. In addition, it should be noted that these solid electrolytes have lower content of traditional glass former (B_2O_3 of 15–25 mol %) that also have significant impact on crystallization ability and ionic conductivity.

Based on above material characterization, it was tested the solid electrolyte as the surface agent of $LiCoO_2$ material by physicochemical and electrochemical analysis as shown in Figs. 3 and 4. At first, impact of the solid electrolyte $Li_2O-LiF-Li_2WO_4-B_2O_3$ (composition of 60: 10: 10: 20, mol%, as shown in Table 1) on crystalline structures

of LiCoO₂ materials was identified by XRD analysis, as shown in Fig. 3a. The XRD patterns of pristine and coated LiCoO₂ materials display a layered structure R3 m (JCPDS, no. 70-2685). The same peak positions of the XRD patterns of coated LiCoO₂ indicate on same layered structure pattern with bare material due to a low amount of the solid electrolyte as a coating material on the surface of the LiCoO₂ particles. The morphology of the bare LiCoO₂ material has similar surface morphology of the LiCoO₂ particles that of the coated by the solid electrolyte as the surface agent (Fig. 3b and c). From TEM analysis shows that the surface of coated LiCoO₂ material is covered by a thin film around 12 nm of the solid electrolyte as a surface agent as shown in Fig. 3b and c. It means that solid electrolyte does not change the original crystal structure and morphology of LiCoO₂ that also confirms credible cycling of LiCoO₂ samples with repeating intercalation and deintercalation of lithium ions into/from the structure, even after using the coating process.

To better understand impact of the solid electrolyte on the surface stability and electrochemical performance of $LiCoO_2$, these materials were cycling at 1 C in the potential range of 3.5-4.4 V. The bare $LiCoO_2$ displayed high initial discharge specific capacity of 127.42 mAh g⁻¹ compared to the coated material (125.85 mAh g⁻¹),



Fig. 4. (a) Cyclic performance and ICP analysis of an organic electrolyte after 100 cycles and Co (cobalt ion) concentration of the bare and coated LCO materials, (b) Nyquist plots and equivalent circuit of the LCO materials at a selected cycle (100th cycle) in Fig. 4b, (c-d) charge-discharge voltage profiles of bare and coated LCO at 1 C in the potential range of 3.5–4.4 V in an organic electrolyte of 1 M LiPF₆ in EC-DMC (1:1 v/v).

however, it should be noted that cycling performance of coated LiCoO₂ were much improved during cycling life thanks to the solid electrolyte on the surface of particles. In addition, the cobalt ions content in an organic electrolyte after cycling of the bare and coated LiCoO₂ electrodes was determined by ICP analysis. From the ICP analysis (Fig. 4a), it is found that the concentration of cobalt ions for the coated $LiCoO_2$ (0.97 ppm) is lower than for the bare (1.45 ppm) that also confirm the stabilization of the structure of LiCoO₂ by the solid electrolyte coating resulting in reduce the dissolution of the cobalt ions and decrease the direct contact an organic electrolyte with particles of the LiCoO₂ material. Therefore, these data can indicate that surface coating of LiCoO₂ cathode material can prevent irreversible surface phase transitions and electrolyte decomposition at a high potential cut-off of 4.4V leading to cycling stability of the bare material. Furthermore, charge-discharge voltage profiles of the coated material display less polarization behavior during cycling life compared to the bare LiCoO₂ as shown in Fig. 4a-d. In addition to electrochemical performance of the bare and coated LiCoO2 materials, the resistances of samples were obtained using EIS measurements after the 100th cycle and fitted by an equivalent circuit, as shown in Fig. 4b. The Nyquist plots of materials consist of two semi-circles, where the high frequency range related to the electrolyte resistance (Relectrolyte), the medium frequency range of transport of Li ions through the surface film (R_{film}) and charge-transfer resistance (R_{ct}) related to the electrochemical reactions, and low frequency range attributed to the Li diffusion into/from LiCoO₂ particles (Z_w). In detail, main parameters are the surface film and charge-transfer resistance, it should be noted that coated LiCoO₂ material has lower value resistances (R_{film} of 11.8 Ω and R_{ct} of 37.5 Ω) compared to the bare sample (R_{film} of 14.6 Ω and R_{ct} of 64.8 Ω). Therefore, these values of resistance strongly indicate that solid electrolyte on the LiCoO₂ surface helps reduce resistances and improves of Li diffusion that leads to enhanced surface stability of the LiCoO₂ material during cycling life (123.85 mAh g^{-1}) compared to the bare (117.59 mAh g^{-1}), as shown in Fig. 3b.

Thus, on basis of the above experimental results, this surface coating process is a simple method for modification of the surface of cathode materials which does not change the layered structure and morphology. Moreover, the solid electrolyte as the surface agent on the surface of $LiCoO_2$ maintain cycling stability of LIBs thank to effectively suppressing the phase transition and side reaction components occurring on the $LiCoO_2$ surface at the high potential cut-off of 4.4 V (vs. Li/Li^*).

Conclusion

In summary, we have synthesized the fast Li^+ conducting glassy solid electrolytes $Li_2O-LiF-Li_2WO_4-B_2O_3$ with the high ionic conductivity from 10^{-7} to 10^{-6} S cm⁻¹ at room temperature. The obtained solid electrolyte $60Li_2O-10Li_2WO_4-20B_2O_3$ with content of LiF is 10 mol% exhibits high ionic conductivity of $1.74 \ 10^{-6}$ S cm⁻¹ than solid electrolyte $50Li_2O-20Li_2WO_4-30B_2O_3$ without LiF is 2.5 10^{-7} S cm⁻¹ at room temperature and compare to widely attractive solid electrolyte "LIPON" with ionic conductivity of $1.6 \ 10^{-6}$ S cm⁻¹. In addition, we can suggest that these novel solid electrolytes Li_2O- LiF– Li_2WO_4 – B_2O_3 can be used for beyond solid-state battery concepts and also for lithium-ion battery system as a promising surface agent for surface stabilization of the surface of high-energy densities electrode materials (LiCOO₂) which request high charge voltage in an organic electrolyte.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jiec.2019.01.030.

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