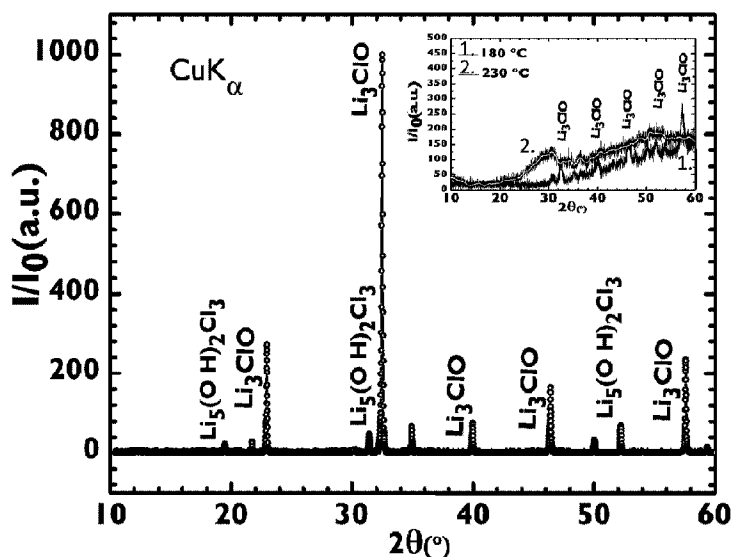




(86) **Date de dépôt PCT/PCT Filing Date:** 2015/02/26
(87) **Date publication PCT/PCT Publication Date:** 2015/09/03
(45) **Date de délivrance/Issue Date:** 2023/08/01
(85) **Entrée phase nationale/National Entry:** 2016/08/24
(86) **N° demande PCT/PCT Application No.:** IB 2015/051440
(87) **N° publication PCT/PCT Publication No.:** 2015/128834
(30) **Priorité/Priority:** 2014/02/26 (PT107482)

(51) **Cl.Int./Int.Cl.** *H01M 10/0562* (2010.01),
H01G 4/06 (2006.01), *H01M 16/00* (2006.01),
H01G 11/56 (2013.01)
(72) **Inventeurs/Inventors:**
SOUSA SOARES DE OLIVEIRA BRAGA, MARIA
HELENA, PT;
DO AMARAL FERREIRA, JOSE JORGE, PT
(73) **Propriétaire/Owner:**
UNIVERSIDADE DO PORTO, PT
(74) **Agent:** MILTONS IP/P.I.

(54) **Titre : VERRE D'ELECTROLYTE SOLIDE POUR CONDUCTION D'IONS DE LITHIUM OU DE SODIUM**
(54) **Title: A SOLID ELECTROLYTE GLASS FOR LITHIUM OR SODIUM IONS CONDUCTION**



(57) **Abrégé/Abstract:**

Glassy electrolyte for lithium or sodium ions conduction The present disclosure relates to the development and improvement of sodium or lithium-ion electrochemical devices, in particular to the development of a new glassy electrolyte comprising high ionic conductivity for batteries, capacitors, and other electrochemical devices comprising a solid electrolyte glass comprising the formula $R_{3-2x}M_xHalO$ wherein R is selected from the group consisting of lithium or sodium; M is selected from the group consisting of magnesium, calcium, strontium or barium; Hal is selected from the group consisting of fluorine, chlorine, bromine, iodine or mixtures thereof; X is the number of moles of M and $0 \leq x \leq 0.01$ and the solid electrolyte glass has a glass transition point.



(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau

(43) International Publication Date
3 September 2015 (03.09.2015)



(10) International Publication Number
WO 2015/128834 A1

(51) International Patent Classification:

H01M 10/052 (2010.01) H01M 16/00 (2006.01)
H01M 10/054 (2010.01) H01G 11/56 (2013.01)
H01M 10/0562 (2010.01)

(21) International Application Number:

PCT/IB2015/051440

(22) International Filing Date:

26 February 2015 (26.02.2015)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

107482 26 February 2014 (26.02.2014) PT

(71) Applicants: UNIVERSIDADE DO PORTO [PT/PT];
Praça Gomes Teixeira, S/n, 4º, S.419, P-4099-002 Porto
(PT). LABORATÓRIO NACIONAL DE ENERGIA E
GEOLOGIA [PT/PT]; Estrada Da Portela, Zambujal, Al-
fragide, P-2720-866 Amadora (PT).

(72) Inventors: SOUSA SOARES DE OLIVEIRA BRAGA,
Maria Helena; Rua De Salgueiros, 651, P-4050-533 Porto
(PT). DO AMARAL FERREIRA, José Jorge; Estrada
Da Portela, Zambujal, P-2720-866 Amadora (PT).

(74) Agent: SILVESTRE ALMEIDA FERREIRA, Luis
Humberto; Edifício Net, Rua de Salazares 842, P-4149-
002 Porto (PT).

(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,
AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY,
BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM,
DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,
HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR,
KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG,
MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM,
PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC,
SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN,
TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GH,
GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ,
TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU,
TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE,
DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU,
LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK,
SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,
GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

[Continued on next page]

(54) Title: A SOLID ELECTROLYTE GLASS FOR LITHIUM OR SODIUM IONS CONDUCTION

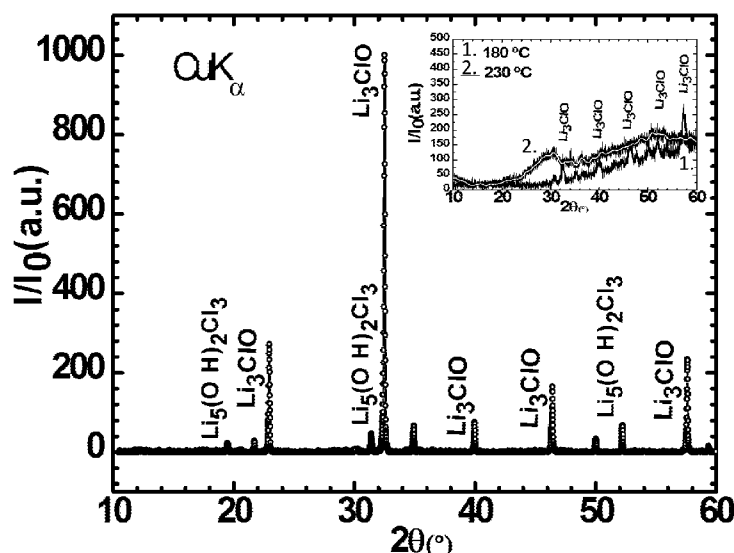


Fig. 1

(57) Abstract: Glassy electrolyte for lithium or sodium ions conduction The present disclosure relates to the development and improvement of sodium or lithium-ion electrochemical devices, in particular to the development of a new glassy electrolyte comprising high ionic conductivity for batteries, capacitors, and other electrochemical devices comprising a solid electrolyte glass comprising the formula $R_{3-2x}M_xHalO$ wherein R is selected from the group consisting of lithium or sodium; M is selected from the group consisting of magnesium, calcium, strontium or barium; Hal is selected from the group consisting of fluorine, chlorine, bromine, iodine or mixtures thereof; X is the number of moles of M and $0 \leq x \leq 0.01$ and the solid electrolyte glass has a glass transition point.

WO 2015/128834 A1



-
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

D E S C R I P T I O N

A solid electrolyte glass for lithium or sodium ions conduction

Technical field

[0001] The present disclosure relates to the development and improvement of sodium or lithium-ion electrochemical devices, in particular to the development of a new solid electrolyte glass comprising a high ionic conductivity and/or a high electrochemical window of stability.

Background

[0002] Four types of next generation batteries are currently being envisaged among the international community: lithium-sulfur, metal-air, and metal-sodium batteries, multivalent cation batteries and all-solid-state battery concepts (M. Tatsumisago and Hayashi, A. Sol. Stat. Ionics, 2012, 225, 342). These battery designs require high-performance, safe and cost effective electrolytes that are compatible with optimized electrode materials. Solid electrolytes have not yet been extensively employed in commercial batteries as they suffer poor ionic conduction at acceptable temperatures and insufficient stability with respect to lithium-metal.

[0003] Chen and co-workers (Z. Chen, Y. Qini, Y. Ren, W. Lu, C. Orendorff, E. P. Roth and K. Amine, *Energy Environ. Sci.* 2011, **4**, 4023) showed that higher graphite negative electrode surface area in a lithium-ion cell can result in more solid electrolyte interphase (SEI) and therefore more heat generation during thermal decomposition. This initial reaction, which occurs at ~110 °C, can further trigger other exothermal reactions in the cell. Therefore, the latest work on graphitic anodes mainly focuses on the development

of a stable artificial solid electrolyte interphase to stabilize the lithiated graphite and improve both safety and cycling performance.

[0004] Recently, lithium batteries using oxygen from air at the positive electrode (lithium-air batteries) have attracted world-wide attention. In this open system, the use of electrolytes with low volatility is strictly required. For the lithium-air batteries a major focus of attention has been the lithium-metal anode protected by a lithium-ion conducting ceramic electrolyte (N.-S. Choi, Z. Chen, S. A. Freunberger, X. Ji, Y.-K. Sun, K. Amine, G. Yushin, L. F. Nazar, J. Cho and P. G. Bruce, *Angew. Chem. Int.* 2012, 51, 9994). LISICON ($\text{Li}_{(1-x-y)}\text{Al}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{(3-y)}\text{O}_{12}$) has been used for the previous purpose with a major inconvenient related to - LISICON being reduced in contact with Li-metal - following-on a Li/ceramic interface difficult to cycle (N.-S. Choi, Z. Chen, S. A. Freunberger, X. Ji, Y.-K. Sun, K. Amine, G. Yushin, L. F. Nazar, J. Cho and P. G. Bruce, *Angew. Chem. Int.* 2012, 51, 9994).

[0005] Promising results were recently obtained with a $\text{Li}_{10}\text{GeP}_2\text{Si}_2$ solid electrolyte (N. Kamaya, K. Homma, Y. Yamakawa, M. Hirayama, R. Kanno, M. Yonemura, T. Kamiyama, Y. Kato, S. Hama, K. Kawamoto and A. A. Mitsui, *Nature Mat.* 2011, 10, 682). In this solid electrolyte medium, Li^+ ions are conducted at 0.012 mScm^{-1} and 12 mScm^{-1} at -100°C and 25°C , respectively, which is considered to be a high conductivity. Mo et al (Y. Mo, S. P. Ong and G. Ceder, *Chem. Mater.* 2012, 24, 15) found that $\text{Li}_{10}\text{GeP}_2\text{Si}_2$ is not stable against reduction by lithium at low voltage or extraction of Li with decomposition at high voltage.

[0006] On a different front, sulfide glasses have been studied due to their high ionic conductivity. A glass of the $\text{Li}_3\text{P}_2\text{O}_4\text{-Li}_2\text{S-SiS}_2$ system is formed at ambient pressure by quenching $0.03\text{Li}_3\text{P}_2\text{O}_4\text{-}0.59\text{Li}_2\text{S-}0.38\text{SiS}_2$ in liquid nitrogen. Its conductivity at room temperature is 0.69 mScm^{-1} (S. Kondo, K. Takada and Y. Yamamura, *Sol. Stat. Ionics* 1992, 53-56(2), 1183) and its stability against electrochemical reduction is as wide as 10 V (A. Hayashi, H. Yamashita, M. Tatsumisago and T. Minami, *Sol. Stat. Ionics* 2002, 148, 381).

[0007] On the other hand, for lithium-ion or sodium-ion electrochemical devices such as capacitors and especially batteries, the safety issue remains a major barrier. Battery manufacturers are now able to produce high-quality lithium-ion cells for consumer electronics, with less than one reported safety incident for every one million cells produced. However, this failure rate is still too high for applications in plug-in hybrid electric vehicles and pure electric vehicles, since several hundred of lithium-ion cells will be needed to power a vehicle. The failure of a single cell can generate a large amount of heat and flame, both of which can then trigger thermal runaway of neighbouring cells, leading to failure throughout the battery pack. Consequently, there is a wide effort to tackle the safety issue of lithium batteries.

[0008] Typically, the conductivity of liquid state of the art electrolytes at room temperature (20 °C) is about 10 mS cm^{-1} , and it increases by approximately 30-40% at 40 °C. The electrochemical window of stability of liquid electrolytes is usually equal or smaller than 4 V, not enabling their use with all the pairs of electrodes.

[0009] The stability of the electrolyte is related to its electrochemical window which is directly related with the electrical band gap. The calculated electronic energy band gap for Li_3ClO crystalline solid is 6.44 eV and does not change more than the decimal value of an eV with low dopant levels up to 0.7 at%. Cyclic voltammetry experiments conducted to determine the window of stability of the glassy samples at 130 °C have shown a stability range of more than 8 V, which allows the application of our electrolyte in next generation high voltage battery cells (5 V).

[0010] These facts are disclosed in order to illustrate the technical problem addressed by the present disclosure.

General description

[0011] The present disclosure relies on a novel type of glasses, which is a disordered amorphous phase presenting a glass transition and showing the highest ionic conductivity of at least 13 mScm^{-1} at 25°C for Li-ion and at least 17 mScm^{-1} for Na-ion at 25°C . These glassy electrolytes for lithium/sodium batteries are inexpensive, light, recyclable, non-flammable and non-toxic. Moreover, they present a wide electrochemical window (higher than 8 V) and thermal stability within the application range of temperatures.

[0012] A lithium-ion or sodium-ion battery is a rechargeable type of battery, wherein lithium/sodium ions move, through the electrolyte, from the negative electrode to the positive electrode during the discharge process and back during the charging process. The battery's electrochemistry is governed by an overall reaction occurring at the positive and negative electrodes and the battery's maximum open circuit potential difference is determined by the cited reaction.

[0013] A lithium-ion or sodium-ion electrical double layer capacitor (EDLC) is a supercapacitor, wherein lithium/sodium ions move, through the electrolyte towards the negative electrode accumulating at the interface and forming a nanometric spaced capacitor with the electrode's negative ions or electrons during charge. At the opposite interface, electrode's positive ions form another EDLC with the negative ions of the electrolyte (which are negative due to lack of Li or Na cations). The capacitor's operating potential difference is determined by the electrolyte's electrochemical window of stability.

[0014] The lithium-ion or sodium-ion batteries and capacitors are lightweight, high energy density power sources for a variety of devices, such as portable devices, power tools, electric vehicles, and electrical grid storage; contain no toxic metals and are therefore characterized as non-hazardous waste.

[0015] The disclosed subject-matter relates to a glassy electrolyte for Li-ion or Na-ion (Li^+ and Na^+ , respectively). The glass is synthesized from a compound with stoichiometry $\text{R}_{3-2x}\text{M}_x\text{HalO}$, wherein R is lithium (Li) or sodium (Na); M is magnesium (Mg), calcium (Ca), strontium (Sr), or barium (Ba); Hal is fluorine (F), chlorine (Cl), bromine (Br) or iodine (I), or a mixture between these elements; O is oxygen. Furthermore, $0 \leq x \leq 0.01$, preferably with $0.002 \leq x \leq 0.007$; preferably with $0.003 \leq x \leq 0.005$.

[0016] The glassy electrolyte, after reaching the vitreous state, is a Li^+ ion or Na^+ ion superconductor in addition to being an electrical insulator demonstrating the essential functional characteristics of an electrolyte. The ionic conductivity in the disclose glassy electrolyte, comprising Li^+ ion or Na^+ ion, improves at least two orders of magnitude comparing with the crystalline material. The electrochemical window becomes also wider from 6 V to more than 8 V. It can, therefore, be applied between the negative and positive electrodes of a lithium battery or capacitor if R in the formula of the compound mentioned above is lithium, or to a sodium battery or capacitor if R in the same formula is sodium.

[0017] This glass has proved to be anti-flammable, to have lightweight, being recyclable, easy to synthesize and of low cost.

[0018] An embodiment of the disclosed subject-matter is relate to solid electrolyte glass comprising formula $\text{R}_{3-2x}\text{M}_x\text{HalO}$ wherein

R is selected from the group consisting of lithium or sodium;

M is selected from the group consisting of magnesium, calcium, strontium or barium;

Hal is selected from the group consisting of fluorine, chlorine, bromine, iodine or mixtures thereof;

X is the number of moles of M and $0 \leq x \leq 0.01$;

and the solid electrolyte glass has a glass transition point.

[0019] In an embodiment the solid electrolyte glass does not have a peak with a half-value width of 0.64° or less in a range of $31^\circ \leq 2\theta \leq 34^\circ$ in measurement by an X-ray diffraction method using a $\text{CuK}\alpha$ ray.

[0020] In an embodiment the $\text{Li}_{3-2x0.005}\text{Ba}_{0.005}\text{ClO}$ glassy electrolyte does not have a peak with a half-value width of 0.64° or less in a range of $31^\circ \leq 2\theta \leq 34^\circ$ in measurement by an X-ray diffraction method using a $\text{CuK}\alpha$ ray.

[0021] In an embodiment the solid electrolyte glass of the present disclosure has a ionic conductivity of at least 13 mScm^{-1} at 25°C wherein R is a ion lithium; preferably an ionic conductivity of $13\text{-}60 \text{ mScm}^{-1}$ at 25°C , more preferably an ionic conductivity of at least 25 mScm^{-1} at 25°C .

[0022] In an embodiment the solid electrolyte glass of the present disclosure has a ionic conductivity of at least 17 mScm^{-1} at 25°C wherein R is a ion sodium; preferably an ionic conductivity of $17\text{-}105 \text{ mScm}^{-1}$ at 25°C , more preferably an ionic conductivity of at least 31 mScm^{-1} at 25°C .

[0023] The ionic conductivity can be measured by standard methods, namely by Electrochemical Impedance Spectroscopy (EIS) at 25°C .

[0024] In an embodiment the solid electrolyte glass of the present disclosure X in the formula may be 0.002, 0.005, 0.007 or 0.01.

[0025] In an embodiment the solid electrolyte glass of the present disclosure Hal may be a mixture of chloride and iodine.

[0026] In an embodiment the solid electrolyte glass of the present disclosure Hal may be $\text{Hal} = 0.5\text{Cl} + 0.5\text{I}$.

[0027] In an embodiment the solid electrolyte glass of the present disclosure wherein R is lithium:

M is barium, Hal is chlorine and x is 0.005 or;

M is barium, Hal is a mixture of chlorine and iodine, x is 0.005.

[0028] In an embodiment the solid electrolyte glass of the present disclosure wherein R is sodium, M is Ba, Hal is Cl and x is 0.005.

[0029] Another aspect of the present disclosure is related to a electrolyte composition, in particular a solid electrolyte glass composition, of the formula $\text{Na}_{3-2x}\text{M}_x\text{HalO}$ wherein

M is selected from the group consisting of magnesium, calcium, strontium or barium;

Hal is selected from the group consisting of fluorine, chlorine, bromine, iodine or mixtures thereof;

X is the number of moles of M and $0 < x \leq 0.01$.

[0030] Another aspect of the present disclosure is related to an electrochemical device comprising a glassy electrolyte describes in the present disclosure.

[0031] Another aspect of the present disclosure is related to a battery comprising a glassy electrolyte describes in the present disclosure.

[0032] Another aspect of the present disclosure is related to a capacitor comprising the glassy electrolyte describes in the present disclosure.

[0033] Another aspect of the present disclosure is related to an electrochemical device comprising at least one capacitor of the present describes in the present disclosure and at least one battery describes in the present disclosure.

[0034] Another aspect of the present disclosure is related to a method for synthesizing a conductive glass electrolyte, in particular for preparing 5 g, comprising a compound of the formula $R_{3-2x}M_xHalO$ wherein

R is lithium;

M is selected from the group consisting of magnesium, calcium, strontium or barium;

Hal is selected from the group consisting of fluorine, chlorine, bromine, iodine or mixtures thereof, in particular Cl;

X is the number of moles of M and $0 \leq x \leq 0.01$;

comprising the following steps:

mixing a stoichiometric quantity of LiHal, LiOH, and one of the following compounds: $Mg(OH)_2$; $Ca(OH)_2$, $Sr(OH)_2$ or $Ba(OH)_2$;

adding to said mixture deionized water and mixing to form a solution in a closed container;

heating said solution up to 250 °C during 2-8h;

opening the container to evaporate the excess of water in the heated product.

[0035] In one embodiment, the method for synthesizing any of the compounds of the previous paragraph may comprise the following step:

introducing the synthesized glassy material between electrodes the electrodes of an electrochemical device;

heating the glassy material up to 170-240 °C and cooling.

[0036] In one embodiment, the method for synthesizing any of the compounds of the previous paragraph may comprise the following step:

a stoichiometry mixture of LiCl, LiOH, and one of the following compounds: $Mg(OH)_2$; $Ca(OH)_2$, $Sr(OH)_2$ or $Ba(OH)_2$, is used; the mixture is introduced in a Teflon reactor with 1-2 drops of deionized water and mixing to form a homogenous paste which is kept closed in the reactor and introduced in a sand bath;

the mixture is heated up to 250 °C and kept for at least 4h;
 the reactor is opened to let the excess of water evaporate;
 a glass material synthetized is introduced between two gold square electrodes with 1 cm wide and pressed with the aid of a clip for the electrolyte to gain a regular thickness equal to 1-3 mm;
 the glass material produced is heated up to 230 °C and cooled down in the sand bath, 2-5 times under the action of a variable potential difference between -10 V and 10 V with variable frequencies between 100 Hz and 5 MHz.

[0037] Another aspect of the present disclosure is related to a method for synthetizing a conductive glass electrolyte, in particular for preparing 5g, comprising a compound of the formula $R_{3-2x}M_xHalO$ wherein

R is sodium;

M is selected from the group consisting of magnesium, calcium, strontium and barium;

Hal is selected from the group consisting of fluorine, chlorine, bromine, iodine or mixtures thereof;

X is the number of moles of M and $0 \leq x \leq 0.01$ of

comprising the following steps:

mixing a stoichiometry quantity of NaHal, NaOH and one of the following compounds: $Mg(OH)_2$; $Ca(OH)_2$; $Sr(OH)_2$ or $Ba(OH)_2$;

adding to said mixture deionized water and mixing to form a solution in a closed container;

heating the solution up to 70-90 °C for 2-8h;

increasing the temperature up to 190-250 °C for 2-8h, maintaining said temperature for at least 2h;

opening the container to evaporate the excess water in the heated product.

[0038] In one embodiment, the method for synthetizing any of the compounds of the previous paragraph may comprise the following step:

introducing the synthesized glass material between electrodes;
heating the glass up to 190-230 °C and cooling.

[0039] In one embodiment, the method for synthesizing any of the compounds of the previous paragraph may comprise the following step:

a stoichiometry mixture of NaCl, NaOH and one of the following compounds: Mg(OH)₂; Ca(OH)₂; Sr(OH)₂ or Ba(OH)₂ or

a stoichiometry mixture of NaCl, NaF, NaOH and one of the following compounds: Mg(OH)₂; Ca(OH)₂; Sr(OH)₂ or Ba(OH)₂ is used;

the mixture is introduced in a reactor with 1-2 drops of deionized water and mixed to form a homogenous paste which is kept closed in the reactor and introduced in a sand bath;

the mixture is heated up to 80 °C for 2h;

the temperature is increased to 120 °C for 24h;

the temperature is increased to 245 °C for 24h;

the temperature is maintained for at least 4h;

the reactor is opened to let the excess of water evaporate;

a glassy material synthesized is introduced between two gold square electrodes with 1 cm wide and pressed with the aid of a clip for the electrolyte to gain a regular thickness equal to 1-3 mm;

the glass material produced is heated up to 230 °C and cooled down in the sand bath;

the glass material is heated up to 140 °C and cooled down in the sand bath 2-5 times under the action of a variable potential difference between -10 V and 10 V with variable frequencies between 100 Hz and 5 MHz.

[0040] Another aspect of the present disclosure is related to a method for synthesizing a ion conductive glassy electrolyte, in particular for preparing 5g, comprising a compound of the formula $R_{3-2x}M_xHalO$ wherein

R is lithium;

M is selected from the group consisting of magnesium, calcium, strontium or barium;

Hal is selected from the group consisting of fluorine, chlorine, bromine, iodine or mixtures thereof;

X is the number of moles of M and $0 \leq x \leq 0.01$ of

comprising the following steps:

mixing a stoichiometry quantity of LiCl, LiOH and one of the following compounds: $\text{Mg}(\text{OH})_2$; $\text{Ca}(\text{OH})_2$; $\text{Sr}(\text{OH})_2$ or $\text{Ba}(\text{OH})_2$;

adding to said mixture deionized water, in particular 5-25 ml or 1-2 drops, and mixed to form a solution, in particular an homogeneous paste, in a closed container;

heating said solution up to 250 °C during 2-8h;

opening the container to evaporate the excess of water in the product;

introducing the glass material synthetized between the electrodes, in particular a glass material synthetized is introduced between two gold square electrodes with 1 cm wide and pressed with the aid of a clip for the electrolyte to gain a regular thickness equal to 1-3 mm;

the glass obtained is heated up to 170-240 °C and cooled down, in particular 2-5 times under the action of a variable potential difference between -10 V and 10 V with variable frequencies between 100 Hz and 5 MHz.

[0041] Another aspect of the present disclosure is related to the use of the composition of the formula $\text{R}_{3-2x}\text{M}_x\text{HalO}$ wherein

R is selected from the group consisting of lithium or sodium;

M is selected from the group consisting of magnesium, calcium, barium or strontium;

Hal is selected from the group consisting of fluorine, chlorine, bromine, iodine or mixtures thereof;

X is the number of moles of M and $0 \leq x \leq 0.01$;

as an enhancer of the ionic conductivity of an electrolyte and/or of the electrochemical window of stability of an electrolyte.

[0042] The disclosed subject matter relates to a glassy electrolyte optimized with ultra-fast ionic conduction based on an $R_{3-2x}M_x\text{HalO}$ stoichiometry, in which R is lithium or sodium ion, M is a higher valent cation such as Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} ; and Hal is a halide anion like F^- , Cl^- , Br^- or I^- or a mixture of halides anions.

[0043] The glass-liquid transition is the reversible transition in amorphous materials from a hard and relatively brittle state into a molten or rubber-like state. The glass transition of a liquid to a solid-like state may occur with either cooling or compression. The transition comprises a relatively smooth increase in the viscosity of a material of about 17 orders of magnitude without any pronounced change in material structure. The consequence of this dramatic increase is a glass exhibiting solid-like mechanical properties on the timescale of practical observation. While glasses are often thought of as rigid and completely immobile, it is well known that relaxation processes of one type or another continue to be measurable all the way down to the cryogenic range. Hundreds of degrees below T_g , on the other hand, there is frequently an important source of dielectric loss in ordinary glass insulators. This is attributed to mobile alkali ions and, to a lesser extent, protons, in the anionic network. In many cases, for example in solid electrolytes, these quasi-free modes of motion are the focus of special materials interest such as advanced solid electrolytes based on freely mobile cations.

[0044] A more operative classification for the glass transition temperature is that at this temperature - or within a few degrees up to for example 50°C - the specific heat, the coefficient of thermal expansion and eventually the dielectric constant change abruptly. In the Differential Scanning Calorimetry (DSC) experiment, T_g is expressed by a change in the base line, indicating a change in the heat capacity of the material. Usually, no enthalpy (latent heat change) is associated with this transition (it is a second order

transition); therefore, the effect in a DSC curve is slender and is distinguishable only if the instrument is sensitive.

[0045] These solid electrolytes undergo a viscous liquid to a solid-like transition, at T_g . Above T_g a non-Arrhenius conductivity regime is observed [$T_g(\text{Li}_3\text{ClO}) \approx 119^\circ\text{C}$, $T_g(\text{Li}_{3-2*0.005}\text{Mg}_{0.005}\text{ClO}) \approx 109^\circ\text{C}$, $T_g(\text{Li}_{3-2*0.005}\text{Ca}_{0.005}\text{ClO}) \approx 99^\circ\text{C}$, $T_g(\text{Li}_{3-2*0.005}\text{Ba}_{0.005}\text{ClO}) \approx 75^\circ\text{C}$, $T_g(\text{Li}_{3-2*0.005}\text{Ba}_{0.005}\text{Cl}_{0.5}\text{I}_{0.5}\text{O}) \approx 38^\circ\text{C}$]. One variant of the solid electrolyte developed by us, $\text{Li}_{3-2x}\text{Ba}_x\text{ClO}$ ($x = 0.005$), has a conductivity of 25 mScm^{-1} , 38 mScm^{-1} and 240 mScm^{-1} at 25°C , 75°C and 100°C , respectively, in the glassy state or supercooled liquid state. Another variant, $\text{Li}_{3-2x}\text{Ba}_x\text{Cl}_{0.5}\text{I}_{0.5}\text{O}$ ($x = 0.005$), has a conductivity of 121 mScm^{-1} at 50°C in the supercooled liquid state.

[0046] Antiperovskite hydroxides, most of them following the general formula $\text{Li}_{3-n}(\text{OH})_n\text{Hal}$ or $\text{Li}_4(\text{OH})_3\text{Cl}$ present ionic conductivities which are surprisingly smaller than the $\text{Li}_{3-2*x}\text{M}_x\text{HalO}$ vitreous electrolytes, achieving the highest ionic conductivity, 0.010 Scm^{-1} , at $\sim 250^\circ\text{C}$ (for $\text{Li}_5(\text{OH})_3\text{Cl}_2$). Nevertheless, they are observed in our samples prior to the formation of the glasses and they may have an surprisingly important role in glass formation since the translational symmetry characteristic of a homogeneous fluid is broken by exposure to an external force field, in the vicinity of a confining surface (which may be regarded as the source of an external field), or in the presence of an interface between coexisting phases.

[0046a] In another aspect, there is provided solid electrolyte glass comprising compound of formula $R_{3-2x}M_x\text{HalO}$ wherein R is selected from the group consisting of lithium and sodium; M is selected from the group consisting of magnesium, calcium, strontium and barium; Hal is selected from the group consisting of fluorine, chlorine, bromine, iodine and mixtures thereof; x is the number of moles of M and $0 < x \leq 0.01$; and the solid electrolyte glass has a glass transition point; wherein a glassy phase of the solid electrolyte glass is obtained by heating-cooling cycles up to 250 °C.

[0046b] In another aspect, there is provided an electrolyte composition comprising a compound of formula $\text{Na}_{3-2x}M_x\text{HalO}$ wherein M is selected from the group consisting of magnesium, calcium, strontium and barium; Hal is selected from the group consisting of fluorine, chlorine, bromine, iodine and mixtures thereof; x is the number of moles of M and $0 < x \leq 0.01$.

[0046c] In another aspect, there is provided a method for synthesizing a glass electrolyte comprising a compound of formula $R_{3-2x}M_x\text{HalO}$ wherein R is sodium; M is selected from the group consisting of magnesium, calcium, strontium and barium; Hal is selected from the group consisting of fluorine, chlorine, bromine, iodine and mixtures thereof; x is the number of moles of M and $0 < x \leq 0.01$; comprising the following steps: mixing a stoichiometry quantity of NaHal, NaOH and one of the following compounds: $\text{Mg}(\text{OH})_2$; $\text{Ca}(\text{OH})_2$; $\text{Sr}(\text{OH})_2$ and $\text{Ba}(\text{OH})_2$; adding to said mixture deionized water and mixing to form a solution in a closed container; heating the solution up to 70-90 °C for 2-8h; increasing the temperature up to 190-250 °C for 2-8h, maintaining said temperature for at least 2h; opening the container to evaporate the excess water in the heated product.

[0046d] In another aspect, there is provided method for synthesizing a glass electrolyte comprising a compound of formula $R_{3-2x}M_x\text{HalO}$ wherein R is lithium; M is selected from the group consisting of magnesium, calcium, strontium and barium; Hal is selected from the group consisting of fluorine, chlorine, bromine, iodine and mixtures thereof; x is the number of moles of M and $0 < x \leq 0.01$; comprising the following steps: mixing a stoichiometry quantity of LiHal, LiOH and one of the following compounds: $\text{Mg}(\text{OH})_2$; $\text{Ca}(\text{OH})_2$; $\text{Sr}(\text{OH})_2$ and $\text{Ba}(\text{OH})_2$; adding to said mixture deionized water and mixing to form a solution in a closed container; heating said solution up to 250 °C during 2-8h; opening the container to evaporate the excess of water in the heated product.

[0046e] In another aspect, there is provided a method for synthesizing a glass electrolyte comprising a compound of formula $R_{3-2x}M_x\text{HalO}$ wherein R is lithium; M is selected from the group consisting of magnesium, calcium, strontium and barium; Hal is selected from the group consisting of fluorine, chlorine, bromine, iodine and mixtures thereof; x is the number of moles of M and $0 < x \leq 0.01$; comprising the following steps: mixing a stoichiometry quantity of LiHal, LiOH and one of the following compounds: $\text{Mg}(\text{OH})_2$; $\text{Ca}(\text{OH})_2$; $\text{Sr}(\text{OH})_2$ and $\text{Ba}(\text{OH})_2$; adding to said mixture deionized water and mixing to form a solution in a closed container; heating said solution up to 250 °C during 2-8h; opening the container to evaporate the excess of water in the heated product.

[0046f] In another aspect, there is provided a use of the composition of formula $R_{3-2x}M_x\text{HalO}$ wherein R is selected from the group consisting of lithium and sodium; M is selected from the group consisting of magnesium, calcium, barium and strontium; Hal is selected from the group consisting of fluorine, chlorine, bromine, iodine and mixtures thereof; x is the number of moles of M and $0 < x \leq 0.01$; as an enhancer of the ionic conductivity of an electrolyte and/or of the electrochemical window of stability of an electrolyte.

Description of the figures

[0047] For a better understanding of the solution, the attached figure are joined, which represent preferred embodiments of the invention which, however, these figures are not intended to limit the scope of the present invention.

[0048] **Figure 1:** XRD diffractogram of a sample of Li_3ClO at room temperature. There is evidence of small amount of an hydroxide phase, possibly $\text{Li}_5(\text{OH})_2\text{Cl}_3$, due to sample manipulation. At 180 °C (graph right above, figure 1 (1)), there is little evidence of the hydroxide but the presence of crystalline Li_3ClO is still clear, although an amorphous phase becomes visible. At 230 °C (graph right above, figure 1 (2)), only an amorphous phase is clearly distinguishable. The XRD radiation used was $\text{CuK}\alpha$.

[0049] **Figure 2:** XRD diffractogram of a Li_3ClO - crystalline sample (the same as in figure 1 (1)) and of $\text{Li}_{3-2*0.005}\text{Ba}_{0.005}\text{ClO}$ – glassy (2) at room temperature after EIS measurements (after six cycles of heating/cooling). Compton's scatter, which is inelastic scattering and amorphous scatter related with the glass is observed. There is evidence of the presence of an hydroxide phase, possibly $\text{Li}_5\text{Cl}_3(\text{OH})_2$ (the same as in figure 1), that due to sample's air exposed manipulation is inevitable and starts to form at the surface.

[0050] **Figure 3:** Differential Scanning Calorimetry (DSC). DSC curves for a sample of $\text{Li}_{3-2*0.005}\text{Mg}_{0.005}\text{ClO}$ during heating and cooling, at 5 °C/min, eventually showing the glass transition (baseline anomaly) and first order transition temperatures (melting corresponds to endothermic incidents (heating curve) and to an exothermic incident on the cooling curve).

[0051] **Figure 4:** EIS experimental and fitted data using the equivalent circuit previously described. Nyquist impedance and correspondent fitting curve for the 2nd cycle of a sample containing $\text{Li}_{3-2*0.005}\text{Ba}_{0.005}\text{ClO}$, at 25 °C. A is the surface area, $A = 1.76 \text{ cm}^2$ and d the thickness, $d = 0.2 \text{ cm}$.

[0052] **Figure 5:** EIS experimental and fitted data using the equivalent circuit previously described. Nyquist impedance for the 2nd cycle of a sample containing $\text{Li}_{3-2*0.005}\text{Ba}_{0.005}\text{ClO}$, at different temperatures after the glass transition. A is the surface area and d the thickness.

[0053] **Figure 6:** Photograph of a glassy sample of $\text{Li}_{3-2*0.005}\text{Ca}_{0.005}\text{ClO}$.

[0054] **Figure 7:** Electrical properties of plain and doped Li_3ClO . **a)** Calculated electronic band structure for the $\text{Li}_{3-2*0.04}\text{Ca}_{0.04}\text{ClO}$ solid crystal within the Brillouin zone directions, using DFT-GGA as implemented in VASP. The band gap of 4.74 eV is highlighted after the Fermi level which corresponds to 0 eV. **b)** Li_3ClO calculated electronic band structure within the Brillouin zone directions, using HSE06. The band gap of 6.44 eV highlights the difference between E_g calculated with DFT-GGA and HSE06. **c)** Voltammetry for different cells and doped electrolytes, at 130 °C, emphasizing the stability of the electrolytes up to 8 V.

[0055] **Figure 8:** Glass transition temperature versus ionic radius (of the Li^+ ion, in Li_3ClO , of the doping ion (M) in $\text{Li}_{3-2*0.005}\text{M}_{0.005}\text{ClO}$, $\text{M} = \text{Mg}^{2+}$, Ca^{2+} , Sr^{2+} , Ba^{2+} and of $\text{Li}_{3-2*0.005}\text{M}_{0.005}\text{Cl}_{0.5}\text{I}_{0.5}\text{O}$). Excluding Sr^{2+} , all glass transition temperatures were obtained by Electrochemical Impedance Spectroscopy (EIS). Ionic radiuses were obtained from the literature.

[0056] **Figure 9:** Ionic conductivities of plain and doped Li_3ClO . **a)** Logarithm of the ionic conductivity of Li_3ClO , $\text{Li}_{3-2*0.005}\text{Mg}_{0.005}\text{ClO}$ and $\text{Li}_{3-2*0.005}\text{Ca}_{0.005}\text{ClO}$ versus $1000/T$ [K] during heating and cooling. **b)** Comparison between the logarithm of the ionic conductivities of hydroxides that can be formed during $\text{Li}_{3-2*x}\text{M}_x\text{HalO}$ synthesis; some known solid electrolytes and a gel electrolyte commonly used in Li-ion batteries; Li_3ClO and $\text{Li}_{3-2*0.005}\text{M}_{0.005}\text{ClO}$ ($\text{M} = \text{Mg}$, Ca , Sr , and Ba) during heating. Line and symbols +, × for $\text{Li}_{3-2*0.005}\text{Ba}_{0.005}\text{ClO}$ glassy samples in their 2nd, 3rd and 4th heating/cooling cycles, respectively. EIS measurements were performed during heating.

[0057] **Figure 10:** $\text{Log}(\sigma T)$ versus $1000/T$ graphs, to highlight identical values for the extrapolated data of the σT term in the solid-like glass and supercooled liquid domains when the temperature, T , approaches infinity; **a)** for a sample of Li_3ClO ; **b)** for a sample of $\text{Li}_{3-2*0.005}\text{Ca}_{0.005}\text{ClO}$.

[0058] **Figure 11:** Pseudo-Arrhenius plot and “apparent” activation energies for a $\text{Li}_{3-2*0.005}\text{Ba}_{0.005}\text{ClO}$ sample during the 4th heating/cooling cycle. The sample was submitted to an EIS cycle on every heating. The sample was glassy and therefore it is not expected an Arrhenius behaviour at least above T_g .

Figure 12: Ionic conductivities of plain and doped Li_3ClO . Logarithm of the ionic conductivity of Li_3ClO (Y. Zhao and L. L. Daemen, *J. Am. Chem. Soc.* 2012, **134**, 15042), $\text{Li}_3\text{Cl}_{0.5}\text{Br}_{0.5}\text{O}$ (Y. Zhao and L. L. Daemen, *J. Am. Chem. Soc.* 2012, **134**, 15042), AgI (H. Mehrer, *Diffusion in Solids Fundamentals, Methods, Materials, Diffusion-Controlled Processes*, Springer Series in Solid-State Sciences, Vol. **155**, 1st ed. 2007), $\text{Li}_{3-2*0.005}\text{Ba}_{0.005}\text{ClO}$ (1st and 4th cycles) and $\text{Li}_{3-2*0.005}\text{Ba}_{0.005}\text{Cl}_{0.5}\text{I}_{0.5}\text{O}$ (1st to 3rd cycles) versus $1000/T$ [K] during heating.

[0059] **Figure 13:** The experimental ionic conductivity versus concentration for $\text{Li}_{3-2*x}\text{Ca}_x\text{ClO}$ and $\text{Li}_{3-2*x}\text{Mg}_x\text{ClO}$. These results were obtained in the stainless steel non-optimized cell. Electrodes were of stainless steel. The sample cannot be pressure tight as in the gold cell, and most likely the samples did not become glasses.

[0060] **Figure 14:** Cycle stability of the solid electrolyte versus Li-metal. **a)** Chronopotentiometry emphasizing cycling stability of a $\text{Li}/\text{Li}_{3-2*0.005}\text{Ca}_{0.005}\text{ClO}/\text{Li}$ cell at 44 °C. V_{oc} stands for open circuit voltage. The applied current (I_{app}) = $\pm 0.1\text{mAcm}^{-2}$. **b)** Zoom of the graph in a) showing the stability of the $\text{Li}/\text{Li}_{3-2*0.005}\text{Ca}_{0.005}\text{ClO}/\text{Li}$ cell.

[0061] **Figure 15:** Lattice vibration spectra of the Li_3ClO . Above: the calculated spectrum and IINS for a brass/ Li_3ClO /brass cell (blocking electrodes). Below: the IINS for a $\text{Li}/\text{Li}_3\text{ClO}/\text{Li}$ cell. The dependence from the applied frequency of the intensity of the spectra peaks highlights the jump frequency. This effect is notorious for the peaks around 350 cm^{-1} . In the calculated spectra, incoherent cross-sections of each element were not weighed. Additionally, calculations did not take into account the overtones.

Detailed description

[0062] The present disclosure describe the novel type of glasses, and method of obtain thereof.

Synthesis, Characterization and Neutron Scattering

[0063] In an embodiment, the preparation of Li_3ClO and corresponding doped solid electrolyte samples consisted in pre-drying LiCl , and Li , Mg , Ca or Ba hydroxides since most of them are highly hygroscopic, weighing the stoichiometric amounts and mixing them. Then, by adding a few deionized water drops, a paste was formed and introduced in a Teflon reactor, which was closed. The reactor was heated at $230\text{-}260^\circ\text{C}$ for 2-3 hours before it was opened to let the water evaporate for approximately 1 h. Then it was closed in glassware and allowed to cool to room temperature. A vacuum pump was used to dry the water out. A few hours are needed for the sample to become 100% of the amorphous Li_3ClO or its doped homolog. Pellets were obtained as well (with a cold press).

[0064] The part of the sample designated for EIS experiments was manipulated in air, after synthesis, since it proportionated the formation of hydroxides that were beneficial to glass formation.

[0065] The cooling processes took place in the sand bath, it was slow, in the screw pressed cell, and most of the times EIS experiments were performed during cooling. Glasses were obtained after hydroxides ran out (eventually this phase works as a confining surface, helping glass formation).

[0066] In an embodiment, samples were submitted to X-ray Diffraction (XRD) in a Panalytical instrument, using $\text{CuK}\alpha$ radiation, to determine the amount of the product present in the sample as observed in figure 1. XRD measurements were also performed after EIS experiments to determine if the material was amorphous. An example of the latter measurements can be observed in figure 2. Mg, Ca, Sr or Ba quantitative analysis was performed by means of Atomic Absorption Spectroscopy (AAS).

[0067] The high sensitivity of ionic conductivity of glasses to chemical composition is well known, therefore different doping elements and compositions $\text{Li}_{3-2x}\text{M}_x\text{HalO}$ (for example, $x = 0$ in Li_3ClO ; $x = 0.002, 0.005, 0.007$ and 0.01 for $\text{M} = \text{Mg}$ and Ca ; $x = 0.005$ for $\text{M} = \text{Ba}$ and $\text{Hal} = \text{Cl}$ or $\text{Hal} = 0.5\text{Cl} + 0.5\text{I}$) were synthesized. To obtain glasses, the samples were mounted into a gold cell (described in ionic and electronic conductivity measurements), in air atmosphere, and performed heating-cooling cycles up to 250°C . Eventually, after the first heating-cooling cycle (sample was slowly cooled down and protected from moisture), the ionic conductivity grows abruptly.

[0068] Differential Scanning Calorimetry experiments (DSC) in alumina closed crucibles and Ar flowing atmosphere, using dried powder and slightly pressed powder, show that after the first cycle, the hydroxide's melting peak cannot be distinguished anymore. The latter also shows a baseline anomaly that is probably due to the glassy transition and a clear first order transition corresponding to the melting peak of $\text{Li}_{3-0.01}\text{Mg}_{0.005}\text{ClO}$ as it can be distinguished in figure 3. A Labsys-Setaram instrument was used to perform the latter measurements.

[0069] The role of the lattice during hopping and diffusion was established by means of neutron inelastic incoherent scattering (IINS). A sample holder stick and a lithium-metal symmetric battery cell (screw brass collectors, quartz glass tube with approximately 2.5 cm of diameter, and about 3 cm of sample - distance between lithium electrodes) were

prepared for these experiments at the Los Alamos Neutron Scattering Center (LANSCE). Temperature, current and applied frequency could vary.

Ionic and Electronic Conductivity Measurements

[0070] Electrochemical Impedance Spectroscopy (EIS) was performed in a cell using either gold or stainless steel (blocking electrodes) that was heated up in a sand bath, in air atmosphere or in a glovebox in Ar and/or air (water vapour < 10%). Our gold symmetric cell has about 1.77 cm² of surface area. It consisted of two disk foils of gold separated by the sample with a thickness of about less than 5 mm (usually 1 - 3.0 mm) and it was pressed tightly with a screw. Our stainless steel cell was bulky and could contain a sample with the same dimensions as the gold one. In the latter cell, blocking electrodes could be stainless steel or copper (just for temperatures near room temperature). This cell was seldom used. The instrument used is a Bio-Logic SP240. Experiments were conducted in the temperature range 25 to 255 °C. The frequency range was 5 MHz–0.1Hz. Ionic conductivity was calculated using Nyquist impedance of an equivalent circuit containing a passive resistance in series with a constant phase element in series with circuit containing a capacitor in parallel with a resistance. The latter resistance is the solid electrolyte's resistance which plays the role of the dielectric in an ideal parallel-plate capacitor. When the resistance to ionic conduction becomes too small and Faraday's induction caused by the cables unavoidable and prominent at high frequencies, a non-ideal inductive element was added in series to the previous circuit. Figures 4 and 5 show EIS measurements' data for a sample containing $\text{Li}_{3-2*0.005}\text{Ba}_{0.005}\text{ClO}$ tested in a symmetric gold cell as previously described, for different cycles and temperatures. Tests in the empty cell and with AgI were performed to control the procedures and establish analysis methods.

[0071] Cyclic voltammetry tests were performed in the stainless steel cell with a lithium electrode as reference electrode and a counter electrode of copper or stainless steel. Chronopotentiometry was performed in a lithium symmetric cell equivalent to the gold

one previously described. Three measurements intercalated by an open circuit interval were performed containing 20 cycles each of 40 minutes (20 minutes at a positive current and 20 minutes at a negative current). Measurements were performed in an Ar-dry glovebox.

Calculations

[0072] In an embodiment, density Functional Theory (DFT) calculations with Projector Augmented Wave (PAW) pseudopotentials as implemented in the Vienna Ab initio Simulation Package (VASP) code, were performed. A plane wave cut-off of 500 eV, and k-mesh of 4×4×4 were used. Calculations were implemented for crystalline electrolytes in real space and were performed within the P1 space group supercells containing at least 134 atoms. Some supercells contained as many atoms as possible, 270 atoms or more, to allow better approximations with the real Ba^{2+} , Ca^{2+} or Mg^{2+} concentrations. The Generalized Gradient Approximation (GGA), and the Perdew–Burke–Ernzerhof (PBE) functional were used, and no magnetic moments were included in the model. The Heyd-Scuseria-Ernzerhof (HSE06) functional was used to calculate band structure and electronic Density of States (DOS) to determine the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO).

[0073] Ionic conduction in solids occurs by ion hopping from a crystal lattice site to another by vacancy mechanism; therefore it is convenient to have a partial occupancy of energetically equivalent or near-equivalent sites. In favourable structures, the defects may be mobile, leading to high ionic conductivity. While the rate of ion transport in a crystalline solid is dictated by the diffusivity and concentration of the vacancies mediating ion transport, the open structure of inorganic glassy materials facilitates the process of ionic hopping and results in enhanced conductivity. Inorganic glasses thus represent an attractive material class for electrolyte applications. An advantage of inorganic glasses is single-cation conduction; they belong to the so-called decoupled

systems in which the mode of ionic conduction relaxation is decoupled from the mode of structural relaxation.

[0074] Comparing the temperature dependence of the relaxation time of the structure and conduction for inorganic glassy liquids with, say, organic polymers shows that the former exhibit a decoupling character capable of yielding higher single ion conduction in the glassy state (figure 6). Single cation conduction is associated with fewer side reactions and significantly wider electrochemical stability windows, which can be up to 10 V.

[0075] Electronic properties, such as the band structure and Density of States (DOS) were also calculated by means of DFT using the GGA functionals and the Hyed-Scuseria-Erznerhof (HSE06) functionals. In figure 7a, electronic band structure calculations using GGA are shown as well as the correspondent band gap of 4.74 eV. Figure 7b shows a HSE06 calculation and its correspondent band gap, E_g , value of 6.44 eV, which indicates a wide range of electrochemical stability for the crystalline material. (The band gap calculated using HSE06 hybrid functional seems to agree more with experiments than the one calculated using GGA functional as generally expected. Figure 7c shows voltammetry graphs correspondent to four experiments in which it can be observed that no substantial oxidation of Li_3ClO or $\text{Li}_{3-2*0.005}\text{Ba}_{0.005}\text{ClO}$ at 130 °C can be detected up to 8 V, which covers all the negative-positive electrode-pair voltage windows for Li batteries. The electrical conductivity was obtained from these voltammetry cycles using the Hebb–Wagner (H-W) method. In a polarization measurement, under steady state conditions, in a $\text{Li}/\text{Li}_3\text{ClO}/\text{Cu}$ cell with a ion blocking electrode such as Cu, $\partial I/\partial V = -A\sigma_e/d$ where I is the electrical current, V is the applied voltage (E in figure 7c), A the cross-sectional area of the electrolyte (with $j = I/A$), d the thickness of the electrolyte and σ_e its electronic conductivity. The derivative $\partial I/\partial V$ yields de electronic conductivity in the electrolyte near the end adjacent to the blocking electrode.

[0076] For Li_3ClO at 130 °C in the 1.4-2.5 V interval, $\sigma_e = 9.2 \times 10^{-9} \text{ Scm}^{-1}$, and in the interval 2.55-2.82 V, $\sigma_e = 1.18 \times 10^{-7} \text{ Scm}^{-1}$. For $\text{Li}_{3-2*0.005}\text{Ba}_{0.005}\text{ClO}$ at 130 °C for the first cycle and over the interval 4.1-5.97 V, $\sigma_e = 6.77 \times 10^{-8} \text{ Scm}^{-1}$. For the second cycle, and in the range 2.07-5.37 V, $\sigma_e = 1.05 \times 10^{-8} \text{ Scm}^{-1}$. The latter yields a transport number, $t_i = \sigma_i / (\sigma_i + \sigma_e)$, near unity as required for good quality solid electrolytes; σ_i is the ionic conductivity.

[0077] From the experimental study and DFT analysis, it was observed that the ionic radius of the doping atom plays an important role in the liquid/solid-like transition; namely, the larger the doping ion radius the lower the glass transition temperature as it is shown in figure 8. This effect arises due to the disorder that the impurity introduces in the crystal structure, especially the part related to the enthalpy. Consequently, very high ionic conductivities can be obtained at relatively low temperatures, e.g. 25 °C or lower, in high ionic radius doped glassy samples.

[0078] Figure 9 shows the ionic conductivities for solid-like and supercooled liquid samples of plain and doped electrolytes. In figure 9a, not only can the glass transitions be observed, but also the ionic conductivity hysteresis resulting from heating the followed by cooling.

[0079] A peak immediately before the ergodicity breaking transition is observed as well. Ionic conductivity dispersion, probably due to decoupling of diffusivity from viscosity, is observed in the non-Arrhenius regime in figures 9a and 9b. For a material with ionic conductivity, σ , that can be measured above and below T_g , the extrapolated data for the σT term in the two domains should give identical values when the temperature, T , approaches infinity. This finding is verified in the current work and can be observed in figure 10.

[0080] Li_3ClO behaves as a solid-like glass (following Arrhenius law) below T_g ; above T_g it becomes a supercooled liquid showing a non-Arrhenius behaviour. It was observed a

similar kind of behaviour for the doped material, although this behaviour depends on the history of the material as well (as it may be observed from the comparisons between the 2nd and 4th cycles in figure 9b for $\text{Li}_{3-2} \cdot 0.005 \text{Ba}_{0.005} \text{ClO}$). Moreover, doping is not necessary to obtain a glass, but it is helpful to get it at lower temperatures.

[0081] A $\text{Li}_{3-2} \cdot 0.005 \text{Ba}_{0.005} \text{ClO}$ sample that slowly cooled down after the 3rd heating/cooling cycle – submitted to EIS measurements on heating – shows unusually high ionic conductivity at 25 °C as expected and as it is shown on figure 9b (+ symbols). In figure 11 the pseudo-Arrhenius curve for the latter sample in the 4th cycle can be observed. Although linear behaviour it is not expected, at least above T_g , activation energies as low as 0.06 eV can be observed in the temperature range of 35 °C to 74 °C. The glass transition can be observed in figure 9b (× symbols) and in figure 11, although it is much smoother than in previous cycles, probably indicating higher similitude between the supercooled liquid and the solid-like material highlighting that the glass dynamics depends very highly of the cooling rate, among other factors.

[0082] Nonetheless, for lithium batteries, the glassy phase, $\text{Li}_{3-2} \cdot x \text{M}_x \text{HalO}$, offers higher ionic conductivity as it is shown in figure 9b and superior chemical stability compared with those materials, as shown in figure 7. Furthermore, unlike Ti and Ge containing materials, $\text{Li}_{3-2} \cdot x \text{M}_x \text{HalO}$ does not react with lithium-metal and offers a wider window of electrochemical stability.

[0083] Moreover, from the air, the only element that should be avoided - at least after synthesizing a highly conductive glass - should be water vapour, which makes our electrolyte an excellent candidate to be used in lithium-air batteries with lithium-metal anode.

[0084] Doping with Ba^{2+} enhances this effect even further since larger doping ion radius in this case results in higher anisotropy of the lattice, and this seems to be in favour of higher ionic conductivity. However, such an enhancement is limited by other

mechanisms such as the hopping ion trapping in the vicinity of the doping ion; which is less likely to occur in $\text{Li}_{3-2x}\text{Ba}_{0.005}\text{Cl}_{0.5}\text{I}_{0.5}\text{O}$ since the presence of I⁻ in the centre of the cube will expand the lattice, as described to occur in $\text{Li}_3\text{Cl}_{0.5}\text{Br}_{0.5}\text{O}$. Figure 13 shows an optimal composition (x) for $\text{Li}_{3-2x}\text{Mg}_x\text{ClO}$ and $\text{Li}_{3-2x}\text{Ca}_x\text{ClO}$.

[0085] A symmetric Li/ $\text{Li}_{3-2x}\text{Ca}_{0.005}\text{ClO}$ /Li cell was configured to demonstrate the cyclability and long-term compatibility of $\text{Li}_{3-2x}\text{Ca}_{0.005}\text{ClO}$ with metallic lithium. Figure 14a and b shows the voltage profile of the cell cycled near room temperature, at 44 °C. At this temperature, the cell presented a voltage of 46.0 mV at a current density of 0.1 mAcm^{-2} . The direct current (dc) conductivity derived from the symmetric cell was 0.27 mScm^{-1} - obtained by chronopotentiometry as shown in figures 14a and 14b - which is relatively close to the alternating-current (ac) conductivity of 0.85 mScm^{-1} obtained from electrochemical impedance spectroscopy measurements extrapolated for 44 °C. Small interfacial resistance between the lithium electrode and the solid electrolyte was observed, further confirming that the $\text{Li}_{3-2x}\text{Ca}_{0.005}\text{ClO}$ is completely compatible with metallic lithium. The cell showed excellent cyclability at 44 °C as illustrated in figures 14a and 14b, not showing signs of resistance increase during more than 460 h being much more stable than many other electrolytes. These results prove the ability of the glass to be used in Li batteries for electronic device.

[0086] Moreover, the ionic conductivity increases until above 220 h, as shown in figure 14a, indicating that, even at 44 °C, the sample will become partially amorphous eventually due to electrochemical cycling.

[0087] The solid electrolyte Li_3ClO structure employs abundant Li^+ (high concentration of mobile charge carriers) and non-toxic elements and is easily processed, using wet chemistry at relatively low temperatures (240 °C to 310 °C), which is another argument for inexpensive and environmentally-friendly fabrication. Samples were annealed in a pressure tight wafer of Au - in the cell setup - at up to 250°C. Seldom was it needed more than one cycle for the sample to become partially vitreous and highly conductor. A glassy

surface and structure is visible to the eyesight after heating and cooling in figure 6 and as denoted in figure 2. The sample can become transparent on melting.

[0088] It is likely that the precursor hydroxides have an important role in product formation promoting the contact between the reagent compounds powders. These hydroxides are antiperovskite structures, most of them following the general formula $\text{Li}_{3-n}(\text{OH})_n\text{Hal}$. Their ionic conductivities are considerably smaller than the $\text{Li}_{3-2*x}\text{M}_x\text{HalO}$ vitreous electrolytes. In fact, the hydroxide recurrently formed was $\text{Li}_5(\text{OH})_3\text{Cl}_2$ and/or $\text{Li}_4(\text{OH})_3\text{Cl}$ but it transforms into $\text{Li}_{3-2*x}\text{M}_x\text{HalO}$ after the first cycle as it can be inferred from Differential Scanning Calorimeter (DSC) measurements shown in figure 3.

[0089] The glass transition of $\text{Li}_{3-2*0.005}\text{Mg}_{0.005}\text{ClO}$ in DSC measurements seems to occur at $T_g \sim 136^\circ\text{C}$ as observed in figure 3, which is in agreement with the ionic conductivity results. Melting of $\text{Li}_{3-2*0.005}\text{Mg}_{0.005}\text{ClO}$ occurs at $T_m = 269^\circ\text{C}$ as the correspondent endothermic peak demonstrates in figure 3. A glass transition, T_g , is linked via an empirical relationship with the melting temperature T_m , $T_g \sim (2/3)T_m$. We obtained, $T_g/T_m \sim 0.75$, by means of DSC, and $T_g/T_m \sim 0.71$, by conductivity measurements, which is a good approximation to the empirical factor of 0.67.

[0090] The phonon density of states was calculated using DFT and compared with Incoherent Inelastic Neutron Spectroscopy (IINS) spectra. The role of the lattice during hopping and diffusion was established experimentally as a function of electrodes' temperature, voltage and applied frequency. Most of the vibration modes maintain a constant intensity with the applied frequency as observed in figure 15. The effect is likely to be associated with the crystalline behaviour since the experimental conditions were not favourable to glass formation.

[0091] For $320\text{-}380\text{ cm}^{-1}$ wavenumbers ($\sim 1013\text{ Hz}$), the intensity varies with the applied frequency, being higher at $f = 100\text{ Hz}$ and lower at $f = 104\text{ Hz}$.

[0092] This is most likely the jump frequency ($\sim 10^{13}$ Hz) as the eigenvectors associated with phonons suggest, which implies that at higher frequencies more ions have jumped already.

[0093] It is important to mention that the Li_3ClO -crystalline density is as low as 2.07 gcm^{-3} ($\text{Li}_{3-2*0.005}\text{Ca}_{0.005}\text{ClO}$ -crystalline is 2.09 gcm^{-3} and $\text{Li}_{3-2*0.005}\text{Ba}_{0.005}\text{ClO}$ -crystalline is 2.28 gcm^{-3}). At 200°C Li_3ClO density is $\sim 1.96 \text{ gcm}^{-3}$. Liquid electrolytes in lithium-ion batteries consist of lithium salts, such as LiPF_6 (1.50 gcm^{-3}) or LiClO_4 (2.42 gcm^{-3}) in an organic solvent, such as ethylene carbonate (1.3 gcm^{-3}) or dimethyl carbonate (1.07 gcm^{-3}).

[0094] Although the cell will not be lighter just by replacing the liquid by equal volume of the solid electrolyte and even if moisture has to be avoided likewise; merely a thin film of solid electrolyte is needed with no separator or sophisticated packaging resulting in a lighter battery.

[0095] The present results show that the new $\text{Li}_{3-2x}\text{M}_x\text{HalO}$ glassy electrolyte or $\text{Na}_{3-2x}\text{M}_x\text{HalO}$ glassy electrolyte (in which M is a higher valent cation like Ca^{2+} , Sr^{2+} , Mg^{+2} or Ba^{2+} , and Hal is a halide like Cl^- , or a mixture of halide ions like F^- , Cl^- , Br^- , I^-) has an extremely high ionic conductivity that is well above the lithium-ion conductivity of any other superionic conductor at $T = 25^\circ\text{C}$ (25 mScm^{-1}).

[0096] It is the first time that a glass formed from an antiperovskite crystal is presented.

[0097] In addition, this new electrolyte is chemically very stable with respect to Li-metal (more than 260 cycles), proving that it can be used in consumer electronic devices, and it is a light, good electronic insulator, non-flammable and contains no pollutants. Moreover, this novel electrolyte is easy to synthesize, thermally stable and electrochemical stable at least up to 8 V. It is thus promising for applications requiring

batteries with high powers and energy densities, especially, for hybrid electric and pure electric vehicles.

[0098] The present invention is not, obviously, in any way restricted to the herein described embodiments and a person with average knowledge in the area can predict many possibilities of modification of the same invention and substitutions of technical characteristics by others equivalent, depending on the requirements of each situation, as defined in the appended claims.

[0099] The embodiments described above can be combined with each other.

CLAIMS

What is claimed is:

1. A solid electrolyte glass comprising compound of formula $R_{3-2x}M_x\text{HalO}$ wherein
R is selected from the group consisting of lithium and sodium;
M is selected from the group consisting of magnesium, calcium, strontium and barium;
Hal is selected from the group consisting of fluorine, chlorine, bromine, iodine and mixtures thereof;
x is the number of moles of M and $0 < x \leq 0.01$;
and the solid electrolyte glass has a glass transition point;
wherein a glassy phase of the solid electrolyte glass is obtained by heating- cooling cycles up to 250 °C.
2. The electrolyte glass according to claim 1 wherein R is lithium.
3. The electrolyte glass according to claim 1 wherein R is sodium.
4. The electrolyte glass according to claim 1 or 2 comprising an ionic conductivity of at least 13 mScm⁻¹ at 25 °C.
5. The electrolyte glass according to claim 4 comprising an ionic conductivity of 13-60 mScm⁻¹ at 25 °C.
6. The electrolyte glass according to claim 1 or 2 comprising an ionic conductivity of 17-105 mScm⁻¹ at 25 °C.
7. The electrolyte glass according to claim 1 or 2 comprising an ionic conductivity of at least 31 mScm⁻¹ at 25 °C.
8. The electrolyte glass according to any one of claims 1 to 7 wherein x is 0.002, 0.005, 0.007 or 0.01.
9. The electrolyte glass according to any one of claims 1 to 8 wherein Hal is a mixture of chlorine and iodine.

10. The electrolyte glass according to any one of claims 1 to 8 wherein $\text{Hal} = 0.5\text{Cl} + 0.5\text{I}$.
11. The electrolyte glass according to any one of claims 1 to 8 wherein Hal is a mixture of fluorine and iodine.
12. The electrolyte glass according to any one of claims 1 to 8 wherein R is lithium, M is barium, Hal is chlorine and x is 0.005.
13. The electrolyte glass according to any one of claims 1 to 8 wherein R is lithium, M is barium, Hal is a mixture of chlorine and iodine, x is 0.005.
14. The electrolyte glass according to any one of claims 1 to 8 wherein R is sodium, M is barium, Hal is chlorine and x is 0.005.
15. An electrochemical device comprising the electrolyte glass referred in any one of the claims 1-14.
16. A capacitor comprising the electrolyte glass referred in any one of the claims 1-14.
17. A battery comprising the electrolyte glass referred in any one of the claims 1-14.
18. An electrochemical device comprising at least one capacitor as referred in claim 16 and at least one battery as referred in claim 17.
19. A method for synthesizing a glass electrolyte comprising a compound of formula $\text{R}_{3-2x}\text{M}_x\text{HalO}$ wherein
 - R is lithium;
 - M is selected from the group consisting of magnesium, calcium, strontium and barium;
 - Hal is selected from the group consisting of fluorine, chlorine, bromine, iodine and mixtures thereof;
 - x is the number of moles of M and $0 < x \leq 0.01$;
 comprising the following steps:

mixing a stoichiometric quantity of LiHal, LiOH, and one of the following compounds: Mg(OH)₂, Ca(OH)₂, Sr(OH)₂ and Ba(OH)₂;

adding to said mixture deionized water and mixing to form a solution in a closed container;

heating said solution up to 250 °C during 2-8h;

opening the container to evaporate the excess of water in the heated product.

20. The method according to claim 19 further comprising:

introducing the synthesized glass electrolyte between electrodes of an electrochemical device;

heating the glass electrolyte up to 170-240 °C and cooling.

21. A method for synthesizing a glass electrolyte comprising a compound of formula R_{3-2x}M_xHalO wherein

R is sodium;

M is selected from the group consisting of magnesium, calcium, strontium and barium;

Hal is selected from the group consisting of fluorine, chlorine, bromine, iodine and mixtures thereof;

x is the number of moles of M and $0 < x \leq 0.01$;

comprising the following steps:

mixing a stoichiometry quantity of NaHal, NaOH and one of the following compounds: Mg(OH)₂, Ca(OH)₂, Sr(OH)₂ or Ba(OH)₂;

adding to said mixture deionized water and mixing to form a solution in a closed container;

heating the solution up to 70-90 °C for 2-8h;

increasing the temperature up to 190-250 °C for 2-8h, maintaining said temperature for at least 2h;

opening the container to evaporate the excess water in the heated product.

22. The method according to claim 21 further comprising:

introducing the synthesized glass electrolyte between electrodes;

heating the glass up to 190-230 °C and cooling.

23. A method for synthesizing a glass electrolyte comprising a compound of formula $R_{3-2x}M_xHalO$ wherein

R is lithium;

M is selected from the group consisting of magnesium, calcium, strontium and barium;

Hal is selected from the group consisting of fluorine, chlorine, bromine, iodine and mixtures thereof;

x is the number of moles of M and $0 < x \leq 0.01$;

comprising the following steps:

mixing a stoichiometry quantity of LiHal, LiOH and one of the following compounds: $Mg(OH)_2$; $Ca(OH)_2$; $Sr(OH)_2$ or $Ba(OH)_2$;

adding to said mixture deionized water and mixing to form a solution in a closed container;

heating said solution up to 250 °C during 2-8h;

opening the container to evaporate the excess of water in the heated product.

24. The method according to claim 23 further comprising:

introducing the synthesized glass electrolyte between electrodes;

heating the glass up to 170-240 °C and cooling.

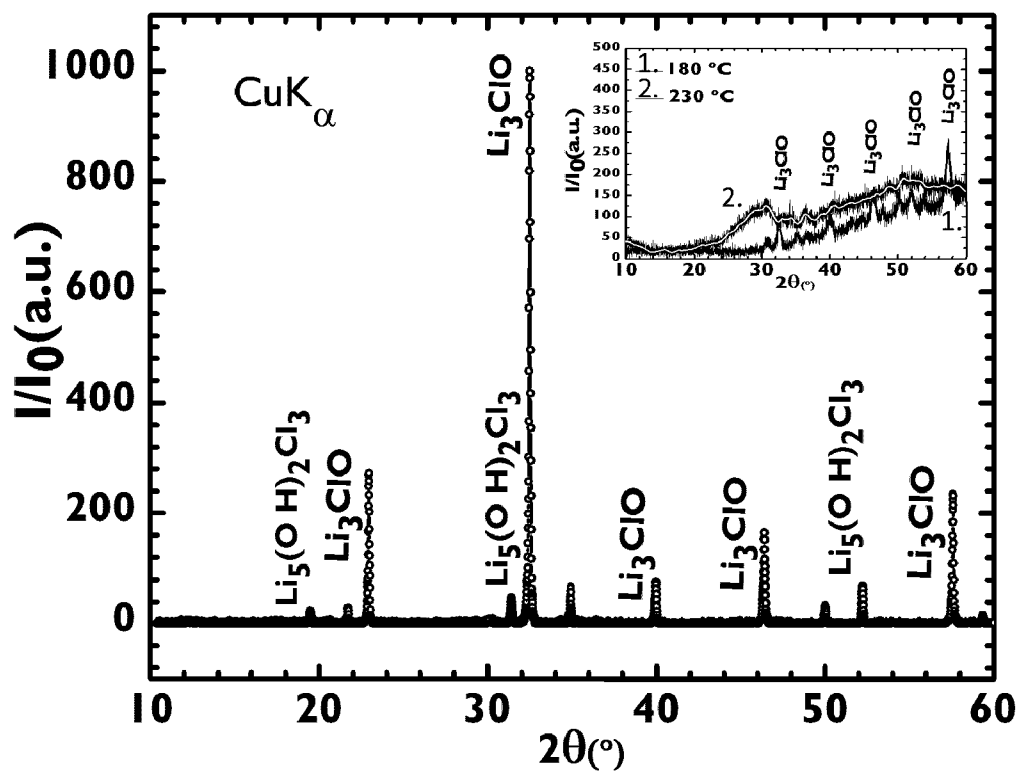


Fig. 1

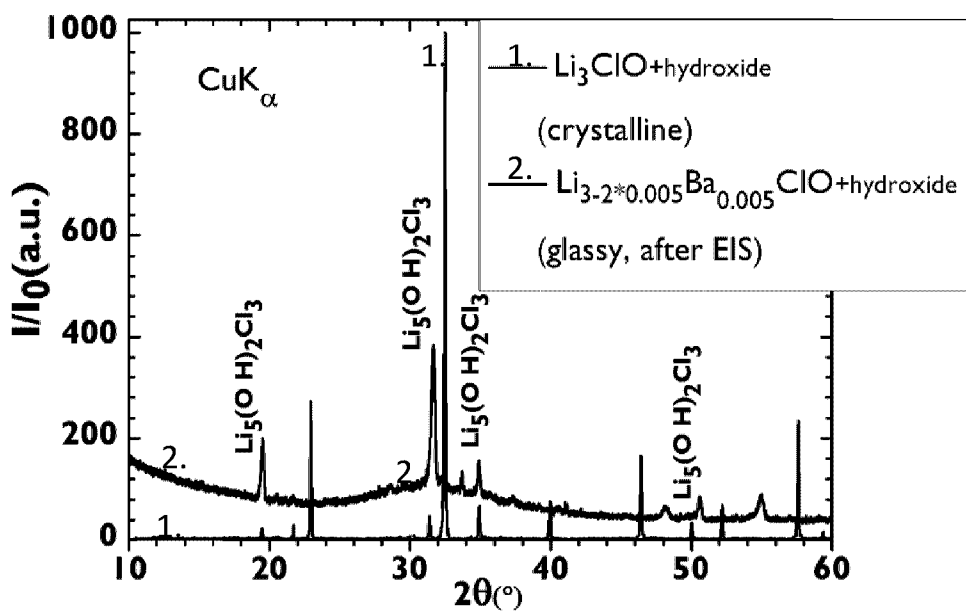


Fig. 2

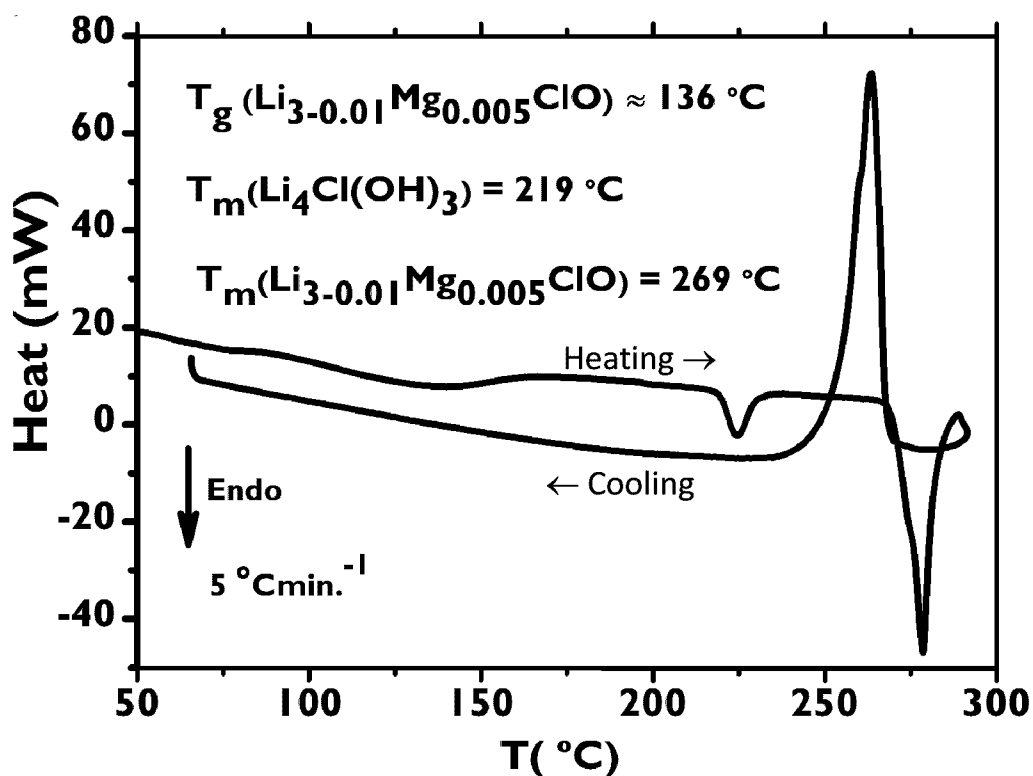


Fig. 3

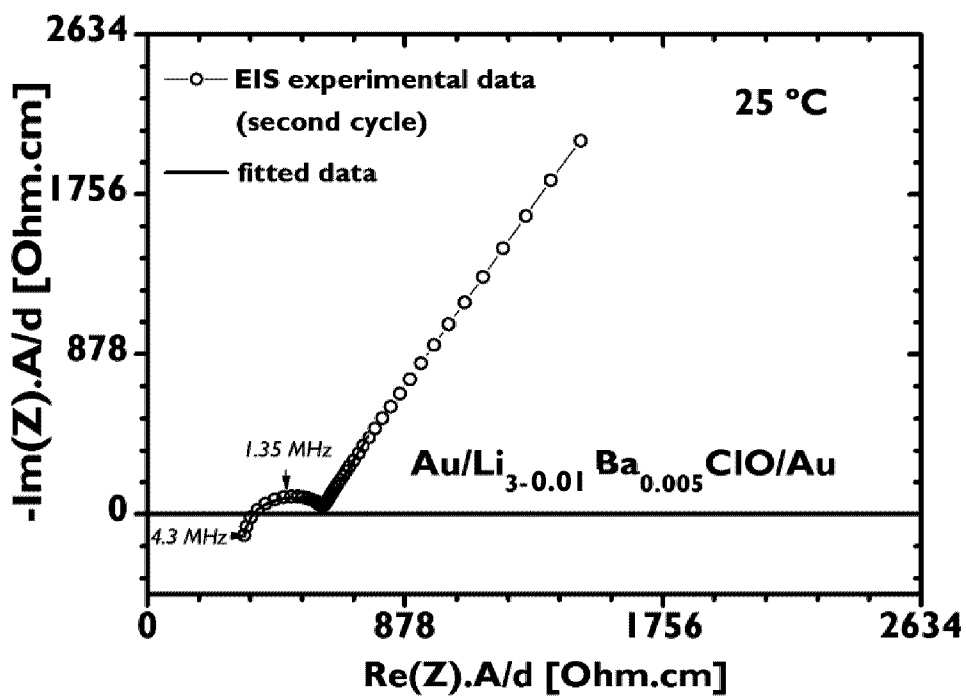


Fig. 4

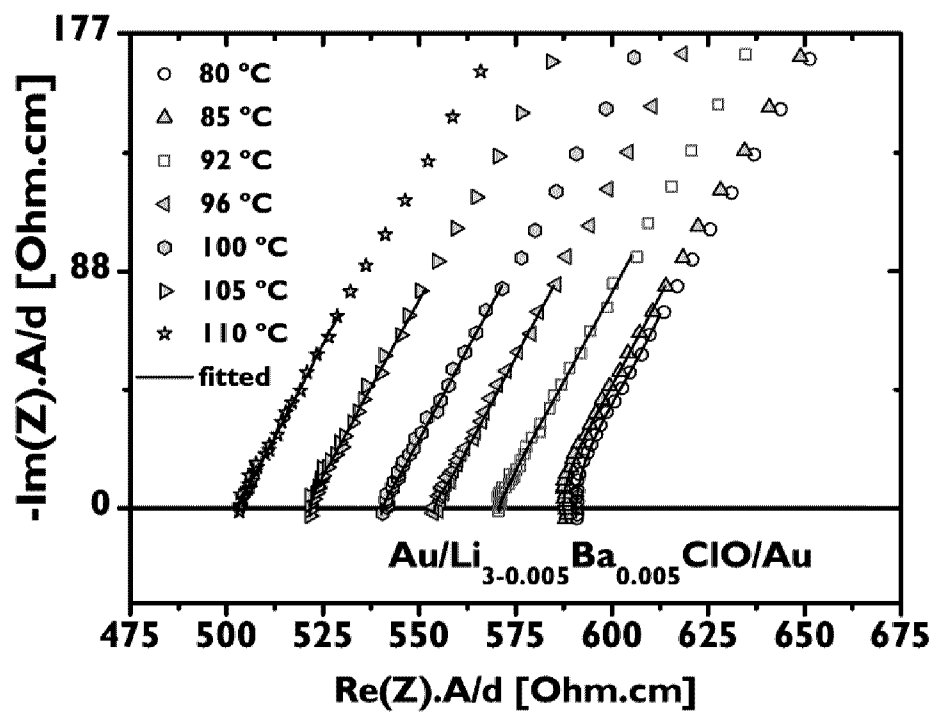


Fig. 5

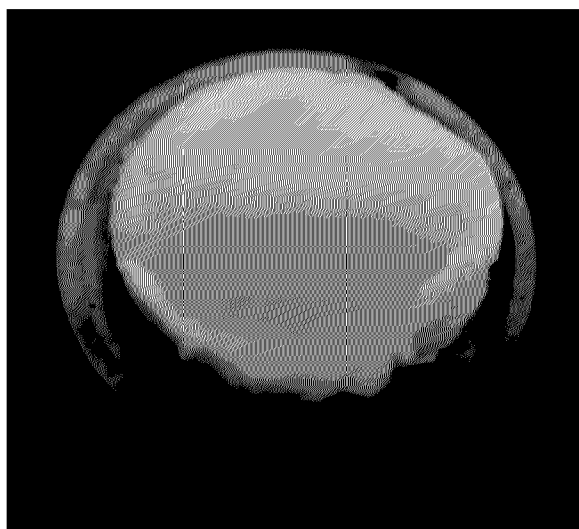


Fig. 6

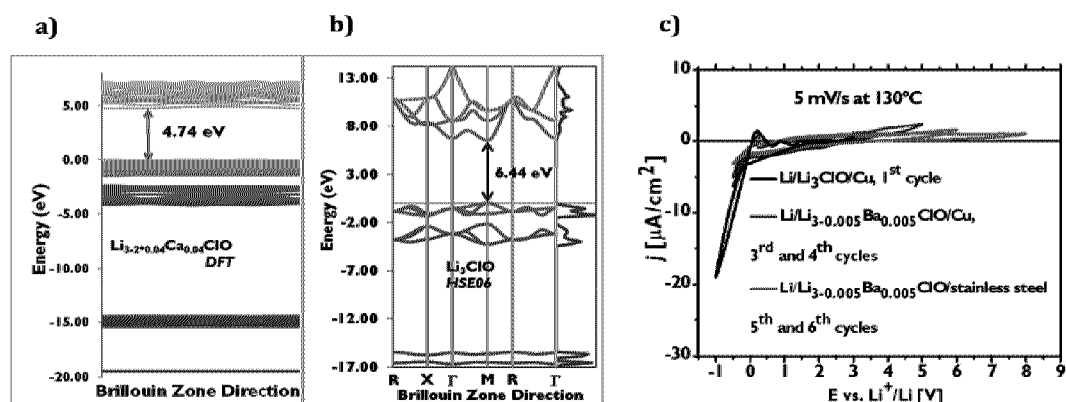


Fig. 7

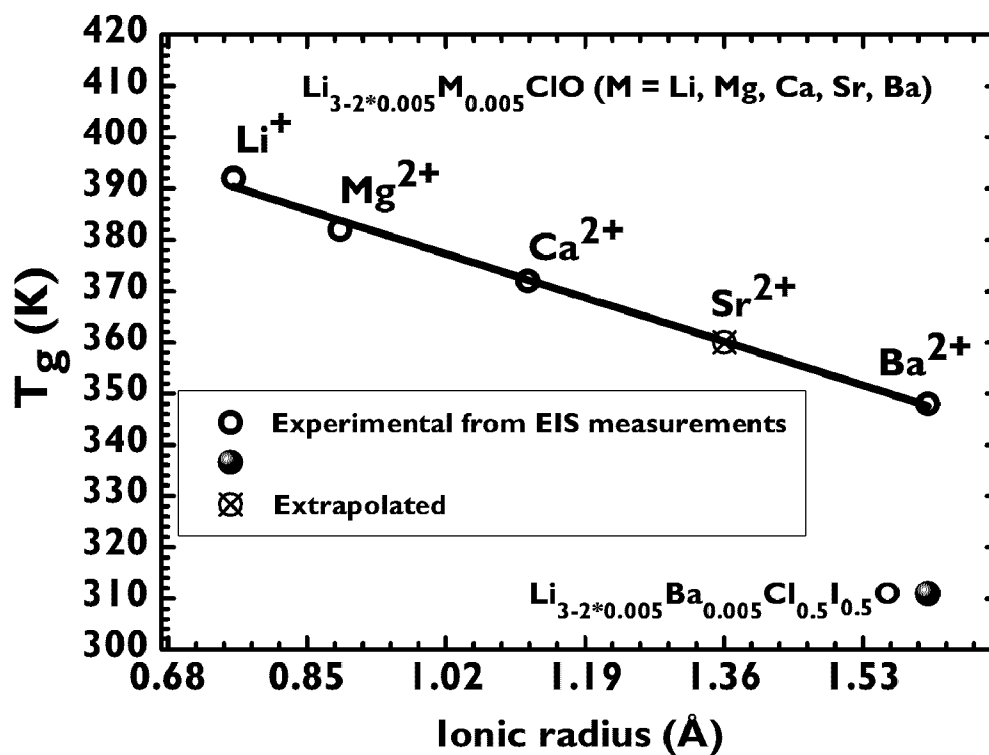


Fig. 8

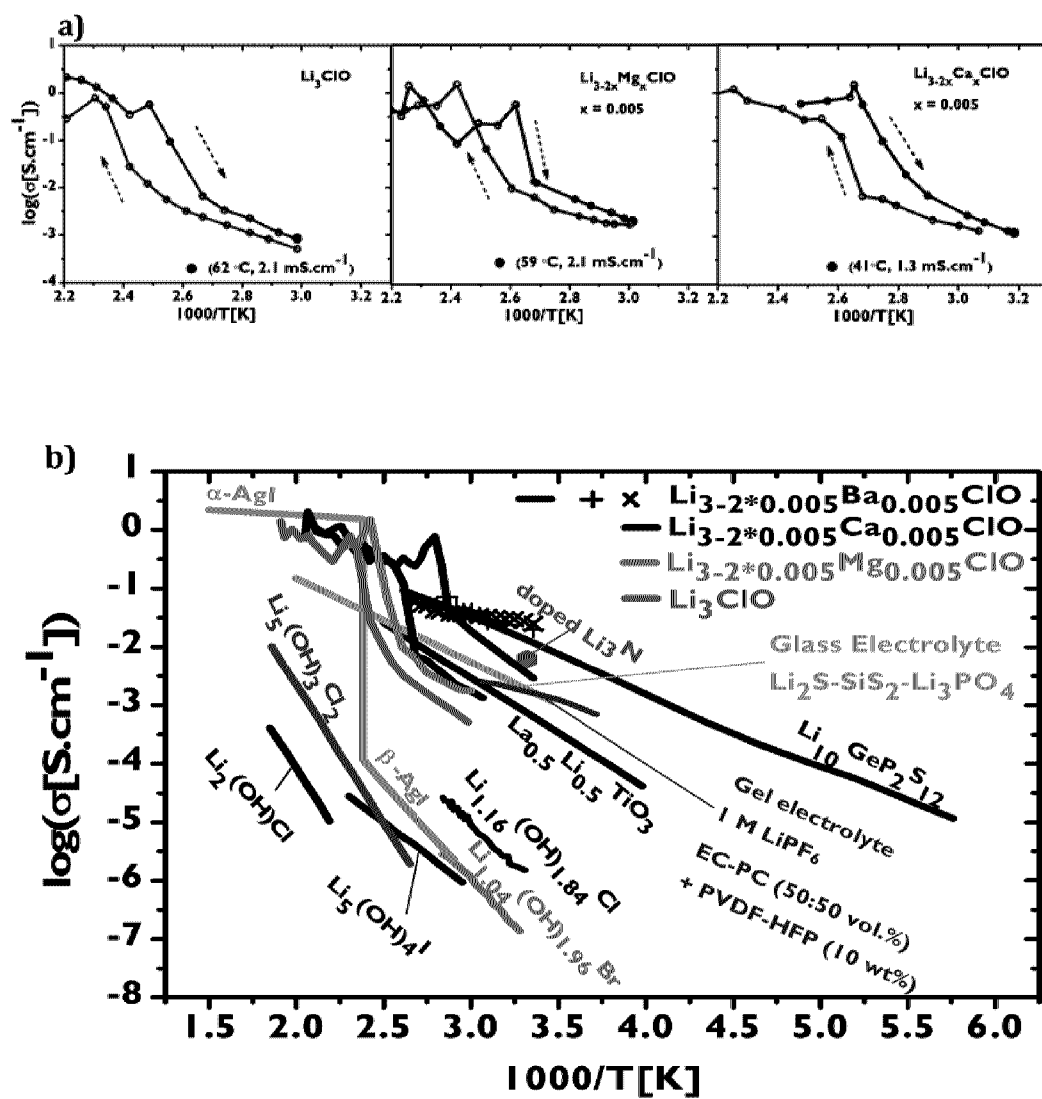


Fig. 9

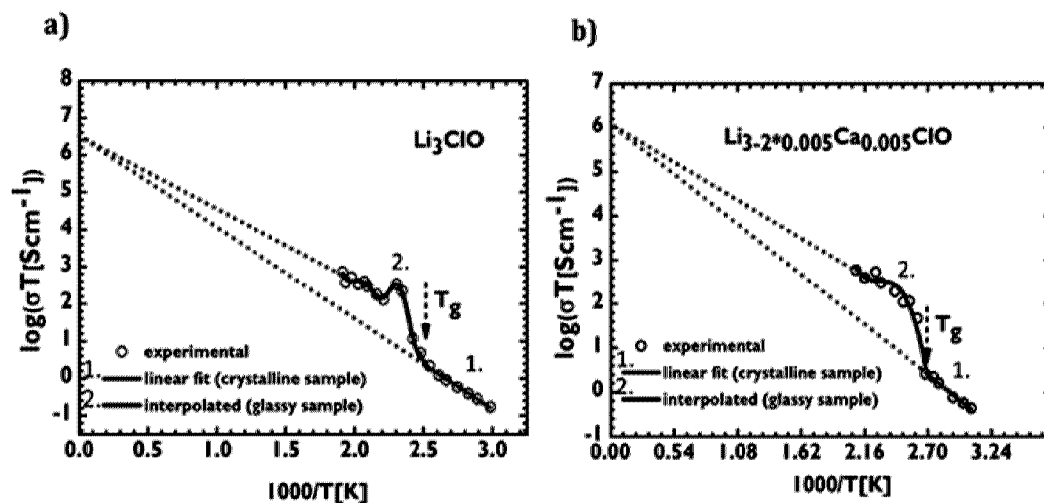


Fig. 10

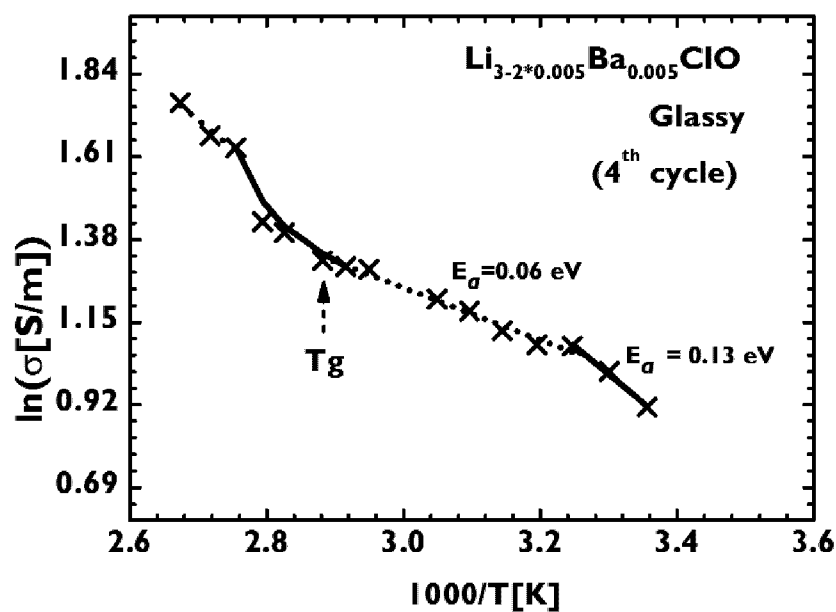


Fig. 11

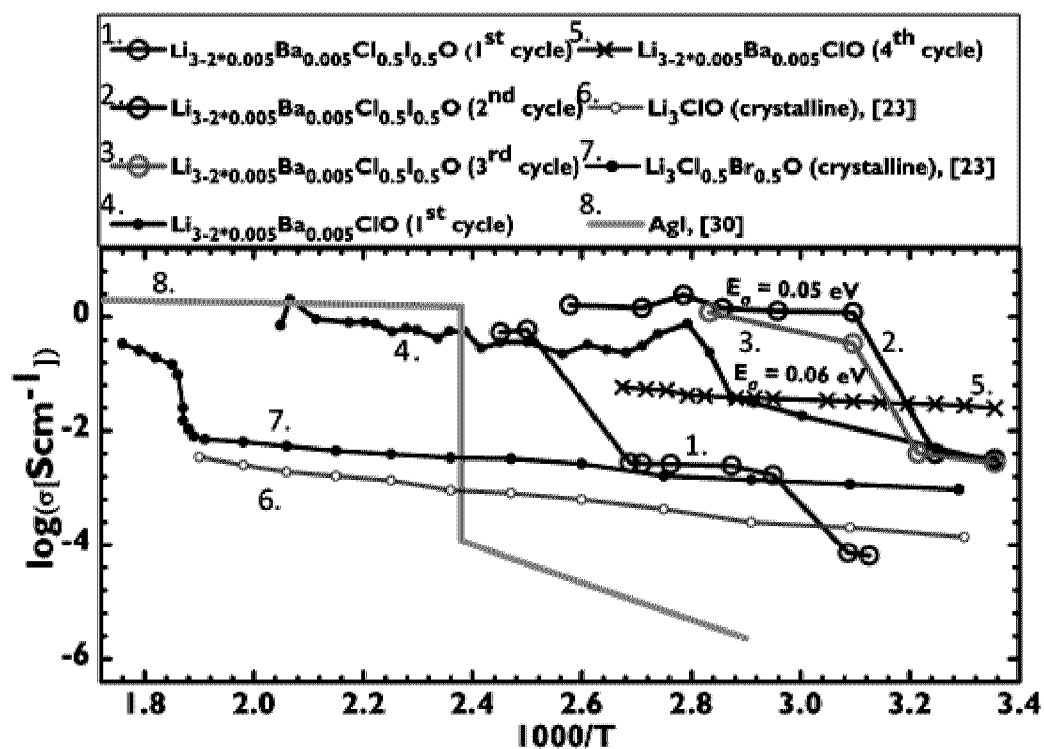


Fig. 12

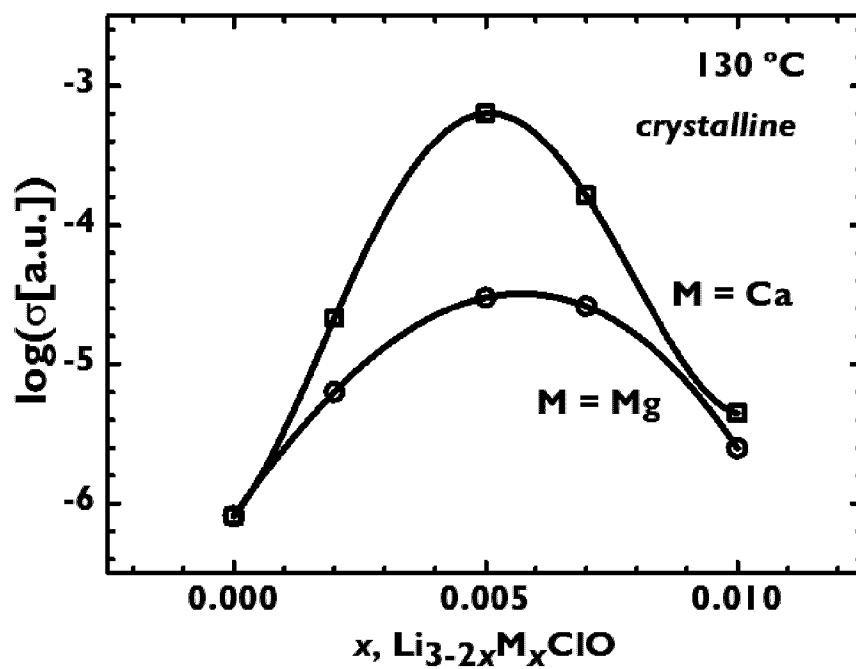


Fig. 13

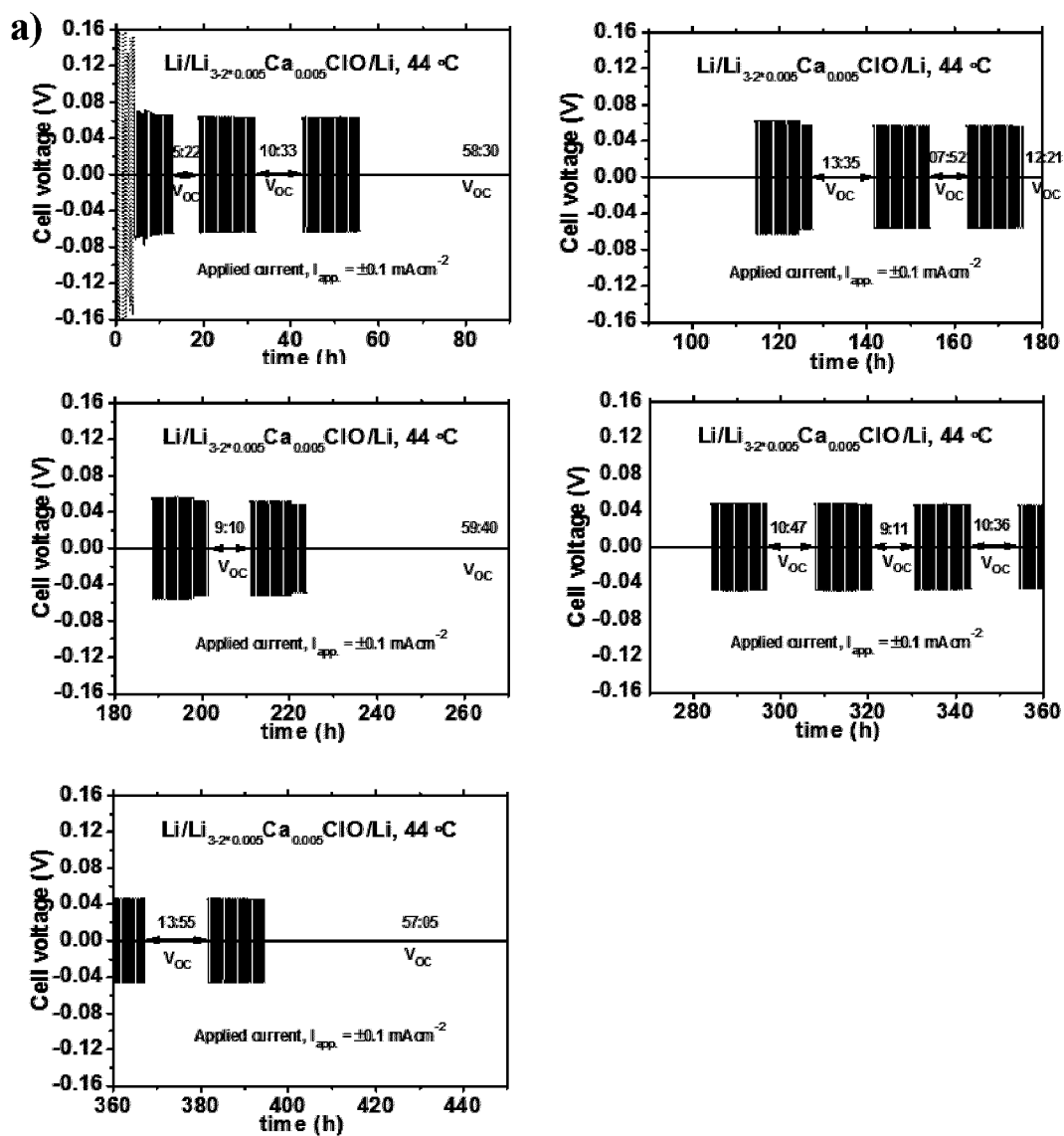


Fig. 14a

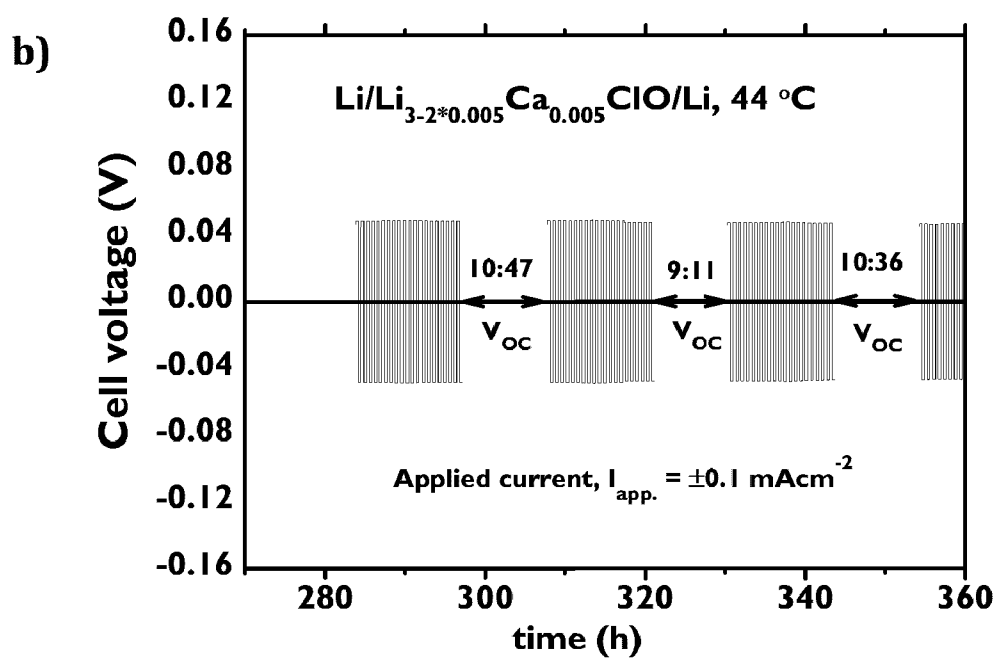


Fig. 14b

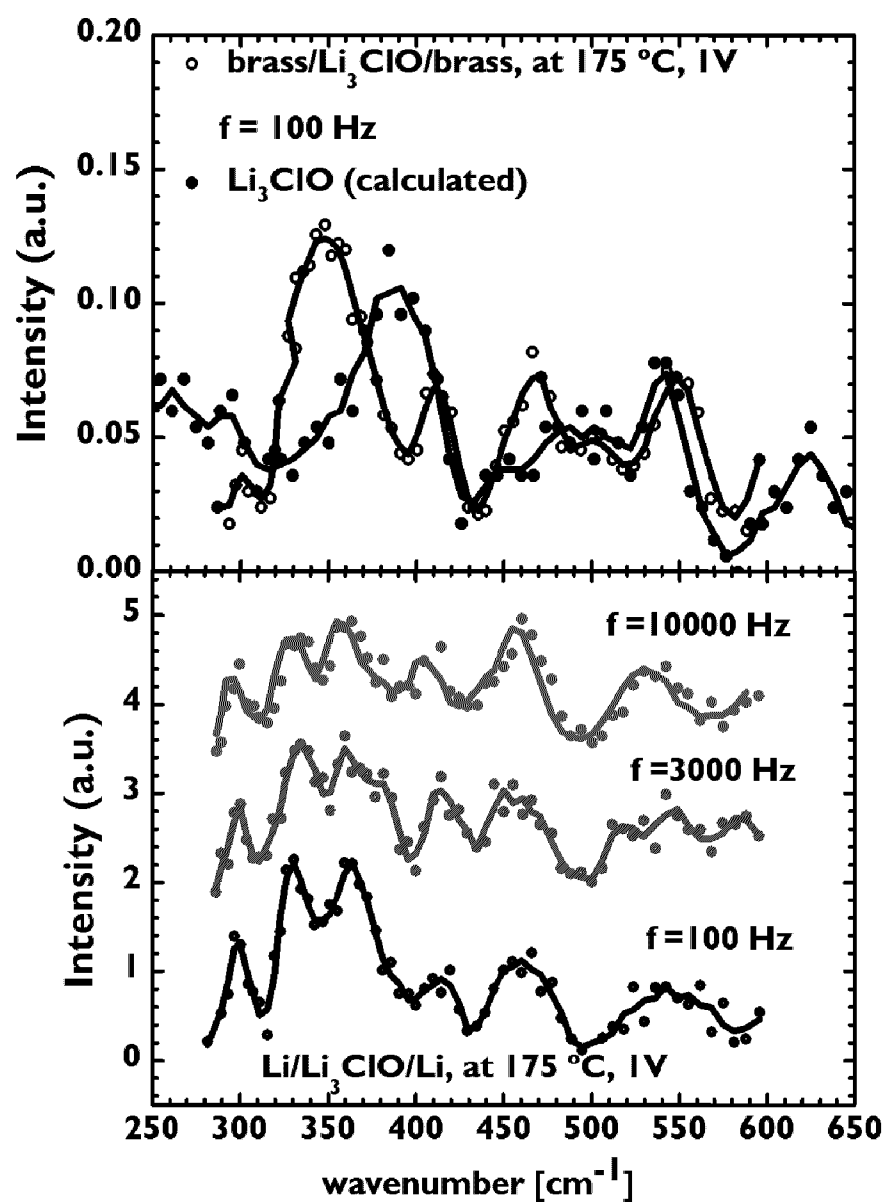


Fig. 15

