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(54) **SOLID-STATE ELECTROLYTES BASED ON LITHIUM HALIDES FOR ALL-SOLID-STATE LITHIUM-ION BATTERY OPERATING AT ELEVATED TEMPERATURES**

(60) Provisional application No. 62/672,445, filed on May 16, 2018.

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(52) **U.S. Cl.**
CPC .. **H01M 10/0562** (2013.01); **H01M 2004/027** (2013.01); **H01M 2300/0068** (2013.01); **H01M 10/052** (2013.01)

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(57) **ABSTRACT**

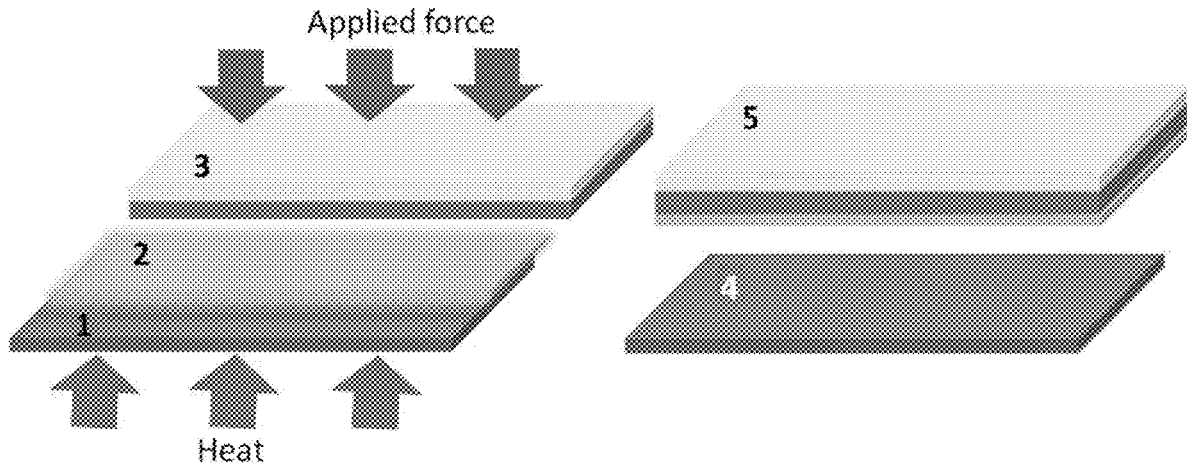
(21) Appl. No.: **16/589,429**

The present disclosure relates to a manufacturing process of the solid-state glass-ceramic electrolytes, known in the art as antiperovskites. Specifically, the disclosure is focused on manufacturing of the solid-state electrolyte from the corresponding precursors directly on the active electrode surface of an electrochemical device, specifically anode or cathode of the lithium-ion or lithium metal batteries.

(22) Filed: **Oct. 1, 2019**

Related U.S. Application Data

(63) Continuation-in-part of application No. 16/413,290, filed on May 15, 2019.



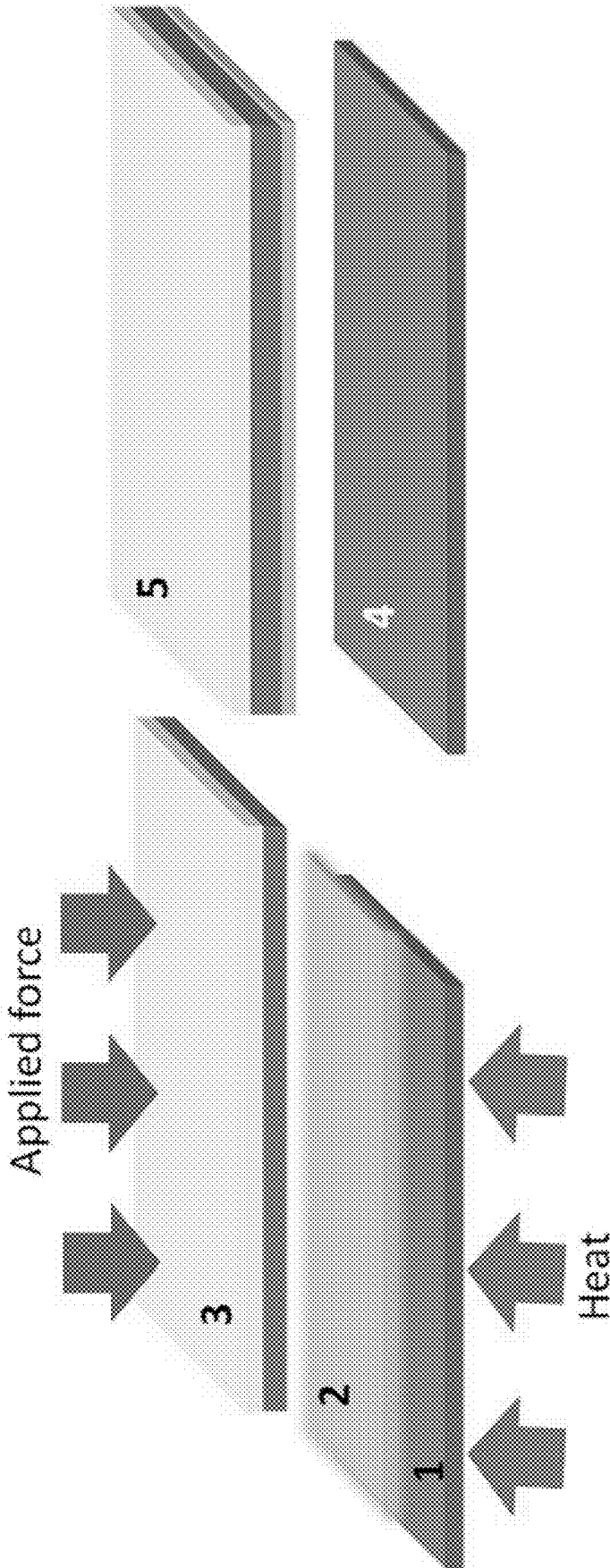


FIG. 1

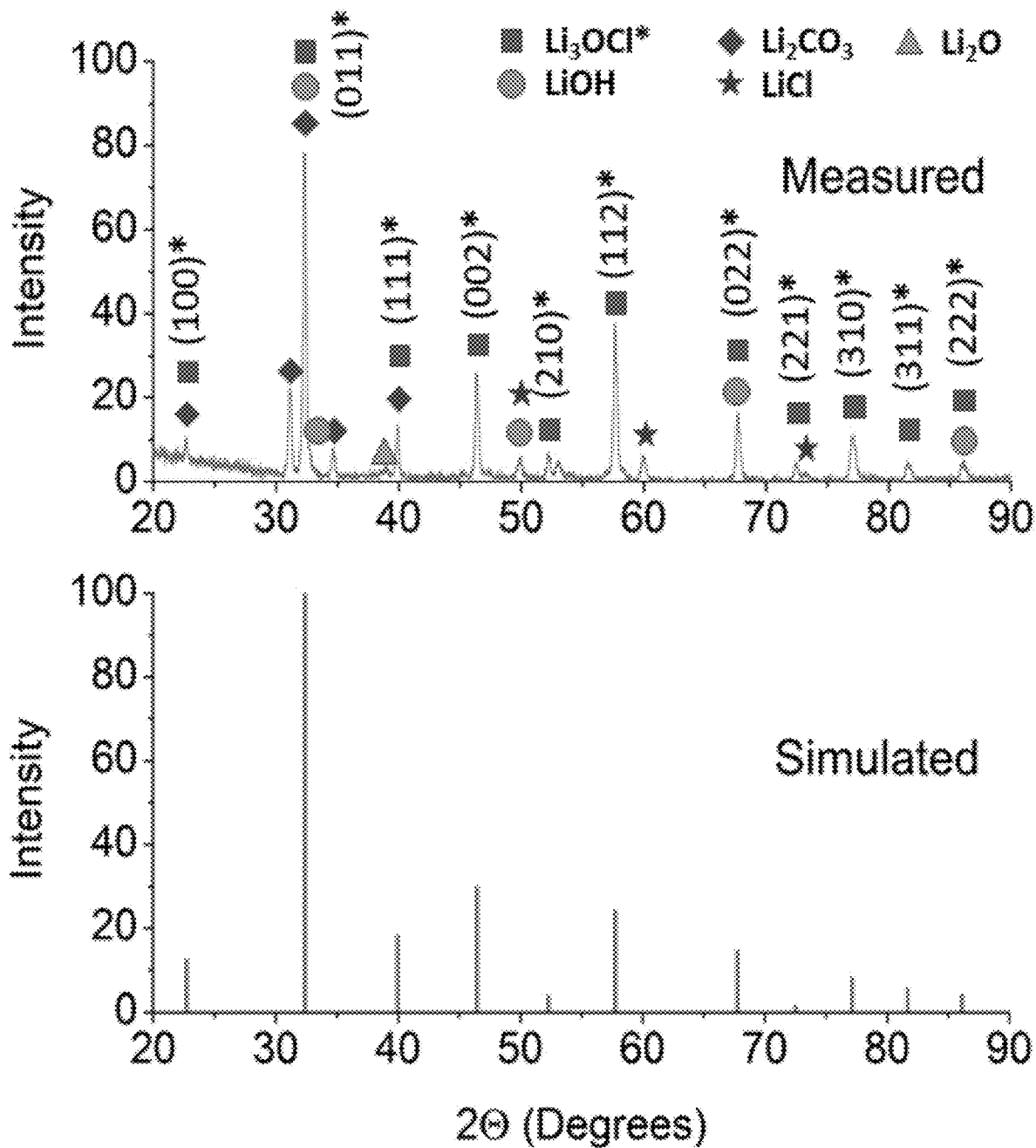


FIG. 2

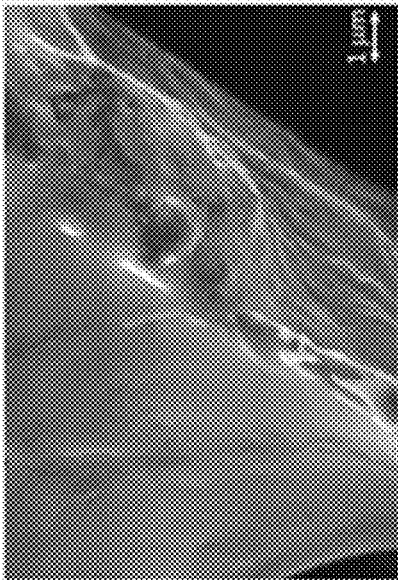


Fig. 3(c)

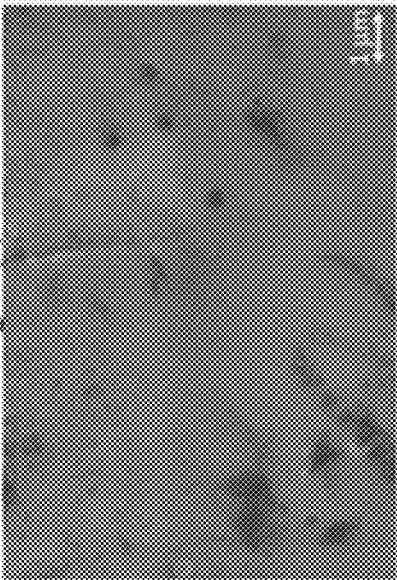


Fig. 3(f)

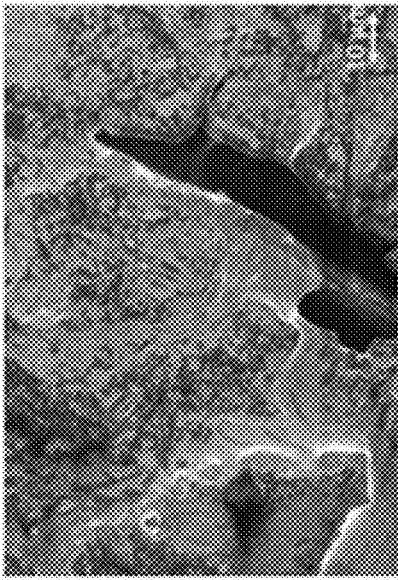


Fig. 3(b)

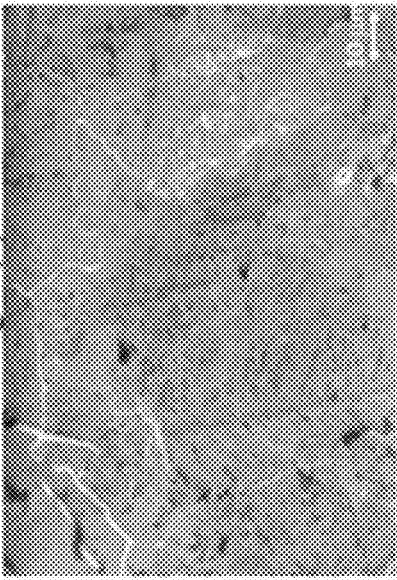


Fig. 3(e)

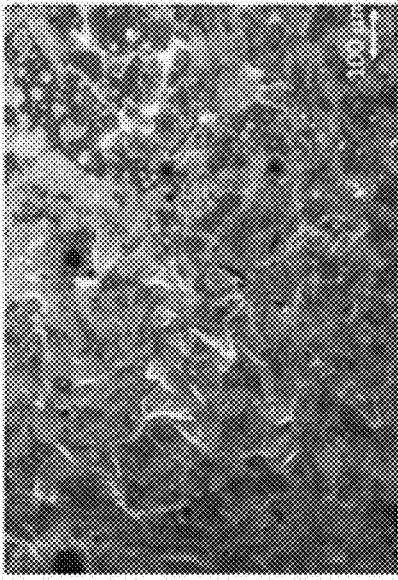


Fig. 3(a)

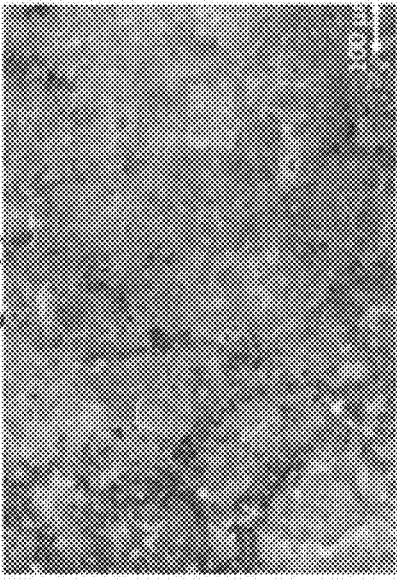


Fig. 3(d)

FIG. 3(a-f)

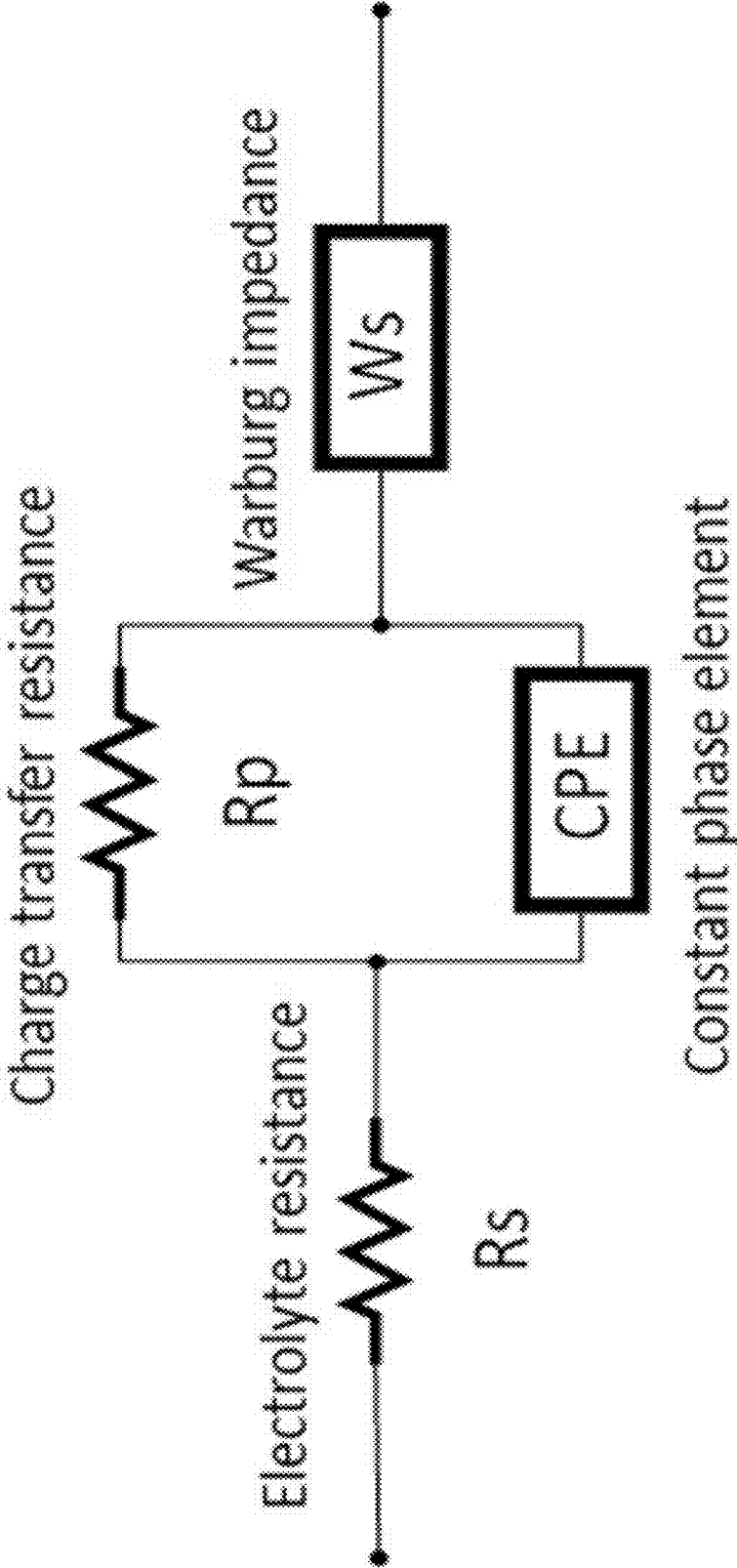


FIG. 4(a)

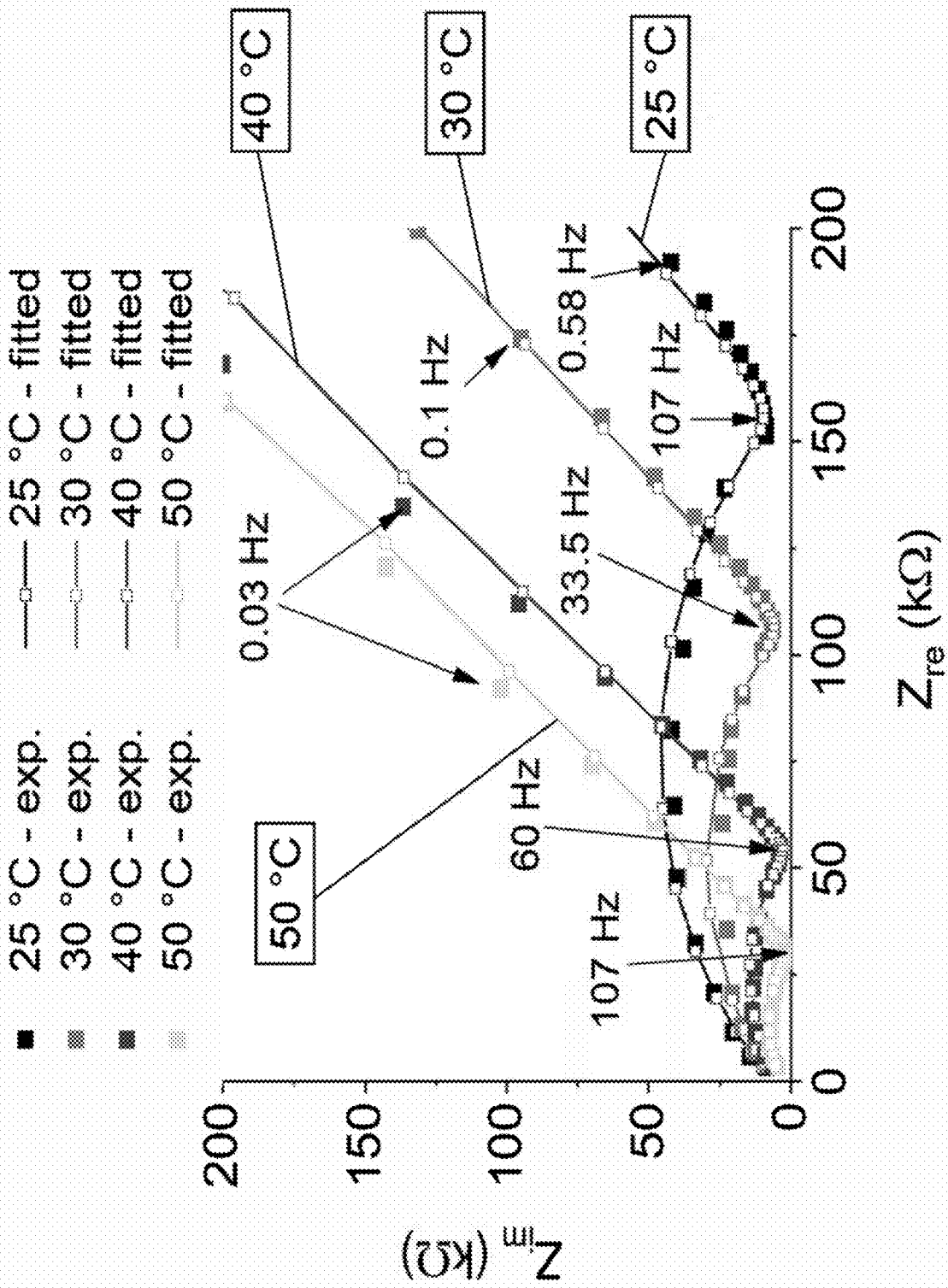


FIG. 4(b)

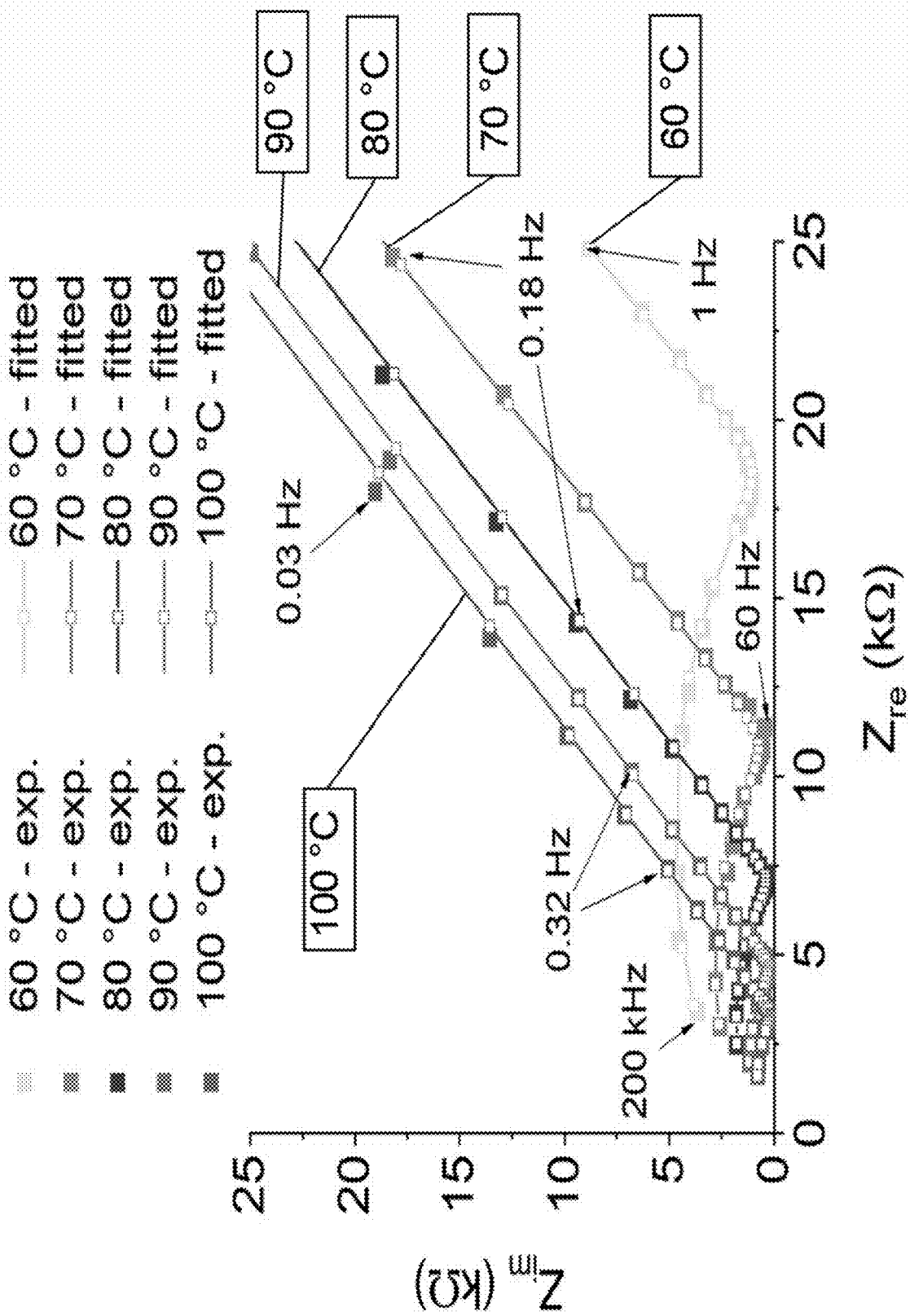


FIG. 4(c)

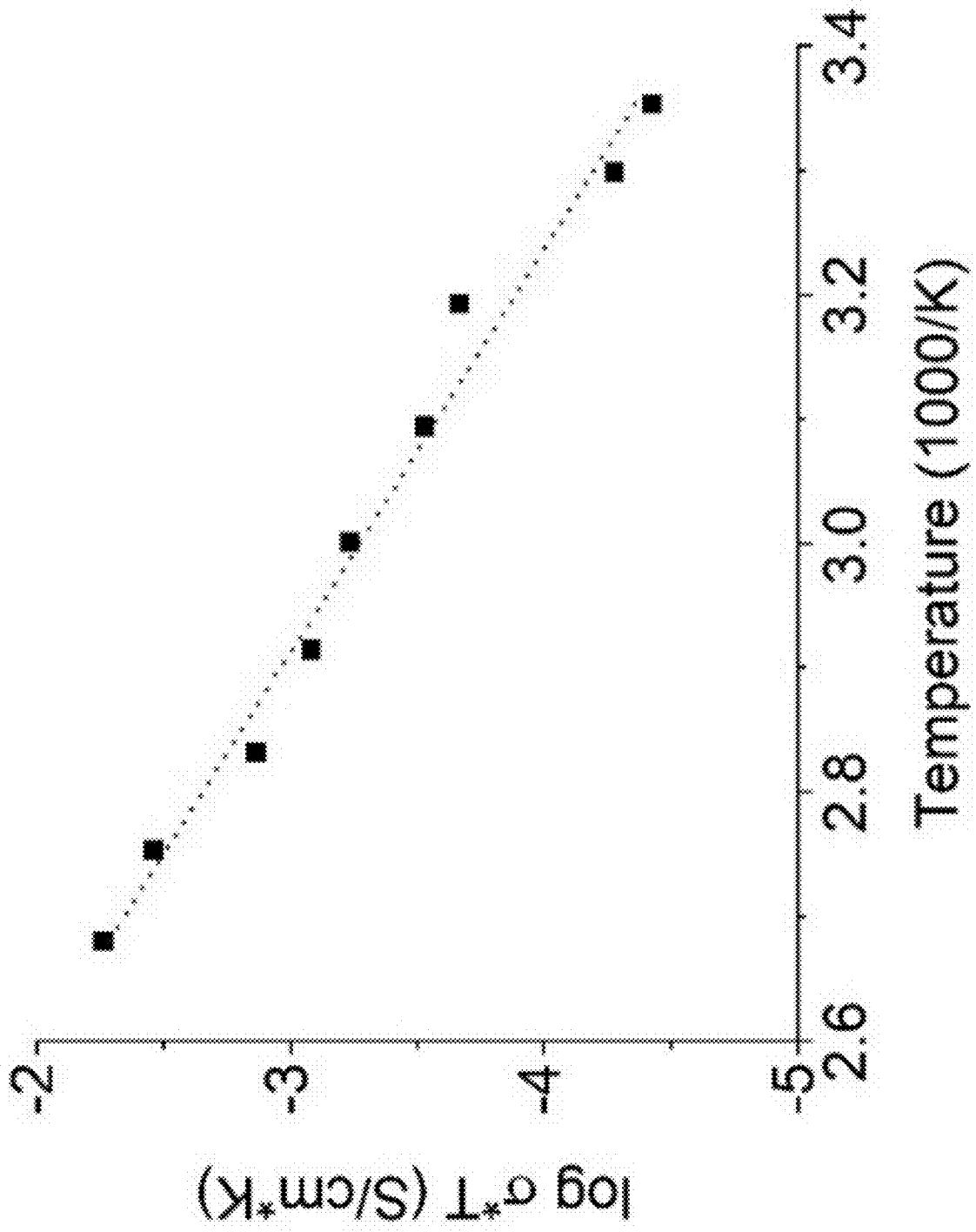


FIG. 5

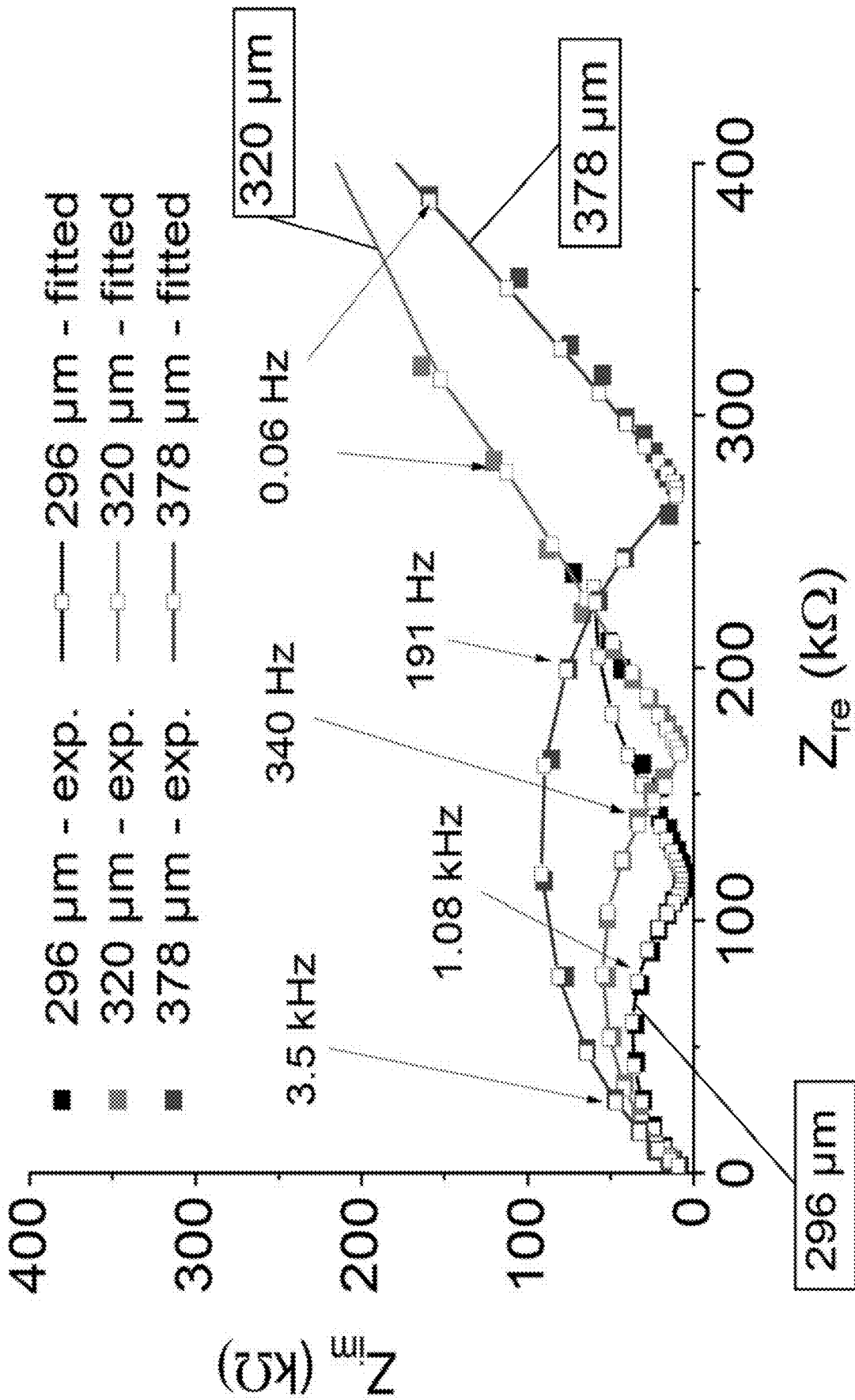


FIG. 6

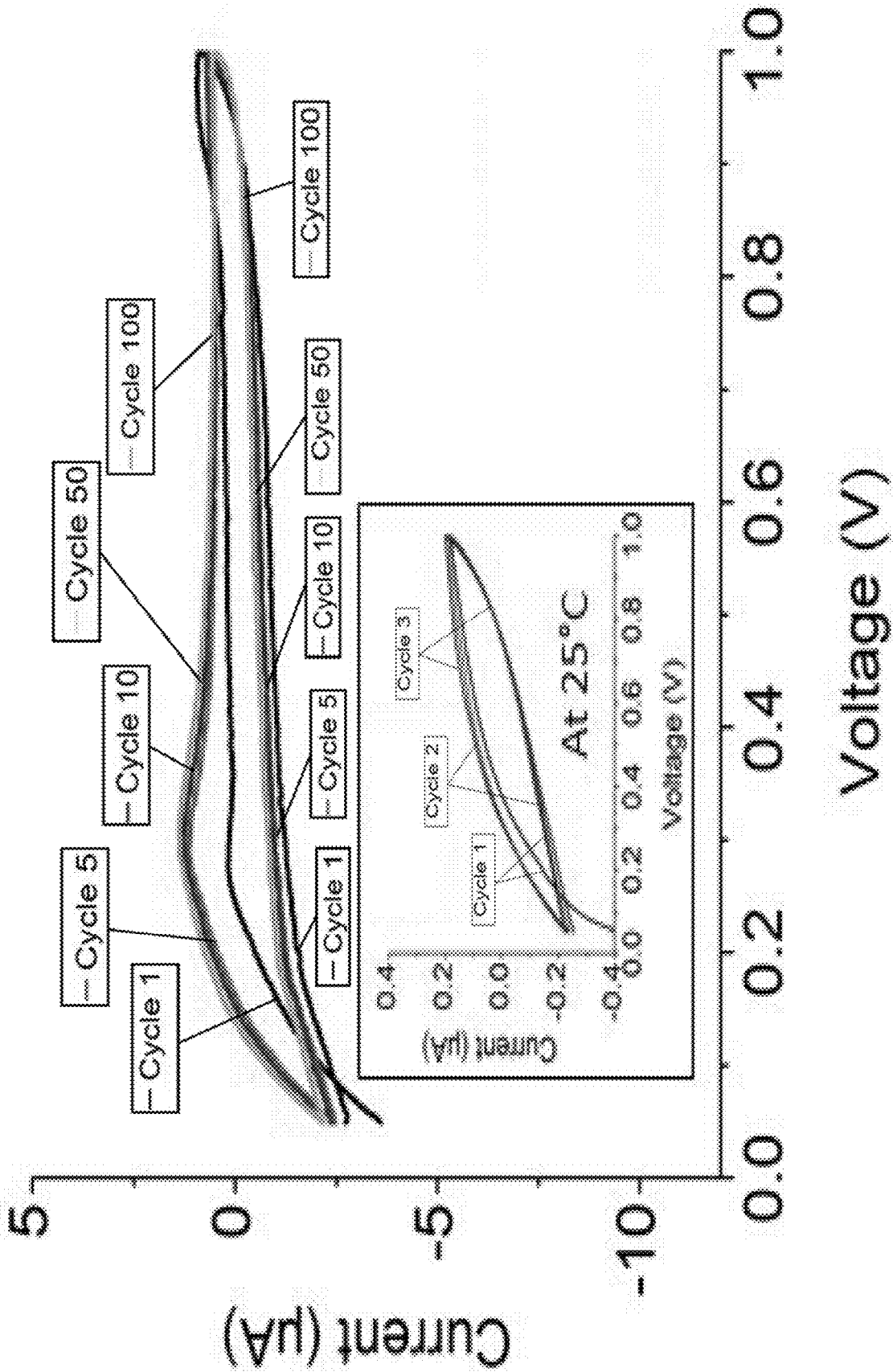


FIG. 7(a)

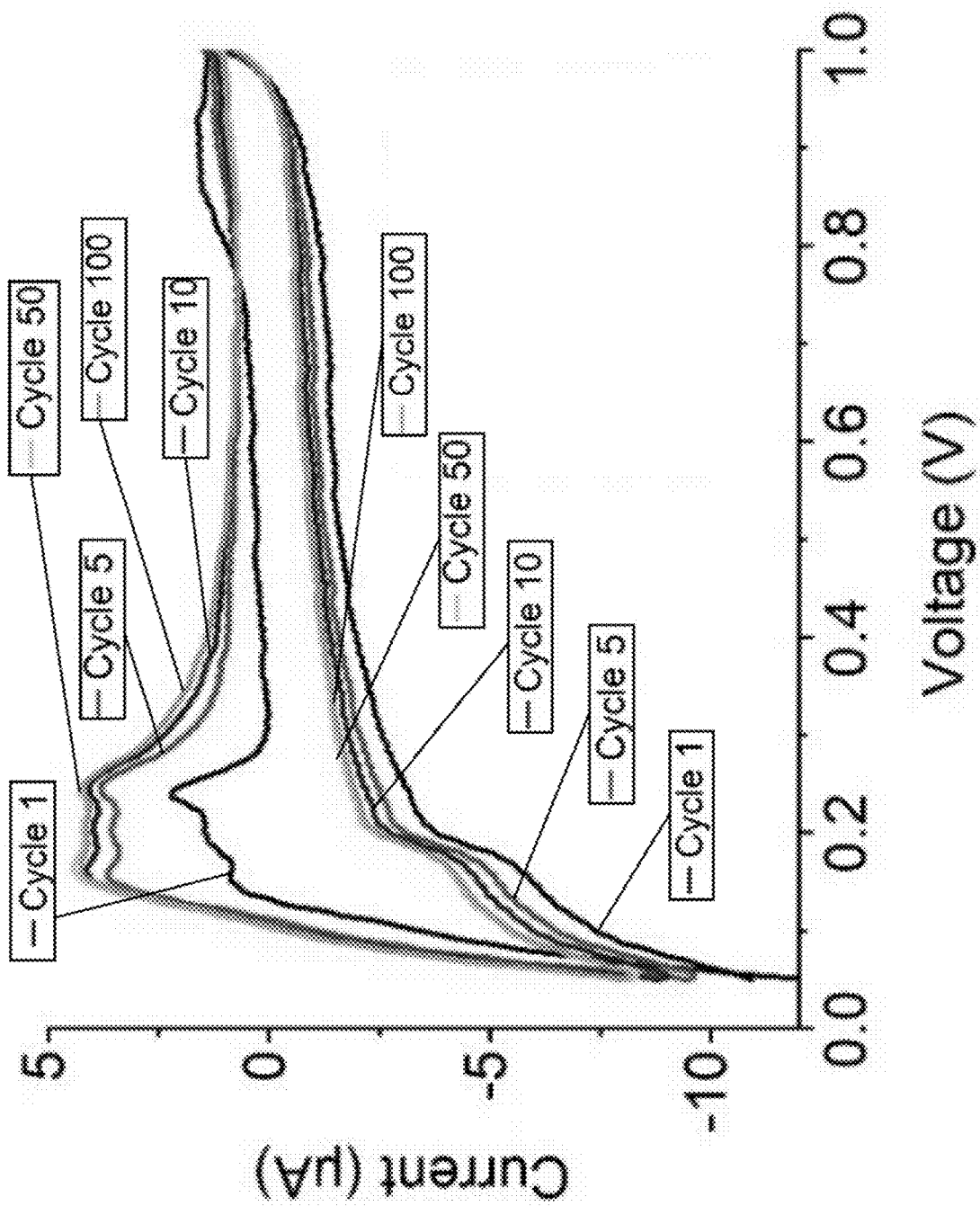


FIG 7(b)

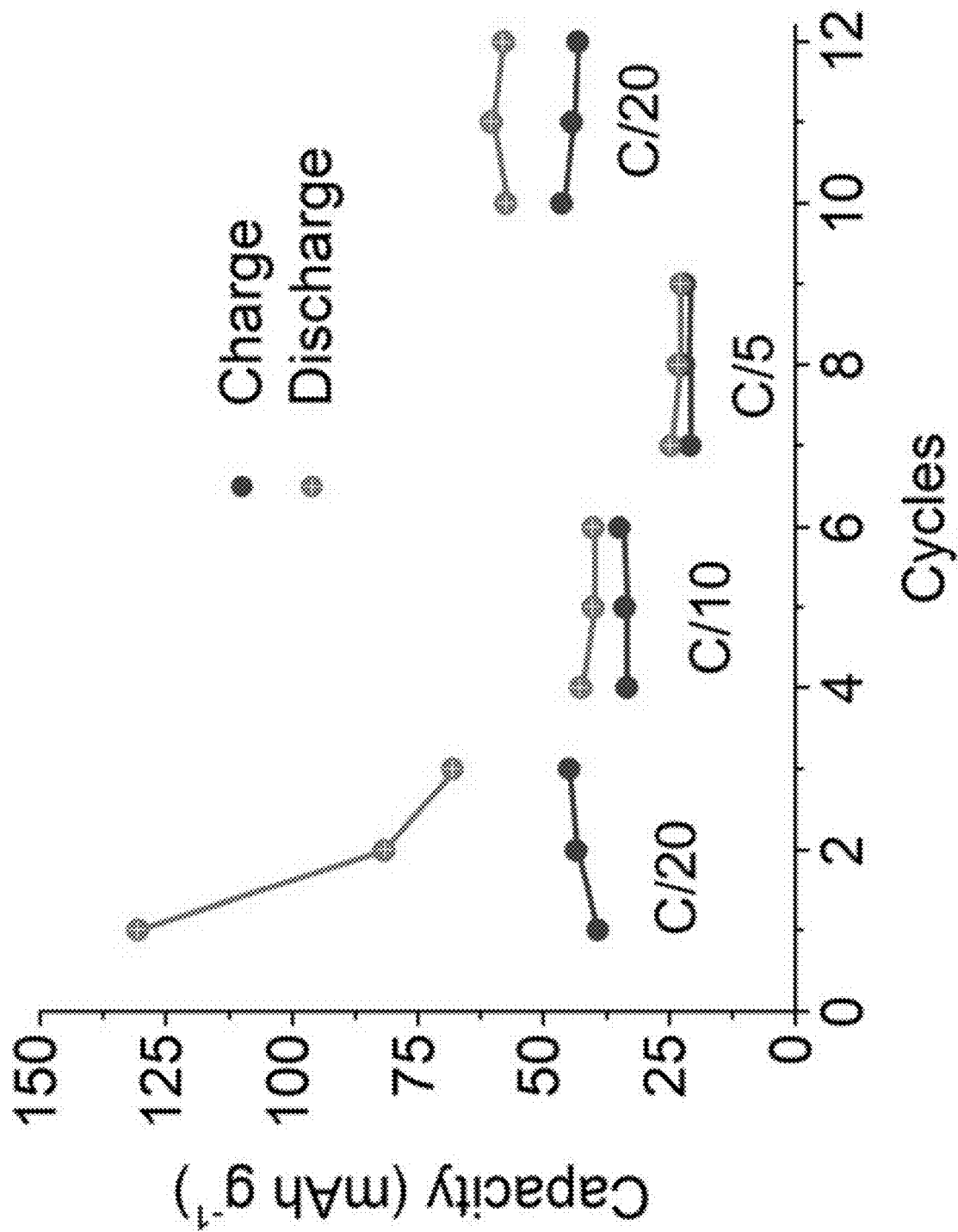


FIG. 8(a)

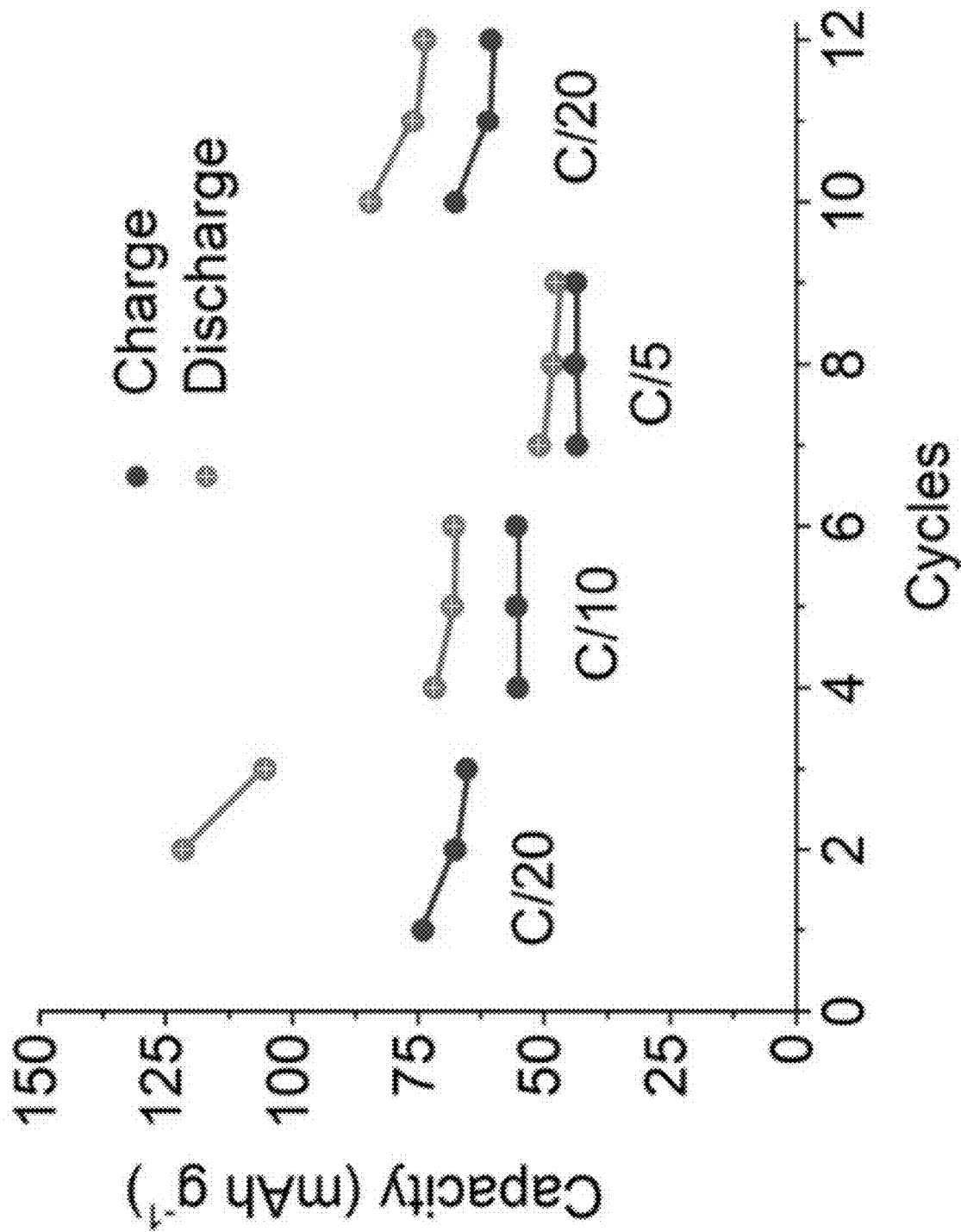


FIG. 8(b)

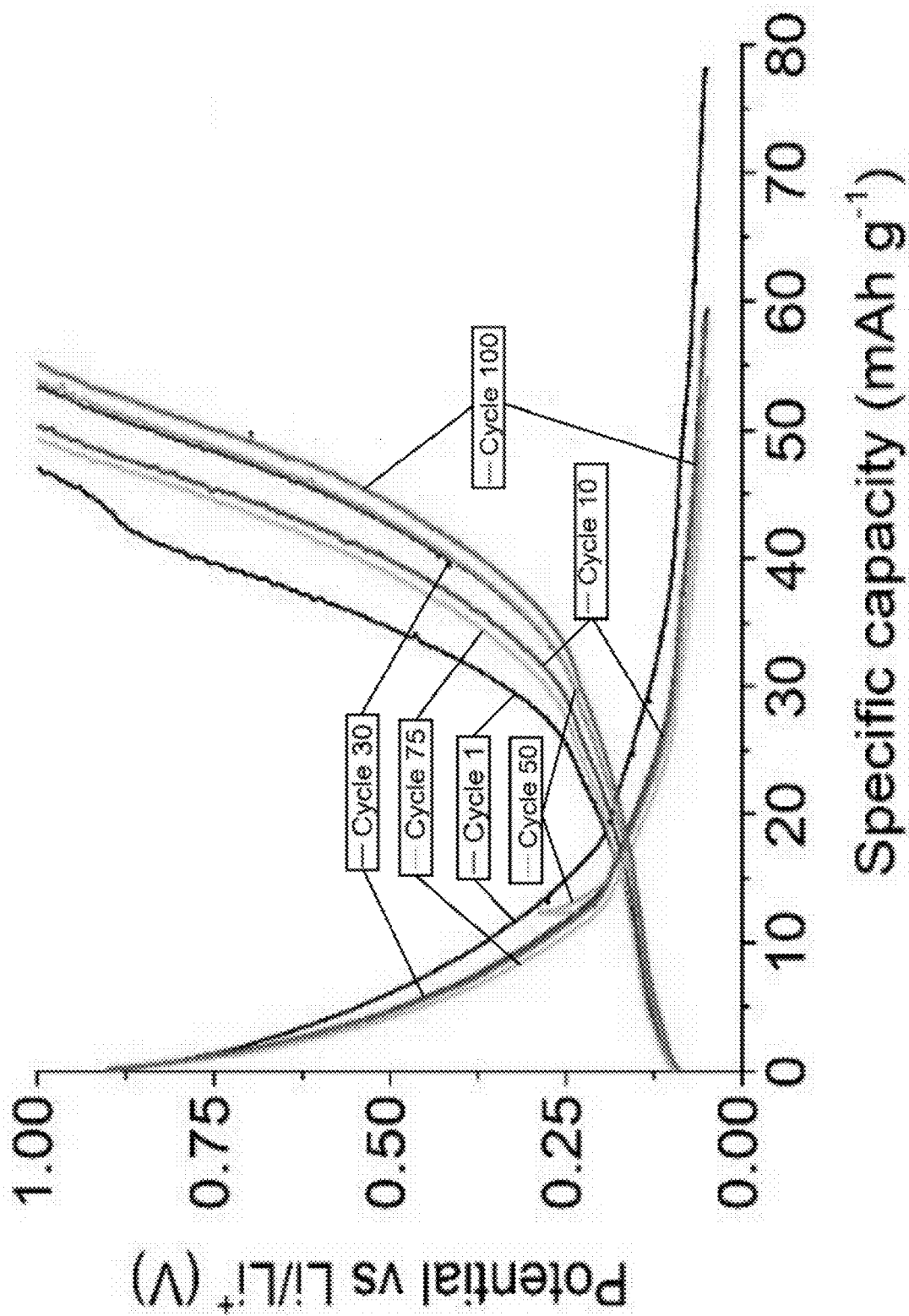


FIG 9(a)

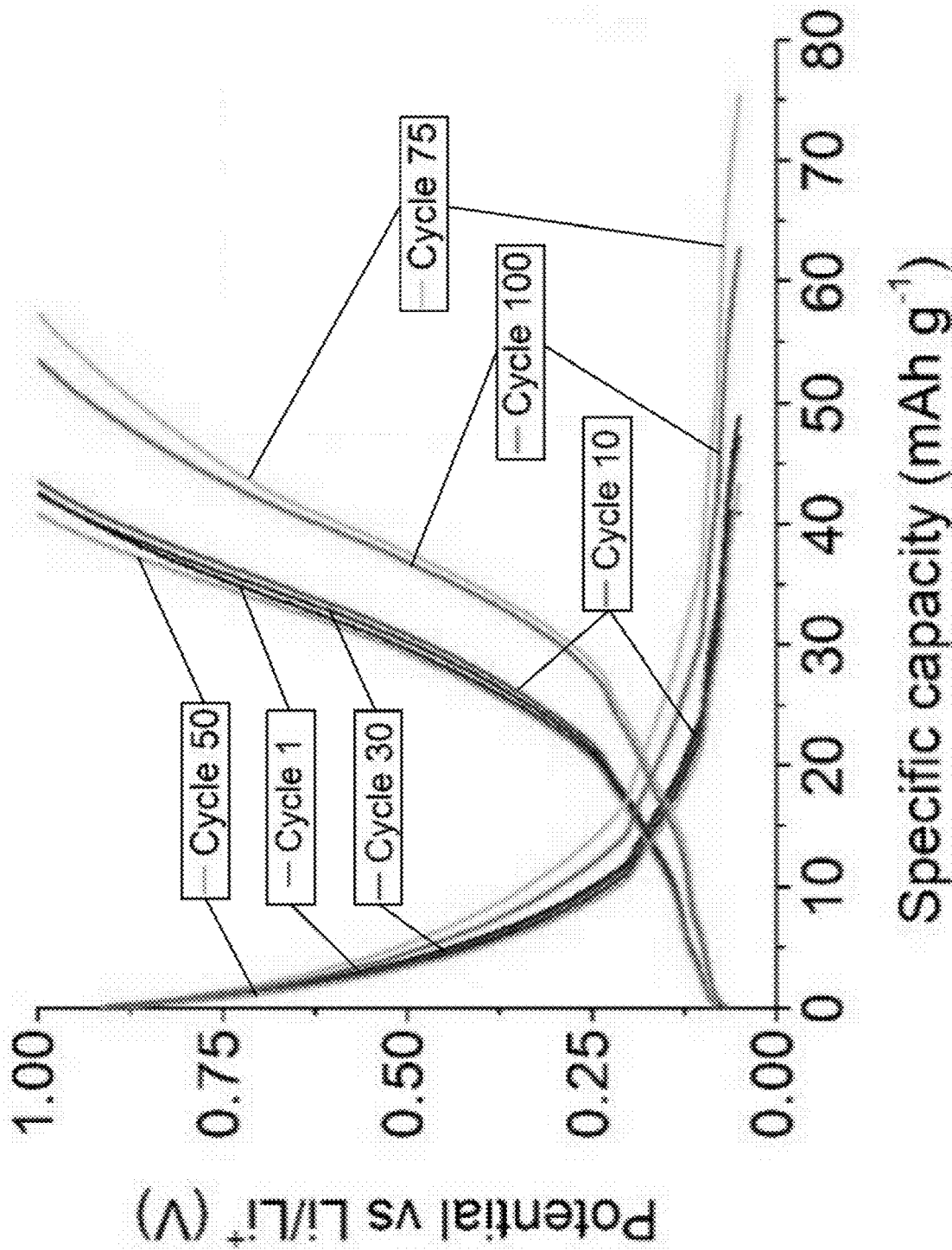


FIG. 9(b)

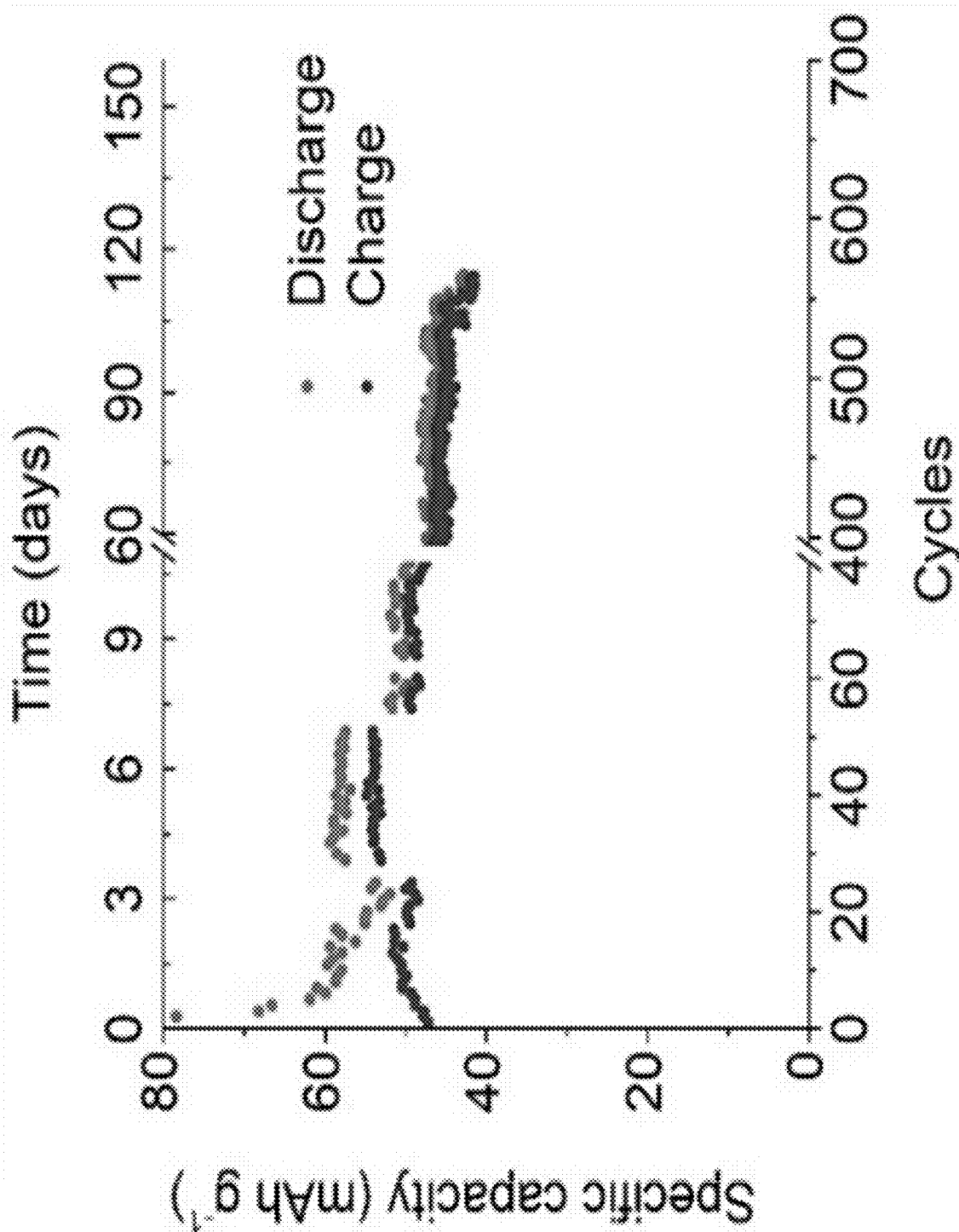


FIG. 10(a)

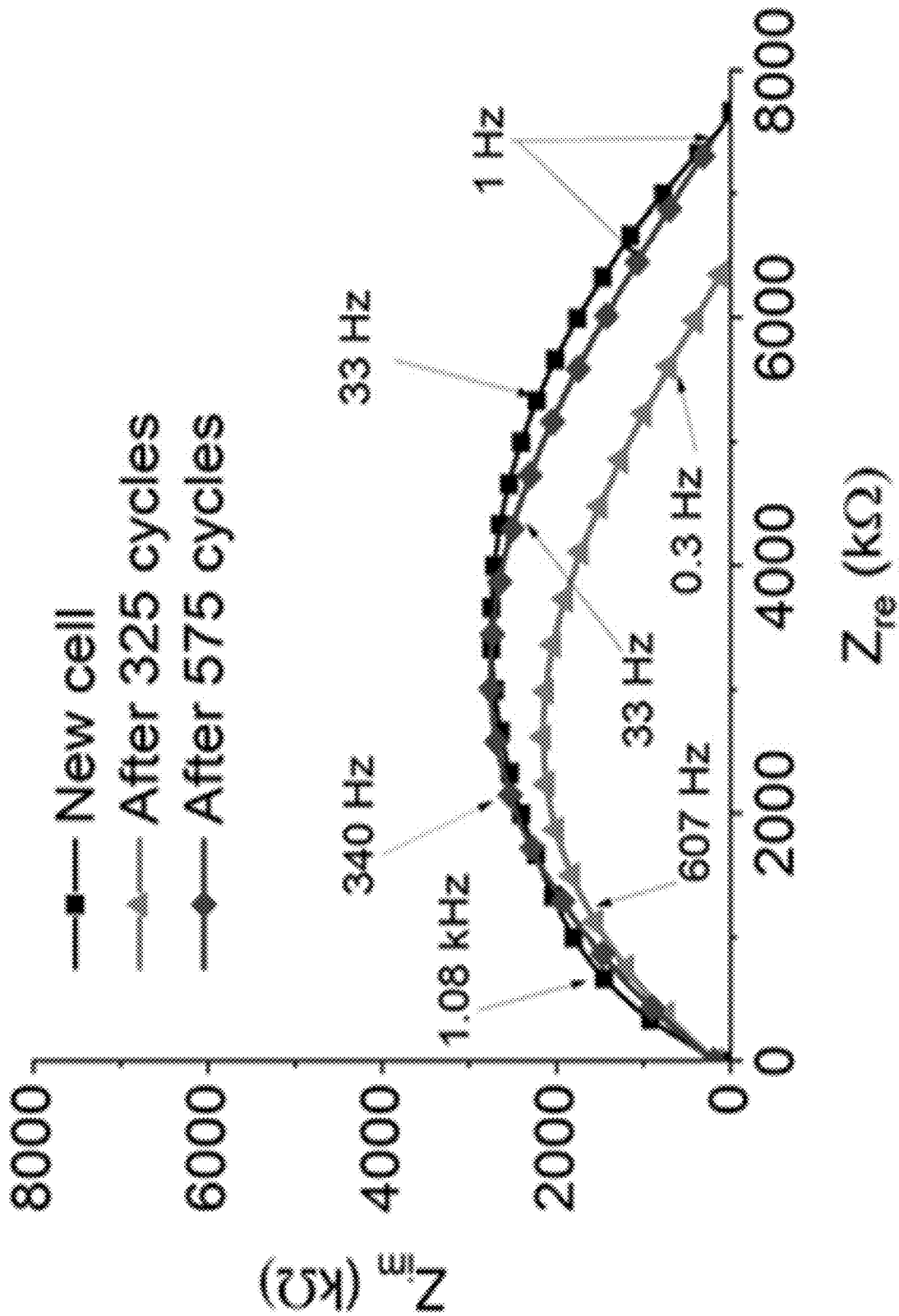


FIG. 10(b)

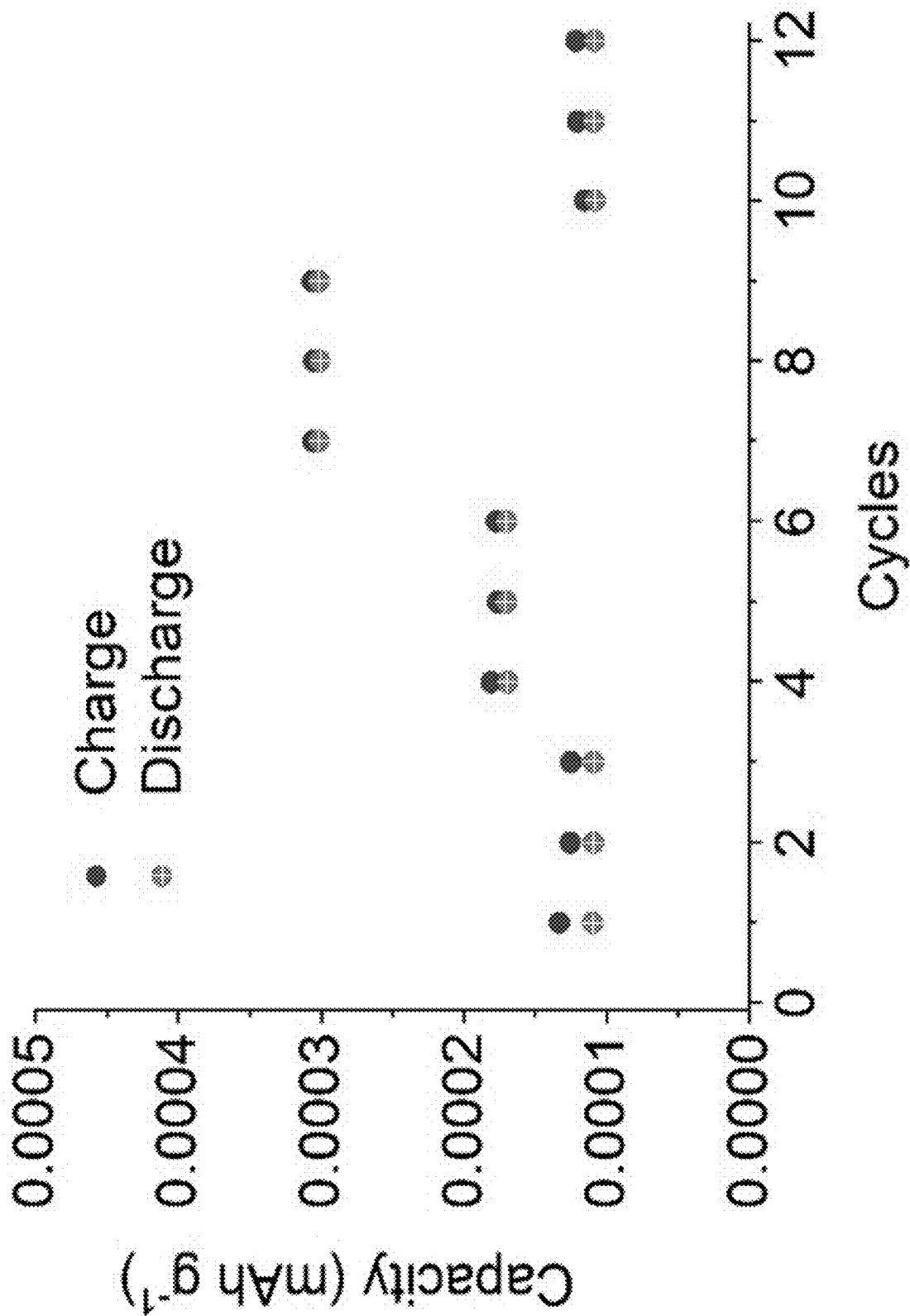


FIG. 11(a)

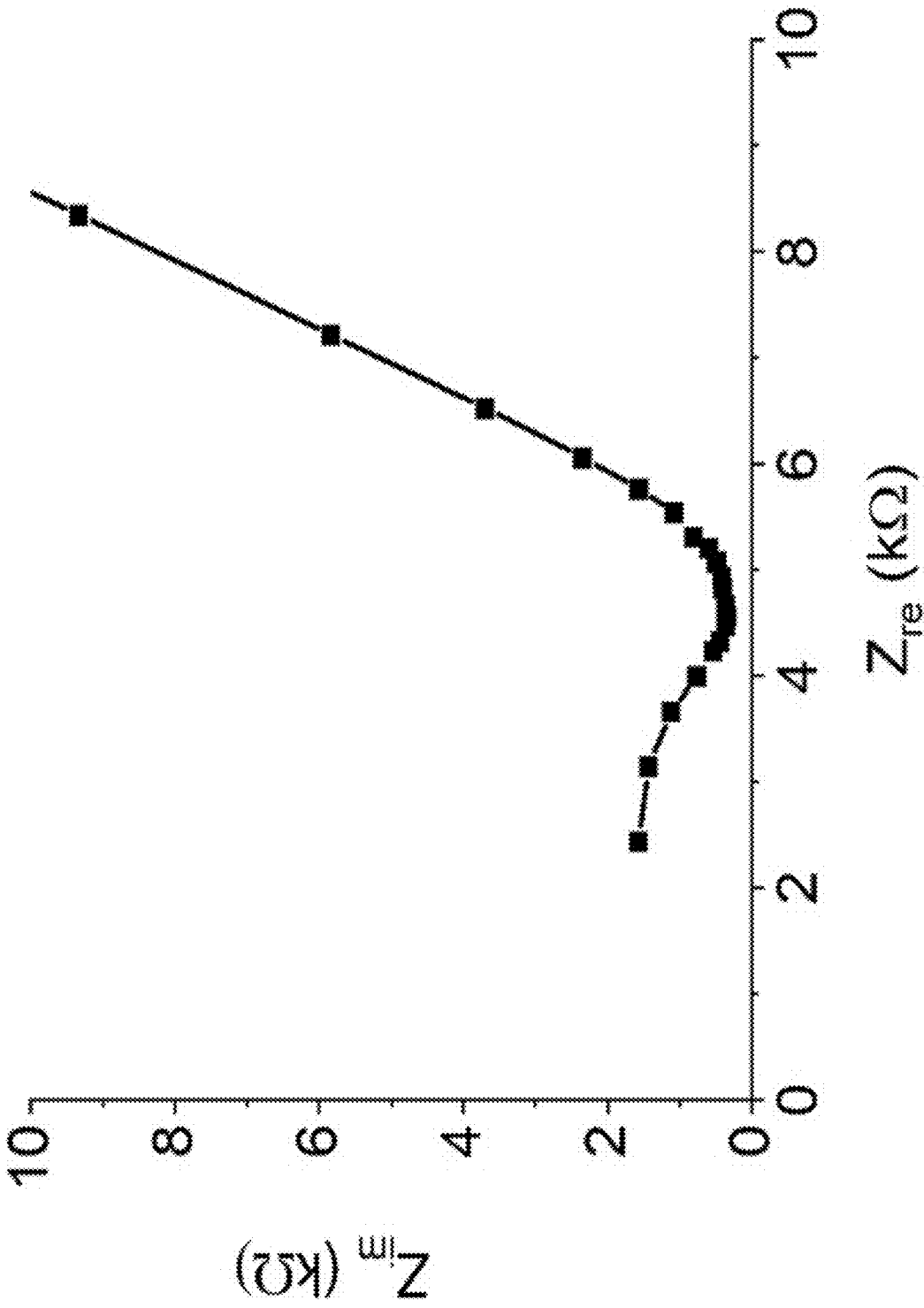


FIG. 11(b)

**SOLID-STATE ELECTROLYTES BASED ON
LITHIUM HALIDES FOR ALL-SOLID-STATE
LITHIUM-ION BATTERY OPERATING AT
ELEVATED TEMPERATURES**

PRIORITY STATEMENT

[0001] This application is a continuation-in-part of and claims priority to U.S. patent application Ser. No. 16/413,290 filed on May 15, 2019, which claims priority to U.S. Provisional Patent Application No. 62/672,445 filed on May 16, 2018 both of which are titled Solid-State Electrolytes Based on Lithium Halides for All-Solid-State Lithium-ion Battery Operating at Elevated Temperatures, all of which are hereby incorporated by reference in their entireties.

GOVERNMENT SUPPORT CLAUSE

[0002] This disclosure was made with government support under NNX14AN22A and N68335-17-C-0016 awarded by National Aeronautics and Space Administration (NASA). The United States government has certain rights in the disclosure.

FIELD OF THE DISCLOSURE

[0003] The present disclosure relates to a manufacturing process of the solid-state glass-ceramic electrolytes, known in the art as antiperovskites. Specifically, the disclosure is focused on manufacturing of the solid-state electrolyte from the corresponding precursors directly on the active electrode surface of an electrochemical device, specifically anode or cathode of the lithium-ion or lithium metal batteries.

TECHNICAL BACKGROUND

[0004] The state-of-the-art lithium-ion batteries demonstrate high energy density, relatively low rate of self-discharge, and low maintenance. However, these batteries experience performance deterioration and formation of solid electrolyte interface (SEI) layers that limit mass transport and lithium-ion conductivity when cycled for extended periods of time [1]. Furthermore, liquid electrolytes, such as conventional LiPF₆-based electrolytes in organic solvents [2] are flammable and corrosive [3]. Because of their narrow electrochemical stability window, liquid electrolytes do not allow the use of high voltage cathodes. Additionally, liquid electrolytes cannot be used with high capacity lithium metal anodes due to dendrite formation [4].

[0005] A number of patents and patent applications disclose the manufacturing processes of the solid-state electrolytes and the batteries made with solid-state electrolytes; among them the batteries made with such solid-state electrolytes as nitrogen-doped LiPO₄ and its derivatives: 0.63Li₂S-0.36SiS₂-0.01Li₃PO₄ (U.S. Pat. No. 7,083,877, 2006)[5], Li_{1.3}Al_{0.3}Ti_{1.7}(PO₄)₃ (U.S. Pat. No. 7,914,932, 2011) [6], Li_{1+x+y}(Al,Ga)_x(Ti,Ge)_{2-x}Si_{3-y}P_{3-y}O₁₂ (U.S. Pat. No. 9,580,320, 2017) [7]. Another group of solid-state electrolytes, specifically garnets (U.S. patent application Ser. No. 15/730,097 [8]), are not economically feasible because of their electrochemical deterioration or prohibitive cost that exceeds the cost of the disclosed glass ceramic materials by over two orders of magnitude. Additional disadvantages of many ceramic materials is high melting point and grain boundary effects that make their application challenging, especially regarding their economic feasibility.

[0006] A broad spectrum of metal oxides, phosphates and sulfides have been tested as solid-state electrolytes for lithium-ion batteries. The primary advantage of oxides is their low charge transfer resistance at the electrolyte-electrode interface [9]. Furthermore, metal oxides, such as Li_{7+x}La₃Zr_{2-x}Y_xO₁₂ [10], Li₅La₃Nb₂O₁₂[11], Li_{5+x}Ba_xLa_{3-x}Ta₂O₁₂ [12], have low ionic conductivity ($\leq 10^{-4}$ S/cm).

[0007] Compared to metal oxides, phosphate- or sulfide-based lithium superionic conductors (LISICONs), such as Li_{1+x-y}Al_x³⁺M_y⁵⁺M⁴⁺_{2-x-y}(PO₄)₃ (where M=Ge; M=Ti, Ge; and M=Ti, Ta) have slightly higher conductivity ($\sim 4 \cdot 10^{-4}$ S·cm⁻¹) than metal oxides. Perovskite structure superfast solid-state ionic conductor Li_{3x}La_{2/3-x}TiO₃ [13] has even higher lithium-ion bulk conductivity ($\sim 1.5 \cdot 10^{-3}$ S/cm [14]), but has elevated grain boundary resistances. Among LISICONs, sulfides (e.g. Li₁₀GeP₂S₁₂) have a theoretical ionic conductivity greater than that of the current liquid LiPF₆-based electrolyte at room temperature ($\sim 10^{-2}$ S/cm) [15]. However, sulfides form interfacial layers with poor ionic conductivity [16, 17]. As a silicon-based analogue of Li₁₀GeP₂S₁₂, Li₁₁Si₂PS₁₂ exhibits high performance and lower activation energy (0.20 eV) due to nearly isotropic lithium ion hopping in the crystalline lattice, but it is not chemically stable [18]. Furthermore, LISICONs in contact with lithium metal form low-conducting interphases [19] that make them less desirable in solid-state battery applications.

[0008] In comparison to oxides and sulfides, lithium-based antiperovskites with a general formula Li_{3-x}M_{3x}C_{1-y}A_{1-z}A'_z, possess the highest ionic conductivity (e.g. $\sim 1.94 \cdot 10^{-3}$ S·cm⁻¹ for Li₃OCl_{0.5}Br_{0.5} [20]) comparable to liquid electrolytes at room temperature [16]. Further tuning of the Li⁺ hopping mechanism for optimized ionic transport can be achieved by A-mixing, M/H-doping, or LiA-depletion. The charge and size of M, C, and A atoms permits to tune Li⁺ ionic conductivity through “vacancy-enhancement” and “distortion-control” of the crystal lattice.

[0009] Additional advantages of antiperovskites are their large electrochemical window and low grain boundary effects due to their glass-ceramic nature [20, 21]. It was demonstrated that mixed halides, e.g. Li₃O(Cl,Br), have higher conductivity than Li₃OBr or Li₃OCl [20]. In the case of Li₃OBr, lower ionic conductivity was explained by the large size of Br anions on dodecahedral A-sites leaving little space for Li⁺ cations to hop into the interstitial spaces. In the case of Li₃OCl, Cl⁻ anions are assumed to distort the crystal structure by octahedral tilting leading to the partial collapse of A sites and the formation of low-symmetry phases with low ionic conductivity.

[0010] In contrast to Li₃O(Cl,Br) [20], partial substitution of lithium atoms by hydrogen atoms in Li₃OClO structure resulting in the Li₂HOCl composition tested at 50-200° C. by Hood et al. (2016) [22] demonstrated significant crystal phase transformation and change in Arrhenius slope at temperatures below 50° C. which does not meet the requirements of a solid-state electrolyte. The electrolyte crystal phase was stable only at higher temperatures (50-200° C.) [22], but revealed relatively high activation energy of 0.56 eV.

[0011] Known in the art, is the phenomenon when the electric conductivity of the solid-state glass-ceramic electrolytes is affected by the cooling rate causing crystal growth and changes in crystal structure and morphology. For example, in case of Li₂OHCl [28], slow cooling from 350 to

250° C. at 8° C./h produced antiperovskite crystal structure, while fast cooling from $\geq 350^\circ$ C. to room temperature resulted in less electrically conductive crystal structures due to overcooling.

[0012] Known in the art, is a phenomenon when solid-state electrolyte interfaces (SEIs) are formed in electrochemical cells, such as lithium-ion batteries. In some cases, for example in batteries with carbon-based anodes, they perform a positive role. However, SEIs can also cause detrimental effects and battery failure due to their low electric conductivity, such as in case of silicon-based anodes. In case of solid-state electrolytes in contact with anodes or cathodes, this effect is not well investigated and understood. An example of SEI formation is presented at the cross section of the lithium metal and Li_2OHCl for a symmetric $\text{Li}/\text{Li}_2\text{OHCl}/\text{Li}$ cell with molten lithium anode tested for 160 cycles at 195° C. [28].

[0013] Lithium dendrites, that form within an electrochemical lithium-ion cell, present a significant battery safety challenge due to increased battery flammability. In case of solid-state electrolytes, lithium dendrite formation was earlier detected along the grain boundaries in garnets [23, 24].

[0014] A few synthesis methods for the glass-ceramic antiperovskites with a general formula $\text{Li}_{3-x}\text{M}_x\text{C}_{1-y}\text{C}'_y\text{A}_{1-z}\text{A}'_z$ are known in the art. The patent WO 2012112229 [25] describes a multi-step process for synthesis of a lithium halide from an aqueous solution containing dissolved precursors. The disclosed steps of the said synthesis include preparation of aqueous solution of inorganic precursors, evaporation of water to produce solids, and a heat-treatment step of the solids in vacuum for at least 48 hr to produce lithium halides. This approach does not meet the requirement for cost-effectiveness and technological viability due to lengthy and complicated procedure.

[0015] Known in the art, is a solid-state electrolyte synthesis via spray-deposition of the aqueous solutions containing dissolved inorganic chemicals on a heated substrate, preferably at 100 to 400° C. (U.S. Pat. No. 8,349,498 B2, 2013) [43]. However, this disclosure includes a number of solid-state electrolyte, such as $\text{Li}_x\text{Al}_{z-y}\text{Ga}_y\text{S}_w(\text{PO}_4)_c$, $\text{Li}_x\text{Al}_{z-y}\text{Ga}_y\text{S}_w(\text{BO}_3)_c$, $\text{Li}_x\text{Ge}_{z-y}\text{Si}_y\text{S}_w(\text{PO}_4)_c$, and $\text{Li}_x\text{Ge}_{(z-y)}\text{Si}_y\text{S}_w(\text{BO}_3)_c$, but does not disclose glass-ceramic antiperovskites.

[0016] The U.S. Pat. No. 10,044,061 B2 (2018) [26] describes a process of pulsed laser beam or sputtering for preparing antiperovskite Li_3OCl electrolyte films by using a composite target manufactured from Li_3OCl inorganic precursors, such as lithium metal oxide and metal halide. The patent (U.S. Ser. No. 15/545,000, 2018)[27] describes lithium-rich antiperovskites for cathode applications. Both patents are not directly related to the present disclosure.

[0017] The U.S. Pat. No. 9,246,188 B2 by Zhao et al. [28] describes antiperovskite electrode compositions that may be prepared by sintering of various solid precursors at elevated pressures and temperatures. The patent does not reveal the claimed electrochemical properties of the solid-state electrolytes in an electrochemical setup.

[0018] Claimed in [22] and the U.S. Pat. No. 8,349,498 (2013) [29], a simple mixing of inorganic precursors at temperatures $< 400^\circ$ C. in argon produced dense membranes, composed for example of Li_2HOCl . The controlled cooling from 350 to 250° C. at 8° C./h yielded anti-perovskite structures (termed “slow-cooled”), while fast cooling from $\geq 350^\circ$ C. to room temperature in ~ 20 min (termed “fast-

cooled”) produced more complex crystal structures with increased defects due to the overcooling effect. However, the compounds were found to undergo a phase transition between 30 and 50° C. that is unacceptable for the lithium-ion battery operating in a broad temperature range up to 100° C. Furthermore, the porosity of the said electrolytes exceeded 20 vol. % that is considered as a significant drawback.

[0019] Based on the examples and references presented above, it can be concluded that none of the prior art techniques describe the disclosed in this disclosure manufacturing process of the solid-state glass-ceramic electrolytes, known in the art as antiperovskites, directly on the active battery electrode surfaces followed by compression of the electrolyte onto the said surface and fast cooling that produce functional electrochemical cells with improved long-term electrochemical properties and durability at elevated temperatures.

SUMMARY

[0020] The present disclosure relates to a method of manufacturing the solid-state electrolyte layers on the surface of an active electrode by direct contact of the said electrode with the melted electrolyte at temperatures above or close to the melting point of the electrolyte.

[0021] The present disclosure relates to a method of manufacturing solid-state electrolyte layers directly on the active electrode surfaces, specifically on the surface of anode or cathode, by direct contact of the said electrodes with the electrolyte at temperatures above or close to its melting point.

[0022] According to one specific embodiment, the said manufacturing method comprises a step when a representative solid-state electrolyte from the class of lithium undoped or doped antiperovskites and their polymorphs [33] with a general formula $\text{Li}_{3-x}\text{M}_x\text{C}_{1-y}\text{C}'_y\text{A}_{1-z}\text{A}'_z$, where M is hydrogen, or a metal from the first three groups of the periodic table of elements and x is defined by the charge of the corresponding metal, C and C' are chalcogens (O, S, Se), and A and A' are halogens (F, Cl, Br, I), or ions, such as BH_4^+ or BF_4^+ , can be applied.

[0023] The present disclosure relates to a group of the said electrically conductive and cost-effective solid-state materials and their nanocomposites that have relatively low melting point temperatures, specifically in the range from 250° C. and up to 600° C. that allows to apply an economically feasible method described in this disclosure.

[0024] According to one specific embodiment, the proposed disclosure describes the method that eliminates grain boundary formation in the said solid-state electrolyte layers directly deposited on the electrode surface due to the applied process of fast cooling. Absence of grain boundaries within the electrolyte layer produced by the said method improves the electric conductivity and the lithium-ion transport in the said solid-state electrolyte.

[0025] According to one specific embodiment, the proposed disclosure describes the method that produces solid-state electrolyte layers that do not undergo phase transformations within the operation temperature range in the range of -20° C. -100° C. Absence of phase transformations within the solid-state electrolyte ensures high lithium-ion transport within the said operation temperature range of the operational electrochemical device.

[0026] According to one specific embodiment, the proposed disclosure describes the method that produces solid-state electrolyte layers on the electrode surface, after a compression force is applied to the electrode located on top of the melted solid-state electrolyte.

[0027] According to one specific embodiment, the proposed disclosure describes the method that produces solid-state electrolyte layers on the active electrode surface, and specifically anode or cathode electrode surface, after a compression force is applied. This method results in intimate contact and minimized interfacial resistance between the said electrolyte and the electrodes.

[0028] According to one specific embodiment, the present disclosure is related to the disclosed disclosure related to the class of lithium undoped and doped antiperovskites and their polymorphs that are produced in a moisture-free environment, such as those containing different inert or noble gases, including but not limited to helium, argon, or nitrogen, or vacuum.

[0029] According to one specific embodiment, the present disclosure is related to a manufacturing process involving a class of lithium undoped and doped antiperovskites and their polymorphs that after melting in a moisture-free environment, can be brought in direct contact with the active anode or cathode electrode surface due low melting point of the said electrolytes.

[0030] According to one specific embodiment, the present disclosure is related to the manufacturing process involving a class of lithium undoped and doped antiperovskites and their polymorphs that can be brought in direct contact with the active anode or cathode electrode surface and compressed by using a metal with low adhesion toward the said electrode, preferably nickel foil.

[0031] The present disclosure relates to a said group of electrically conductive and cost-effective solid-state materials and their nanocomposites, formed by the direct exposure of the battery electrodes to the melted electrolyte with addition of polymer-based, inorganic, or organic materials for mechanical electrolyte phase integrity with a specific feature of chemical, electrochemical, and crystal phase stability at elevated temperatures, and more specifically from room temperature (RT) and up to at least 100° C.

[0032] Different from other disclosures in the field, the present disclosure relates to the electrically conducting solid-state antiperovskite electrolytes produced in the said way that do not form interfacial phases in contact with lithium metal anodes. These low conducting interfacial phases known in the art as Solid Electrolyte Interface (SEI) layers have not been detected for the solid-state electrolyte layers formed on the active electrode surface using the method disclosed in this disclosure.

[0033] Different from other disclosures in the field, the present disclosure relates to the electrically conducting solid-state electrolytes with antiperovskite crystal structures that are produced in a moisture-free environment on the active positive or negative battery electrode surface or both and the performance of the battery made in the said way.

[0034] Different from other disclosures in the field, the present disclosure relates to the electrically conducting solid-state electrolytes with antiperovskite crystal structures that are produced in a moisture-free environment on the active positive or negative battery electrode surface or both and the performance of the battery made in the said way at elevated temperatures.

[0035] The applications of the present disclosure described in this disclosure are relevant but are not limited to the electrochemical energy generation and storage devices and specifically the electrode materials of the said devices; among them batteries, dye-sensitized solar cells, fuel cells, supercapacitors, or combination thereof. Yet other application areas may also include touchscreens, organic light-emitting diodes, flexible organic solar cells, and organic electrochemical transistors. Furthermore, the disclosed solid-state electrolyte can be used in hole-injecting transparent plastic and flexible electrodes for polymer light emitting diodes, field-effect transistors, and photovoltaic cells.

[0036] While conventional techniques use the expensive precursors and high-temperature synthesis for manufacturing of the solid-state electrolytes, the disclosed disclosure is related to the antiperovskite-based materials with a general formula $\text{Li}_{3-x}\text{M}_{3x}\text{C}_{1-y}\text{C}'_y\text{A}_{1-z}\text{A}'_z$, where M is H, alkali, or alkali earth metal, C and C' are chalcogens (O, S, Se), and A and A' are halogens (F, Cl, Br, I) or ions, such as BH_4^+ or BF_4^+ . The disclosure is specifically focused on a process of an electrolyte or an electrolyte-based nanocomposite manufacturing in a moisture-free environment that possess constant crystal structure within the entire range of operation temperatures (-20° C.-100° C.) and do not produce additional solid-state phases, such as those detected earlier along the grain boundaries in garnets [23, 24]. Specifically, a process of an electrolyte or an electrolyte-based nanocomposite manufacturing process in a moisture-free environment resulting in an electrochemically stable, highly conductive electrolyte in absence of the phase transformations in a broad temperature range produced by the said method is disclosed.

[0037] The present disclosure demonstrates a manufacturing process of an solid-state electrolyte layer by the said method resulting in an improved electrode-electrolyte interface due to the direct contact with melted electrolyte in a moisture-free controlled environment favorable for solid-state lithium-ion batteries operating in a broad temperature range and at least up to 100° C. by utilizing the melting point value of the antiperovskite, e.g. lithium halide (-282° C.) [20]. The embodiments disclosed herein, successfully tested the manufacturing process of the solid-state glass-ceramic electrolytes, known in the art as antiperovskites, directly on the active either positive or negative battery electrode surface, followed by compression of the electrolyte onto the said surface and fast cooling, that results in improved long-term electrochemical durability observed in contact with lithium metal at the elevated temperatures. These embodiments validate, that the said solid-state electrolyte-electrode interfaces can be produced on the surface of metal, e.g. nickel foil, resulting in a grain-free electrolyte morphology and long-term electrochemical stability of the electrolyte in contact with lithium metal.

BRIEF DESCRIPTION OF THE DRAWINGS

[0038] Illustrated embodiments of the disclosure are described in detail below with reference to the attached drawing figures, which are incorporated in reference herein, and where:

[0039] FIG. 1 is a pictorial representation of a drawing explaining the manufacturing process of the solid-state glass-ceramic electrolyte, known in the art as antiperovskites, directly on the active either positive or negative

battery electrode surface, followed by compression of the electrolyte onto the said surface and fast cooling, that results in enhanced long-term electrochemical performance and durability observed in contact with lithium metal at the elevated temperatures.

1. Metal foil, preferably nickel foil;
2. Electrolyte melted on the surface of the metal foil;
3. Copper-supported anode or aluminum-supported cathode;
4. Ni foil peeled off from the electrolyte surface after compression;
5. Copper-supported anode with attached layer of the solid-state electrolyte in intimate contact with the anode active, e.g. graphite or silicon-based composite layer.

[0040] FIG. 2 is a pictorial representation of an experimental and simulated XRD spectra of Li_3OCl electrolyte deposited directly on the surface of the lithium-ion battery anode with the corresponding Miller indices along with the detected admixture peaks of LiOH [30-32], Li_2O [31, 32], Li_2CO_3 [30], and LiCl [32].

[0041] FIGS. 3A-3F are a set of the SEM images of the Li_3OCl electrolyte deposited directly on the nickel foil without compression (a-c) and after compression (d-f) at 100, 1000, and 10000 magnification.

[0042] FIGS. 4A-4C are a pictorial representation of (a) An equivalent circuit for CR2025 half-cells with Li_3OCl solid-state electrolyte, graphite working electrode, and lithium metal as a reference. AC Impedance spectra of Li_3OCl half-cells at variable temperatures from 25° C. to 60° C. (b) and 70° C. to 100° C. (c). The frequency range is from 200 kHz to 0.01 Hz with a total of 30 points spaced logarithmically. The symbols and the lines represent the experimental and the fitting data, respectively.

[0043] FIG. 5 is a pictorial representation of Arrhenius plot for Li_3OCl solid-state electrolyte derived from the AC Impedance data.

[0044] FIG. 6 is a pictorial representation of the AC Impedance spectra measured at room temperature for the electrochemical half-cells with Li_3OCl solid-state electrolyte membrane having variable membrane thicknesses. The symbols and the lines represent the experimental and the fitting data, respectively.

[0045] FIGS. 7A-B are a pictorial representation of the cyclic voltammetry scans for the electrochemical half-cells with Li_3OCl solid-state electrolyte ($l=360 \mu\text{m}$), graphite-based anode, and lithium metal reference electrode at (a) 50° C., and (b) 100° C. The CV data at 25° C. is provided in the inset.

[0046] FIGS. 8A-B are a pictorial representation of the specific capacity at various C-rates, specifically C/20, C/10, C/5, and C/20 (3 cycles each, 1st C/20 cycle was used to discharge the cells from OCV and is not shown on the graphs) vs. the cycle number for the solid-state electrochemical half-cell with lithium metal reference electrode and C/Cu working electrode (WE) at 50° C. (a) and 100° C. (b).

[0047] FIGS. 9A-B are a pictorial representation of the galvanostatic charge-discharge voltage vs. capacity profiles of the half cells with Li_3OCl electrolyte ($l=350 \mu\text{m}$) in the voltage range of 0.05-1.0 V (vs. Li metal) at C/5 rate measured at (a) 50° C. and (b) 100° C.

[0048] FIGS. 10A-B are a pictorial representation of the cyclability data at 50° C. (a) and for the electrochemical half-cells at C/5 rate and the corresponding AC impedance

profiles measured at room temperature for the cells after long-term experiments at 50° C. (b).

[0049] FIGS. 11A-11B are a pictorial representation of the specific capacity at various C-rates, specifically C/20, C/10, C/5, and C/20 vs. the cycle number for the solid-state electrochemical half-cell with lithium metal reference electrode and Al/NMC cathode at 100° C. (a) and the corresponding impedance data for the fully integrated electrode-electrolyte architecture with lithium metal as an anode.

DETAILED DESCRIPTION

[0050] The following discussion is presented to enable a person skilled in the art to make and use the present teachings. Various modifications to the illustrated embodiments will be clear to those skilled in the art, and the generic principles herein may be applied to other embodiments and applications without departing from the present teachings. Thus, the present teachings are not intended to be limited to embodiments shown but are to be accorded the widest scope consistent with the principles and features disclosed herein. The following detailed description is to be read with reference to the figures, in which like elements in different figures have like reference numerals. The figures, which are not necessarily to scale, depict selected embodiments and are not intended to limit the scope of the present teachings. Skilled artisans will recognize the examples provided herein have many useful alternatives and fall within the scope of the present teachings. While embodiments of the present invention are discussed in terms of a manufacturing process of the solid-state glass-ceramic electrolytes, it is fully contemplated embodiments of the present invention could be used in most any solid-state glass-ceramic electrolytes application without departing from the spirit of the invention.

[0051] The manufacturing process includes compression of the melted electrolyte onto the said electrode surface followed by fast cooling, resulting in improved morphology at the electrolyte-electrode interface, absence of grain boundary effects and long-term electrochemical durability observed in contact with lithium metal at elevated temperatures. The disclosed invention does not require multiple manufacturing steps or moisture by-product removal. It is demonstrated the solid-state electrolyte produced by the method on the surface of graphite-based anodes or metal oxide-based cathodes meets the requirements for reversible lithium-ion intercalation and deintercalation during charge-discharge processes. Long-term cyclability tests at elevated temperatures confirm the absence of chemical or electrochemical processes at the solid-state electrolyte-electrode interfaces when the solid-state electrolyte is deposited by the said method.

[0052] The disclosed invention is different from other inventions known in the art, especially those using other types of solid-state ceramic electrolytes, such as garnets, perovskites, LISICONS etc. having extremely high melting points, prohibitive cost, and grain boundary effects due to their ceramic nature.

[0053] In comparison to disclosures regarding antiperovskites, the advantage of the proposed method is in the manufacturing of the electrolyte layers directly on the active electrode from a melted phase leading to strong adhesion between electrolyte and the active electrode surfaces, absence of grain boundary effects due to fast cooling, extended cyclability at elevated temperatures and absence of

chemical and electrochemical deterioration in presence of lithium metal when the said method is applied.

[0054] The disclosed method of the solid-state electrolyte manufacturing can be utilized in electrochemical energy generation and storage systems, such as lithium-ion or lithium-metal batteries, integrated solar-self-charging batteries, electrolyzers, supercapacitors, and combinations thereof. Furthermore, possible applications can also include sensors and photo- or bioelectrochemical devices require high ionic conductivity combined with mechanical integrity and electrochemical stability.

[0055] The present invention relates to a method of manufacturing the solid-state electrolyte layers on the surface of an active electrode by direct contact of the said electrode with the melted electrolyte at temperatures above or close to the melting point of the electrolyte.

[0056] The present invention also relates to a method of manufacturing solid-state electrolyte layers directly on the active electrode surfaces, specifically on the surface of anode or cathode, by direct contact of the said electrodes with the electrolyte at temperatures above or close to its melting point.

[0057] According to one specific embodiment, the manufacturing method comprises a step when a representative solid-state electrolyte from the class of lithium undoped or doped antiperovskites and their polymorphs with a general formula $\text{Li}_{3-x}\text{M}_x\text{C}_{1-y}\text{C}'_y\text{A}_{1-z}\text{A}'_z$, where M is hydrogen, or a metal from the first three groups of the periodic table of elements and x is defined by the charge of the corresponding metal, C and C' are chalcogens (O, S, Se), and A and A' are halogens (F, Cl, Br, I), or ions, such as BH_4^+ or BF_4^+ , can be applied.

[0058] The present invention also relates to a group of the said electrically conductive and cost-effective solid-state materials and their nanocomposites have relatively low melting point temperatures, specifically in the range from 250° C. and up to 600° C. allowing application of an economically feasible method described in this invention.

[0059] According to one embodiment, the proposed invention describes the method eliminating grain boundary formation in the solid-state electrolyte layers directly deposited on the electrode surface due to the applied process of fast cooling. Absence of grain boundaries within the electrolyte layer produced by the said method improves the electric conductivity and the lithium-ion transport in the said solid-state electrolyte.

[0060] According to one specific embodiment, the proposed invention describes the method producing solid-state electrolyte layers not undergoing phase transformations within the operation temperature range in the range of -20° C.-100° C. Absence of phase transformations within the solid-state electrolyte ensures high lithium-ion transport within the said operation temperature range of the operational electrochemical device.

[0061] According to one embodiment, the proposed invention describes the method produces solid-state electrolyte layers on the electrode surface, after a compression force is applied to the electrode located on top of the melted solid-state electrolyte.

[0062] According to one embodiment, the proposed invention describes the method producing solid-state electrolyte layers on the active electrode surface, and specifically anode or cathode electrode surface, after a compression force is

applied. This method results in intimate contact and minimized interfacial resistance between the said electrolyte and the electrodes.

[0063] According to one embodiment, the present disclosure is related to the disclosed invention related to the class of lithium undoped and doped antiperovskites and their polymorphs are produced in a moisture-free environment, such as those containing different inert or noble gases, including but not limited to helium, argon, or nitrogen or vacuum.

[0064] According to one embodiment, the present disclosure is related to a manufacturing process involving a class of lithium undoped and doped antiperovskites and their polymorphs after melting in a moisture-free environment, can be brought in direct contact with the active anode or cathode electrode surface due low melting point of the said electrolytes.

[0065] According to one specific embodiment, the present disclosure is related to the manufacturing process involving a class of lithium undoped and doped antiperovskites and their polymorphs can be brought in direct contact with the active anode or cathode electrode surface and compressed by using a metal with low adhesion toward the said electrode, preferably nickel foil.

[0066] The present invention relates to a group of electrically conductive and cost-effective solid-state materials and their nanocomposites, formed by the direct exposure of the battery electrodes to the melted electrolyte with addition of polymer-based, inorganic, or organic materials for mechanical electrolyte phase integrity with a specific feature of chemical, electrochemical, and crystal phase stability at elevated temperatures, and more specifically from room temperature and up to at least 100° C.

[0067] Different from other disclosures in the field, the present invention relates to the electrically conducting solid-state antiperovskite electrolytes produced in the said way do not form interfacial phases in contact with lithium metal anodes. These low conducting interfacial phases known in the art as Solid Electrolyte Interface (SEI) layers have not been detected for the solid-state electrolyte layers formed on the active electrode surface using the method disclosed in this invention.

[0068] Different from other disclosures in the field, the present invention relates to the electrically conducting solid-state electrolytes with antiperovskite crystal structures produced in a moisture-free environment on the active positive or negative battery electrode surface or both and the performance of the battery made in the said way.

[0069] Different from other disclosures in the field, the present invention relates to the electrically conducting solid-state electrolytes with antiperovskite crystal structures are produced in a moisture-free environment on the active positive or negative battery electrode surface or both and the performance of the battery made in the said way at elevated temperatures.

[0070] The applications of the present invention described in this disclosure are relevant but are not limited to the electrochemical energy generation and storage devices and specifically the electrode materials of the said devices; among them batteries, die-sensitized solar cells, fuel cells, supercapacitors, or combination thereof. Yet other application areas may also include touchscreens, organic light-emitting diodes, flexible organic solar cells, and organic electrochemical transistors. Furthermore, the disclosed

solid-state electrolyte can be used in hole-injecting transparent plastic and flexible electrodes for polymer light emitting diodes, field-effect transistors, and photovoltaic cells.

[0071] While conventional techniques use the expensive precursors and high-temperature synthesis for manufacturing of the solid-state electrolytes, the disclosed invention is related to the antiperovskite-based materials with a general formula $\text{Li}_{3-x}\text{M}_{3x}\text{C}_{1-y}\text{C}'_y\text{A}_{1-z}\text{A}'_z$, where M is H, alkali, or alkali earth metal, C and C' are chalcogens (O, S, Se), and A and A' are halogens (F, Cl, Br, I) or ions, such as BH_4^+ or BF_4^+ . The invention is specifically focused on a process of an electrolyte or an electrolyte-based nanocomposite manufacturing in a moisture-free environment possess constant crystal structure within the entire range of operation temperatures (-20°C .- 100°C .) and do not produce additional solid-state phases, such as those detected earlier along the grain boundaries in garnets. Specifically, a process of an electrolyte or an electrolyte-based nanocomposite manufacturing process in a moisture-free environment resulting in an electrochemically stable, highly conductive electrolyte in the absence of the phase transformations in a broad temperature range produced by the said method is disclosed.

[0072] The present invention demonstrates a manufacturing process of an solid-state electrolyte layer by the said method resulting in an improved electrode-electrolyte interface due to the direct contact with melted electrolyte in a moisture-free controlled environment favorable for solid-state lithium-ion batteries operating in a broad temperature range and at least up to 100°C . by utilizing the melting point value of the antiperovskite, e.g. lithium halide ($\sim 282^\circ\text{C}$.). The inventors of the embodiments disclosed herein, successfully tested the manufacturing process of the solid-state glass-ceramic electrolytes, known in the art as antiperovskites, directly on the active either positive or negative battery electrode surface, followed by compression of the electrolyte onto the said surface and fast cooling, results in improved long-term electrochemical durability observed in contact with lithium metal at the elevated temperatures. These embodiments validate, the solid-state electrolyte-electrode interfaces can be produced on the surface of metal, e.g. nickel foil, resulting in a grain-free electrolyte morphology and long-term electrochemical stability of the electrolyte in contact with lithium metal.

EXAMPLES FOR VARIOUS ASPECTS OF THE PRESENT DISCLOSURE

Example 1: Confirmation of the Crystal Structure of the Solid-State Antiperovskite Electrolyte Formed on the Surface of Metal that can be Delaminated after Fast Cooling

[0073] Disclosed in this example, is the first step of melting the solid-state electrolyte precursors on the surface of a metal, more preferably nickel foil, that does not adhere to the said electrolyte after cooling down to room temperature and can be easily delaminated in the end of the manufacturing process. The XRD data (FIG. 2) represents the crystal structure of the antiperovskite, specifically solid-state lithium halide Li_3OCl electrolyte formed on the surface of the nickel foil from the corresponding inorganic precursors. The experimental XRD spectrum of the Li_3OCl fits the simulated spectra with the major peaks corresponding to (011), (002), and (112) Miller indices as well as two smaller

peaks with (111) and (022). The experimental XRD spectrum matches the Li_3OCl XRD spectrum reported earlier [20] for alternative Li_3OCl synthesis conditions. However, a number of admixtures, such as LiCl , LiOH , Li_2O , and Li_2CO_3 [30-32] were detected in the original XRD samples. Besides the identified compounds, other compounds could be present, e.g. Li_2OHCl which XRD peaks align with the XRD patterns shown in FIG. 2 and depend on the speed of the cooling process [18]. The data suggests that specific precautions should be considered to avoid contact with atmospheric moisture and CO_2 , ensure complete conversion of the precursors into Li_3OCl antiperovskite, and pay specific attention to the synthesis parameters.

Example 2: Confirmation of the Electrolyte Grain Boundary-Free Morphology after Compression

[0074] The SEM images of the antiperovskite, and specifically lithium halide electrolyte (FIG. 3), demonstrate the effect of compression after melting the said electrolyte at 350°C . on the nickel foil surface. The rough surface of the uncompressed electrolyte after peeling off the nickel foil becomes more visible at higher magnifications. On the contrary, the surface of the compressed electrolyte is uniform without significant morphological changes across the surface. It appears to be more homogenous with no evidence of crystal structure formation that could potentially occur without compression or due to temperature variations because of the complex behavior of viscous liquids close to their glass transition temperatures [34].

Example 3: Manufacturing of the Antiperovskite Electrolyte on the Graphite-Based Anode Surface and Delamination of the Metal Foil Substrate

[0075] For manufacturing of the solid-state electrolyte, specifically lithium halide Li_3ClO , on the commercial anode surface, lithium chloride and lithium hydroxide precursors were mixed in an agate mortar inside an argon MBraun glovebox with ≤ 1 ppm H_2O and ≤ 1 ppm O_2 . A hotplate inside the glovebox with a surface temperature of 350°C . was used to heat the electrolyte precursor powder on the nickel foil until the powder completely melts. The Cu/C electrodes with diameter $d=17.0$ mm and thickness $l=0.012$ mm were degassed overnight in vacuum and pressed upon the molten electrolyte for a short period of time, and specifically for 15 seconds. The multilayer structure comprising of nickel foil with the molten electrolyte and Cu/C working electrode (WE) was taken off the hotplate and allowed to cool. The nickel foil was delaminated from the solid-state electrolyte resulting in Cu/C half-cell with adhered solid-state electrolyte layer.

Example 4: Demonstration of the Lithium Ion Transport in the Antiperovskite Electrolyte Layers in Absence of the Crystal Phase Transformations at Elevated Temperatures

[0076] The electrochemical half-cells were assembled with the Cu/C working attached to the solid-state electrolyte in contact with lithium metal foil. The active surface area of the half-cells defined by the area of lithium metal disks was ~ 1.13 cm^2 . A stainless-steel spacer (0.5 mm) and a wave-spring were placed on top of the lithium disk before crimping the cell at 1000 psi in argon glovebox with ≤ 1 ppm H_2O and ≤ 1 ppm O_2 . The AC impedance data was sampled with

30 points taken over a frequency range of 200 kHz-1 mHz using logarithmic point spacing at AC amplitude of 5.00 mV.

[0077] The AC impedance experimental and fitted data using the equivalent circuit (FIG. 4a) is presented in FIG. 4b,c. Z-view software from Scribner Associates Inc. was used to model the equivalent circuit (FIG. 4a). The same equivalent circuit was then used to fit all data obtained from the experiments at various temperatures. FIG. 3b,c shows that the experimental and the fitted data are in good correlation indicating a functional equivalent circuit.

[0078] The observed AC impedance spectra for half-cells with a solid-state electrolyte membrane (360 μm thick) at different temperatures within the range of 20-100° C. demonstrates the lithium-ion charge transfer represented by the semicircles and the Warburg impedance at lower frequencies responsible for the lithium-ion diffusion. At room temperature (FIG. 4b) the charge transfer resistance is extremely high reaching ~ 130 kOhm/cm² and does not allow for adequate lithium-ion half-cell battery performance evaluation. With temperature increase to 100° C., a significant decrease in the solid-state electrolyte resistance down to ~ 2.6 kOhm/cm² is observed (FIG. 4c). The corresponding Arrhenius plot (FIG. 5) is linear which indicates the absence of the crystal phase transformations reported earlier for the garnet-type solid-state ceramic [35] and Li₂OHCl electrolytes [22]. The AC impedance data for the Li₃OCl solid-state electrolyte at RT demonstrates a linear dependence vs. membrane thickness (FIG. 6). As expected, the charge transfer resistance of the Li₃OCl solid-state electrolyte decreases with distance traveled by lithium ions and reaches the value of 106 kOhm/cm² for the 296 μm thick electrolyte membrane.

Example 5: Antiperovskite Solid-State Electrolyte Performance at Elevated Temperatures by Cyclic Voltammetry

[0079] The temperature effect was investigated by cyclic voltammetry in a temperature range up to 100° C. (FIG. 7a,b). At room temperature, due to high charge transfer resistances in relatively thick solid-state electrolyte membranes, the peaks relevant to lithium ion intercalation-deintercalation within graphite phase are not visible. On the contrary, at 50° C. (FIG. 7a) the lithiation peaks are detected at 0.20V in correlation with those reported earlier [36]. At 100° C. (FIG. 7b) the lithiation peaks have higher resolution due to significant drop in the charge transfer resistance (FIG. 4b,c). Furthermore, at 100° C. three peaks at 0.17V, 0.21V, and 0.25V are visible corresponding to different activation energies of the lithium ions participating in the intercalation process within the graphite anode. Overall, the current density at 100° C. is an order of magnitude higher than at 50° C. indicating more efficient lithium-ion transport, which is in direct correlation with the impedance data (FIG. 4).

Example 6: Antiperovskite Solid-State Electrolyte at Elevated Temperatures: C-Rate Capability and Galvanostatic Cycling

[0080] The solid-state electrolyte was evaluated in a half-cell configuration in the voltage window of 0.05 V-1V. The tests performed at 50° C. and 100° C. (FIG. 8a, b) confirm the performance reproducibility in the electrochemical cells, absence of the specific capacity losses within graphite, and,

the capability of the antiperovskite solid-state electrolyte to provide lithium-ion transport.

[0081] The discharge-charge cycles were carried out at 50° C. and 100° C. in the voltage window of 0.05-1.0 V (vs. Li metal) at a rate of C/5 corresponding to the current density of 7.3 mA g^{-1} (FIG. 9). For clarity, only selected cycles are shown. During the first discharge and the following cycles, almost no voltage loss was detected. Within the first cycles, the charge curves shift towards the higher capacity values (FIG. 9b) and merge during the following 10th-50th cycles. The stable capacity values were reached only after 10-15 cycles, which could be due to the enhancement of the ionic transport kinetics within the antiperovskite electrolyte. It is assumed that the conditioning effect extending up to the 10-15th cycle is due to lithium intercalation/deintercalation within the graphite structure that requires several charge-discharge cycles to establish conduction pathways for lithium ions within the graphite and at the graphite-solid electrolyte interphase.

Example 7: Long-Term Continuous Cyclability Tests in Presence of Lithium Metal

[0082] The tests performed over a four-month period at a rate of $\sim C/5$ (FIG. 10) reveal a specific capacity retention of 80% within 575 cycles at 50° C. (FIG. 10a). On contrary to the drastic capacity losses observed earlier for the antiperovskite thin-film cells after only a dozen cycles [37], these results prove, for the first time, the ability of the antiperovskite electrolyte to transport lithium ions during long periods of time at elevated temperatures in presence of lithium metal reference electrode. The corresponding impedance data evaluated for different cycling times at 50° C. (FIG. 10b) indicate almost constant charge transfer resistances over the time required to perform 575 cycles at 50° C. (FIG. 10b). This performance is significantly superior to the percnore of the electrochemical cells with liquid electrolytes that are known to form SEI layers [1].

Example 8

[0083] A full cell assembled by the disclosed method in which instead of copper-supported anode an NMC-based cathode has been used (FIG. 11). The C-rate capability tests demonstrate reproducible data (FIG. 11a) that confirms the validity of the disclosed manufacturing method and the capability of the full electrochemical cell to transfer lithium ions from anode to cathode through the solid-state electrolyte and intercalate the cathode during discharge. During he discharge process lithium-ions are transferred back to the anode that is reflected in the corresponding values of the charge transfer resistance (FIG. 11b).

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What is claimed is:

1. A method of creating a solid-state glass-ceramic electrolyte, comprising the step of:

manufacturing an electrochemical device, specifically a battery with a metal with low adhesion to the solid-state glass-ceramic electrolyte.

2. The method of claim 1, further comprising the step of: demonstrating a low adhesion between the solid-state glass-ceramic electrolyte and the nickel surface, more preferably a nickel foil.

3. The method of claim 1, further comprising the step of: separating, by peeling off, the metal foil in the end of the manufacturing process with low adhesion to the solid-state glass-ceramic electrolyte and the nickel foil.

4. The method of claim 1, further comprising the step of: melting, on the surface of the metal foil, the inorganic precursors of the solid-state glass-ceramic electrolyte.

5. The method of claim 2, wherein lithium undoped or doped antiperovskites and their polymorphs with a general formula $\text{Li}_{3-x}\text{M}_x\text{C}_1-y\text{C}'_y\text{A}_1-z\text{A}'_z$, where M is hydrogen, or a metal from the first three groups of the periodic table of elements, x is defined by the charge of the metal, C and C' are chalcogens (O, S, Se), and A and A' are halogens (F, Cl, Br, I) or positive ions like BH_4^+ and BF_4^+ , can be used for the disclosed manufacturing process.

6. The method of claim 2, further comprising the step of: melting, on the metal foil surface in moisture-free inert atmosphere or in vacuum, the inorganic precursors for the solid-state glass-ceramic electrolyte.

7. The method of claim 2, further comprising the step of: melting, on the metal foil surface in a moisture-free controlled humidity atmosphere, such as dry air, argon, helium, nitrogen, or in vacuum the solid-state glass-ceramic electrolyte inorganic precursors.

8. The method of claim 2, further comprising the step of: melting the electrolyte inorganic precursors, directly on the said metal foil and brought in direct contact with electrodes of the electrochemical cell, such as aluminum-supported cathode or anode including copper-supported various graphite-, silicon-, or metal oxide-based nanocomposites.

9. The method of claim 2, further comprising the step of: bringing the electrolyte inorganic precursors in direct contact with aluminum-supported cathode or copper-supported anode and compressing forming a fully integrated electrode-electrolyte multilayer architecture half-cell further used to construct a full cell.

10. The method of claim 2, further comprising the step of: removing quickly from the heat source for fast cooling the fully integrated electrode-electrolyte architecture.

11. The method of claim 2, further comprising the step of: removing the metal foil of the fully integrated and quickly cooled multilayer configuration.

12. The method of claim 2, further comprising the step of: removal of the metal foil from the fully integrated electrode-electrolyte architecture with the electrolyte layer free of grain boundary morphology.

13. A solid-state glass-ceramic electrolyte, comprising: a metal foil layer having an upper and lower surface; a solid-state electrolyte layer compressed upon the upper surface of the metal foil;

an anode layer coupled to the electrolyte layer.

14. The solid-state glass-ceramic electrolyte of claim 14, wherein the solid-state electrolyte layer is melted onto the upper surface of the metal foil layer.

15. The solid-state glass ceramic electrolyte of claim 14, wherein the metal foil is comprised of nickel.

16. The solid-state glass ceramic electrolyte of claim 14, wherein the metal foil does not adhere to the solid-state electrolyte layer.

17. A method of manufacturing an antiperovskite, comprising the steps of:

melting an electrolyte onto an upper surface of a metal foil;

compressing an anode layer to the electrolyte on a surface opposite of the metal foil;

cooling the electrolyte; and

delaminating the metal foil from the electrolyte.

18. The method of claim 17, wherein the metal foil is made of nickel and has a low adhesion to the electrolyte, which is a solid-state glass ceramic electrolyte.

19. The method of claim 17, wherein inorganic precursors of the solid-state glass-ceramic electrolyte are melted on the surface of the nickel foil.

20. The method of claim 19, wherein the solid-state glass-ceramic electrolyte comprise lithium undoped or doped antiperovskites and their polymorphs with a general formula $\text{Li}_{3-x}\text{M}_x\text{C}_1-y\text{C}'_y\text{A}_1-z\text{A}'_z$, where M is hydrogen, or a metal from the first three groups of the periodic table of elements, x is defined by the charge of the metal, C and C' are chalcogens (O, S, Se), and A and A' are halogens (F, Cl, Br, I) or positive ions like BH_4^+ and BF_4^+ .

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