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Review—Solid Electrolytes in Rechargeable Electrochemical Cells

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Rechargeable electrochemical cells convert chemical energy into electric power on discharge and store electric power as chemical energy on charge. The chemical reaction between a reductant at the anode and an oxidant at the cathode has an electronic and an ionic component. The electrolyte of a cell conducts inside the cell the working ion of the reaction and forces the electronic component to traverse a circuit outside the cell to deliver a discharge electric power \( P_{\text{dis}} = I_{\text{dis}} V_{\text{dis}} \) for a time \( \Delta t_{\text{dis}} \), where \( I_{\text{dis}} \) is the electric current delivered at a voltage \( V_{\text{dis}} = V(q)_{\text{dis}} \); the cell voltage is constant with \( q \) for two-phase electrode reactions, but for a single-phase reaction in one electrode it decreases with the state of charge \( q \) of the cell. The chemical reaction is completed after a time \( \Delta t_{\text{dis}} \), where \( \Delta t_{\text{dis}} \) depends on \( I_{\text{dis}} \).

In a rechargeable cell, the chemical reaction is reversed by the application of a charging power \( P_{\text{ch}} = I_{\text{ch}} V_{\text{ch}} \). The voltages are:

\[
V_{\text{dis}} = V_{\text{oc}} + \eta_{\text{ch}} (I_{\text{ch}}) \quad \text{and} \quad V_{\text{ch}} = V_{\text{oc}} - \eta_{\text{dis}} (I_{\text{dis}})
\]

where the open-circuit voltage \( V_{\text{oc}} = (\mu_A - \mu_C)/e \) is the difference between the electrochemical potentials of the electrons in the two electrodes divided by the magnitude of the electronic charge \( e \). The \( \eta_{\text{ch}} \) and \( \eta_{\text{dis}} \) are called, respectively, the overvoltage and the polarization. The \( \eta(q) = I R_{\text{cell}} \) depend on the resistances \( R_{\text{cell}} = R_{\text{el}} + R_{\text{ch}} \) where \( R_{\text{el}} \) is the resistance to the ionic conductivity \( \eta_{\text{ch}} = q / \eta_{\text{ch}} \) in the electrolyte and \( R_{\text{ch}} \) is the resistance to ionic transport across any electrolyte/electrolyte interfaces. The \( R_{\text{ch}} \) at the anode and the cathode interface with the electrolyte are different from one another and the charge transport across an interface is also different between charge and discharge, so \( \eta_{\text{ch}} \neq \eta_{\text{dis}} \). The efficiency of storage of electric power in a rechargeable battery is 100 \( P_{\text{dis}}/P_{\text{ch}} \% \).

The capacity of a battery cell is the amount of charge per unit weight or volume passed between the electrodes on a complete cell reaction at a constant current \( I = dq/\Delta t \):

\[
Q(I) = \int_0^{\Delta t} I \, dq = \int_0^{Q(I)} d\delta \quad [2]
\]

An irreversible capacity loss in a charge/discharge cycle, i.e. a \( \Delta t_{\text{dis}}(n+1-1) < \Delta t_{\text{dis}}(n) \) where \( n + 1 \) and \( n \) are cell cycle numbers, represents a capacity fade with cycling; the coulomb efficiency of the cell \( 100 \Delta t_{\text{dis}}(n+1)/\Delta t_{\text{dis}}(n) \% \) is a measure of the cycle life before a rechargeable battery capacity fades to 80% of its original capacity.

The energy density of a battery cell is

\[
\Delta E = \int_0^{\Delta t} I V \, dt = \int_0^{Q(I)} V(q) \, dq = (V(q))Q(I) \quad [3]
\]

Rechargeable batteries with solid or molten electrodes store chemical energy within the electrodes of the cell; but with flow-through redox electrodes and with gaseous electrodes, the chemical energy may be stored externally to give a much greater energy store for a stationary battery than for a conventional portable battery in an electric vehicle or a hand-held wireless device.

For a given chemical reaction between the two electrodes of a rechargeable electrochemical cell, a small \( R_{\text{el}} \) requires a thin electrolyte with a sufficient density \( n_{\text{el}} \) of mobile working ions carrying a charge \( q_i \) with a high mobility \( \mu_i \). Since the electronic conductivity of a good metal is orders of magnitude greater than any electrolyte ionic \( \eta_{\text{ch}} \), electrochemical cells are fabricated with a thin electrolyte between electronically conducting electrodes of large area that need not be very thick or have a high electronic conductivity so long as they contact a large-area current collector that is an excellent metal. The \( R_{\text{ch}} \) can be made small across a solid/liquid interface, but it is increased where a mismatch between the \( \mu_A \) and \( \mu_C \) of a solid electrode and the LUMO or HOMO of a liquid electrolyte requires formation of a passivating solid-electrolyte-interphase (SEI) layer on the electrode; the working ion must transfer across the SEI layer also. For gaseous reactants at a solid-electrolyte surface, a low \( R_{\text{ch}} \) requires a high catalytic activity for the dissociation of the gas and its chemisorption into the electrolyte or the extraction of the working ion from the electrolyte. The realization of a small \( R_{\text{ch}} \) across a solid/solid interface appears to require that at least one solid be soft and/or that a soft conductor of the working ion be in the interface. Even at an alkali-metal anode where plating only changes the electrode dimension perpendicular to the interface, a soft interface layer that is chemically stable on contact with the two solids may be needed. If the electrode consists of small particles into which the working ion is inserted, from which it displaces an atom, or with which it alloys, the volume changes of a solid electrode particle on charge/discharge cycling normally prevent maintenance of a solid/solid interface on cycling even if the solid electrolyte is melted on fabrication to wet all the surface of the electrode particles. The latter constraint prevents, in our view, realization of a large capacity all-solid-state rechargeable battery unless the electrolyte is an elastomer or the volume changes of the electrode particles are small (\( \lesssim 1 \% \)); but what makes a battery cell unsafe with a flammable liquid electrolyte is the growth of dendrites from the anode to the cathode to create an internal short-circuit. If anode dendrites are prevented from forming by plating the anode reversibly across a solid electrolyte and/or are blocked from reaching the cathode by the separator, the use of a flammable catholyte should not be a safety concern. Moreover, a similar management of a stack of cells in a large battery would be required with/without a flammable catholyte if the cathodes evolve oxygen on overcharge.
In the following sections, different classes of solid electrolytes are discussed from the point of view of their potential for application to a rechargeable electrochemical cell. In the case of fuel cells, the double negative charge on the $O^{2-}$ ion makes it difficult to obtain an electrolyte of the solid oxide fuel cell with an oxide-ion conductivity $\sigma_o > 10^{-4} \text{ S cm}^{-1}$ at an operating temperature $T_{OP} < 500^\circ\text{C}$, but the single charge of the $H^+$ ion invites a search for a solid proton electrolyte with a $\sigma_H \approx 10^{-2} \text{ S cm}^{-1}$ below $100^\circ\text{C}$. The Nafion separator now used as the proton-exchange membrane in a PEM fuel cell is unstable above $70^\circ\text{C}$ and too expensive. To date, crystalline proton conductors contain either liquid water, or the water occupies oxygen vacancies where it transfers an $H^+$ to an oxide ion in an equivalent site, in which case the protons only move as $\text{OH}^-\text{ ions}$ in what is termed "vehicular transport". Crystalline alkali-ion electrolytes can be used in an all-solid-state battery, but the solid-electrolyte/solid-cathode interface limits capacity and cycle life. With molten electrodes, crystalline electrolytes of sufficient mechanical strength operate at a $T_{OP} \gtrsim 350^\circ\text{C}$. Today's batteries with liquid electrodes consisting of flow-through redox molecules operating at a $T_{OP} < 100^\circ\text{C}$ use a Nafion separator that leaks redox molecules between anolyte and catholyte. To date, oxide glass electrolytes containing polyanions have not exhibited sufficient alkali-ion or proton conductivity to be competitive with crystalline electrolytes. After an evaluation of these different existing solid electrolytes and their applications, we introduce a new electrolyte concept: dry cation ($\text{Li}^+$, $\text{Na}^+$, $\text{H}^+$) glass/amorphous electrolytes or dielectrics based on dissolving water into a crystalline electronic insulator. Fabrication of these water-solvated glass/amorphous electrolytes into a paste that reforms on drying into a continuous glassy/amorphous solid can facilitate application of the electrolyte over a large surface area. Rechargeable batteries with a high energy density can then be envisaged with a variety of cathode strategies. Where ionic transport across a current-collector/electrolyte interface requires a large activation energy, it is possible to use these ionic conductors as dielectrics with a large dielectric constant for an electrochemical capacitor or an electronic application.

### Solid Oxide-Ion Conductors

Solid oxide-ion conductors are used as the electrolyte in solid oxide fuel cells, for gas separations, and as mixed-oxide/electronic conductors for heterogeneous catalytic cathodes of a fuel cell. With a two-electron charge on the mobile ion, fast diffusion of the $O^{2-}$ ion has only been found above $500^\circ\text{C}$ in a crystalline solid oxide. The earliest structures were oxygen-deficient fluoride oxides, and yttria-stabilized zirconia (YSZ) has remained the most commonly used; but YSZ operates at a $T_{OP} \gtrsim 800^\circ\text{C}$, which has restricted commercialization of the solid oxide fuel cell.1 Oxygen-deficient perovskites based on the brownmillerite structure,2 Fig. 1, use cations stable in both octahedral and tetrahedral sites, which favors oxide-ion mobility where there are fewer oxygen vacancies than in the brownmillerite ABO$_{3-x}$. This concept is illustrated by the La$_{1-x}$Sr$_x$Ga$_{1-y}$Mg$_y$O$_{3-x/2}$ (LSGM) oxide-ion electrolyte3,4 in which the mobile vacancies only begin to become ordered in clusters below $600^\circ\text{C}$.5 However, this strategy can be plagued by absorption of water into the oxygen vacancies. An alternative strategy is to use a disordered lone pair on Bi$^{3+}$ in Bi$_2$O$_3$, which has an oxide-vacancy fluoride structure; Bi$_2$O$_3$ has also been extensively studied.6 Lowering the temperature of a fuel cell further appears to require use of a solid proton electrolyte. The single charge on the $H^+$ ion allows fast $H^+$ conduction at much lower temperatures; but as discussed below, the challenge is to find a dry solid proton conductor.

### Crystalline Alkali-Ion Conductors

It has been widely assumed that ionic mobilities should be greater in crystalline solids than in a glass or a polymer since they can move in a periodic array in a crystalline phase. Crystalline oxides offer a large enough energy gap between a conduction and a valence band for a chemically stable electrolyte of a high-voltage ($V \approx 5$ V) cell; but metallic lithium should not reduce the cation of an oxide in contact with it unless a conversion-reaction anode is desired. A crystalline alkali-ion electrolyte of an all-solid-state battery needs to be chemically stable on contact with the two cell electrodes and consist of an electronically insulating host framework structure within which a percolating interstitial space is partially occupied by only mobile alkali ions.

A $\text{Li}^+$ ion is small enough that the percolating interstitial space may consist of empty tetrahedral sites bridged by face-sharing empty octahedral sites of a close-packed oxide-ion array as is illustrated by the layered MO$_2$, the spinel [M$_2$]O$_4$, and the garnet A$_3$M$_2$O$_{12}$ host frameworks, Fig. 2. Fast mixed Li$^+$/electronic transport has been demonstrated in layered Li$_{1.4}$CoO$_2$ and the spinel Li$_{1+x}$[Mn$_2$]O$_{4-x}$.

![Figure 1. The brownmillerite structure.](image1)

![Figure 2. The 3D connection of Li sites within the interstitial space of the Li$_{7.5}$La$_3$Zr$_2$O$_{12}$ garnet structure for Li$^+$ ordered on half the tetrahedral sites and octahedral-site Li$^+$ displaced toward the empty tetrahedral sites; the interstitial space consists of tetrahedra bridged by face-sharing octahedra.](image2)
however, viable Li⁺ electrolytes with these structures have not been identified. On the other hand, garnet Li⁺ electrolytes have been identified with a Li⁺ concentration between 6 and 7 per host formula unit;¹⁰ bulk Li-ion conductivities have reached σ₁ > 10⁻³ S cm⁻¹ at room temperature.¹¹ However, the garnet electrolytes are unstable on exposure to air if they contain more than 3 Li⁺/formula unit, corresponding to ordering of the Li⁺ on all the tetrahedral sites. With more than 3 Li⁺/formula unit, some excess Li⁺ migrate from the bulk of a garnet host containing Zr(IV) cations to react with adsorbed water or CO₂ on the surface of the garnet particles or grains. Moreover, the Li⁺ conductivity at room temperature in a crystalline ceramic remains too low to allow use of a thick crystalline Li⁺ electrolyte with a close-packed oxide-ion sublattice, which has restricted their use since thin ceramic membranes are not mechanically robust unless supported or in a composite with a polymer. Although a Lithium anode can be plated across membranes are not mechanically robust unless supported or in a composite with a polymer. Although a Lithium anode can be plated across a dense garnet film from which water and CO₂ have been removed, low-cost fabrication of large-area garnet Li⁺ electrolytes on a copper current collector remains a challenge.

The Na⁺ ions are too large to occupy a 3D interstitial space of a close-packed oxide-ion array, but they can occupy a 2D interstitial space between the strongly bonded MO₂ layers of a layered host. The MO₂ layers can be shifted with respect to one another to place the Na⁺ gallery is not fully occupied. However, Na⁺ ions either attract water into the Na⁺ galleries where Na-OH₂ molecules are formed or Na⁺-Na⁺ interactions in electronic insulators stabilize ordered Na⁺ phases in which the Na⁺ are not mobile.

On the other hand, host 3D framework structures formed by replacing O²⁻ by (XO₄)³⁻ polyoxions have a larger interstitial space where the alkali-ion interaction with water is not a problem, as has been illustrated by the NASICON structure of Na₃₋ₓZrₓ(P₁₋ₓSixO₄)₃, Fig. 3. However, the Li⁺ ion is too small for the hexagonal NASICON structure unless the volume of the interstitial space is reduced by smaller framework cations, as has been illustrated by the LISICON electrolyte₁² Li₁₋ₓ(Al₁₋ₓT₁ₓ)₀(PO₄)₃ and by transition-metal electrode compounds with the hexagonal LISICON structure.¹³ Although a LISICON electrolyte separator in a dual liquid-electrolyte system has been demonstrated,¹⁴ its Ti(V) ion is reduced on contact with a metallic-lithium anode and by protons from an aqueous electrolyte with a pH < 7.¹⁵ Nevertheless, LISICON has been shown to support an air cathode with a buffered aqueous electrolyte in a dual-electrolyte cell.¹⁶

Although Li-sulfide electrolytes with a large σ₁ have been identified,¹⁷ᵃᵇ they have not exhibited the stability needed in the presence of a liquid electrolyte or the needed sulfide/solid-cathode interfaces for a high-capacity all-solid-state battery. A commercially viable crystalline alkali-ion electrolyte has yet to be demonstrated, but as discussed in the last section, a water-solvated glass/amorphous alkali-ion electrolyte may prove viable.

### Composite Oxide/Polymer-Gel Separators

A separator needs to transport the working ion of a cell, to be inexpensive, and to be chemically inert on contact with the two electrodes of a cell. The requirement that they also be mechanically robust and, preferably, flexible as thin membranes has prompted exploration of composite oxide/polymer-gel membranes. Polymer-gel electrolytes are inexpensive and excellent alkali-ion conductors; they can be formed into mechanically robust, flexible membranes especially if they are in the form of a cross-linked mesh with a mesh size small enough to retain small oxide particles or the polymer is cast onto a glass-fiber paper. These composite membranes that support oxides (soggy sand electrolyte)¹⁸ block dendrites from an alkali-metal anode; they may also block soluble redox molecules of a liquid flow-through cathode, and an associated osmosis problem can be overcome by introducing a concentration of inactive anolyte molecules to balance that of the catholyte redox molecules.

An initial oxide/polymer-gel separator used low-cost thiolenic chemistry to create, under mild conditions, a square (30×30 Å²) polymer-mesh with a tetra-ethylene crosslinker and links of di(ethylene glycol)divinylether (DEGDVE) with ethylene oxide (EO) that is strong enough to retain Al₂O₃ particles.¹⁹ With about 45% by weight Al₂O₃ loading, the polymer remains flexible, Fig. 4, blocks dendrites from an alkali-metal anode, and absorbs an organic-liquid battery electrolyte. The glass transition temperature of this Al₂O₃/PEG composite is Tg ≃ −30°C and has a melt temperature Tm ≃ 63°C. A Tg well-below room temperature facilitates the incorporation of the liquid electrolyte into the amorphous polymer structure. The liquid electrolyte provides a faster Na⁺ than Li⁺ diffusion because of the stronger affinity of Li⁺ for the oxygen of the EO units. Despite a σ₁, approximately two orders of magnitude lower than that with a conventional polypropylene (PP) separator (Celgard 2500), the Al₂O₃/PEG separator can be made thin enough to have an adequate conductance. Its ability to block dendrites from a Li⁺ anode was demonstrated, and a 6-bromohexylferrocene molecule for a redox flow-through cathode was shown to be blocked from migrating to the anode side of the membrane. Poly(ethylene glycol)dimethylether (PEGDME) added to the anode side of the membrane balanced the concentration of the redox molecule on the cathode side and eliminated problems with cell osmosis. This electrolyte strategy offers the possibility of realizing a high-capacity cell with a flow-through cathode. However, with a conventional organic liquid electrolyte contacting the anode, a Li⁺ or Na⁺ anode forms dendrites on charge that grow on cycling; as the dendrites grow on charge, they form fresh surface that needs to be pacified by an SEI layer, and the Li⁺ of the SEI layer comes from the cathode. Therefore, even if the initial SEI layer is lithiated on the...
initial charge by an additive in the cathode, the formation of a new SEI layer on each cycle introduces a capacity fade that limits the cycle life of the cell. Therefore, it appears necessary to develop a solid electrolyte that is not reduced by an alkali-metal anode and through which an alkali-metal can be plated reversibly on a current collector if we are to have a safe, long-cycle-life rechargeable cell having an alkali-metal anode. On the other hand, by choosing different links of the tetraethyl cross-linked mesh on the cathode side of a separator, it is possible to trap reversibly the soluble intermediates of a sulfur cathode.19

A composite gel-polymer/glass-fiber-paper membrane impregnated with a conventional Li+ or Na+ battery electrolyte has also been prepared.20 Rolled into a thin membrane, this low-cost electrolyte does not shrink at higher temperatures as does the conventional polypropylene (PP) separator Celgard 2500; it also blocks dendrites from a metallic lithium or sodium anode. The conduction band or LUMO of the composite is at a high enough energy that it is not reduced on contact with a metallic lithium or sodium anode, and it can support a cathode with a redox voltage 4.8 V below a metallic-sodium anode, making it suitable for use in a high-voltage cell. The polymer is a porous polyvinylidenedifluoro-co-hexafluoropropylene (PVDF-HFP) having its surface properties modified by a thin coating of adhesive polydopamine (PDA) to improve the liquid electrolyte flow; the PDA coat is thin enough that it does not block the channels and pores of the glass-fiber paper (GF) after coating of the fibers of the GF/PVDF-HFP/PDA composite membrane. This membrane retains its mechanical strength and thermal stability up to 200°C.

**Traditional Glass/Amorphous and Water-Soluble Acid Electrolytes**

Polymer electrolytes can provide acceptable interfaces with solid electrodes for an all-solid-state battery, but to date the ionic conductivities of the polymers have been too low for competitive ambient-temperature operation. Glasses, on the other hand, can be alkali-ion rich or proton solid electrolytes with little, if any, grain-boundary contribution to the resistance. Those with a low melting temperature rich or proton solid electrolytes with little, if any, grain-boundary electrodes for an all-solid-state battery, but to date the ionic conduc-

**Water-Solvated Glass/Amorphous Cation (Li+, Na+, H+) Electrolytes or Dielectrics**

A solid ionic conductor that is an electronic insulator acts as an electrolyte where it conducts ions between electrodes in a battery or a fuel cell, but it is a dielectric where the mobile ions remain in the electrolyte as in an electrochemical capacitor. A crystalline electronic insulator containing a large concentration of alkali ions (Li+ and/or Na+) bonded to oxygen and/or halide atoms X = Cl, Br, and/or I may be converted inexpensively into a water solvated glass/amorphous solid alkali-ion electrolyte/dielectric by the addition of water up to or less than its solubility limit in the solid. The transition from a crystalline solid to a glass/amorphous solid alkali-

**Figure 5.** An Arrhenius plot of the Li+ conductivity and the temperature dependence of the dielectric constants of a glass/amorphous solid Li+ electrolyte/dielectric formed by adding BaO and water to Li3.4H4ClO4, after M. Helena Braga.30
Li$_{1.3}$H$_2$OCl by water and 0.005 BaO/formula unit. The temperature dependence of the dielectric constant (permittivity) of the product, also shown in Fig. 5, show a $T_\alpha \approx 50^\circ$C.

(2) Fig. 6 shows the room-temperature charge/discharge of a capacitor with the water-solvated glass/amorphous solid Na$^+$ electrolyte sandwiched between two aluminum-plate electrodes; the dielectric was relatively thick. The initial discharge, which occurred in less than a second, could not be recorded with the available apparatus; a second discharge occurred within about two seconds and the third slow component, a second, could not be recorded with the available apparatus; a second component of the discharge occurred over several minutes. We speculate that the initial fast discharge originates from a randomization of dipole orientations, the second discharge step reflects the Na$^+$ diffusion, and the slow discharge the slower OH$^-$ diffusion.

(3) Crystalline BaKPO$_4$ was transformed into a water-solvated glass/amorphous solid H$^+$ electrolyte/dielectric having a proton conductivity $\sigma_H \approx 10^{-2}$ S cm$^{-1}$ below 100$^\circ$C, see Fig. 7, by exposing the crystalline solid to water vapor at 80$^\circ$C. The (PO$_4$)$_3$$^-$ ions do not attract a second H$^+$ ion, although the hydrophilic, the solid proton conductor can be used as a capacitor with the water-solvated glass/amorphous solid Na$^+$ electrolyte sandwiched between two aluminum-plate electrodes; the dielectric was relatively thick. The initial discharge, which occurred in less than a second, could not be recorded with the available apparatus; a second discharge occurred within about two seconds and the third slow component of the discharge occurred over several minutes. We speculate that the initial fast discharge originates from a randomization of dipole orientations, the second discharge step reflects the Na$^+$ diffusion, and the slow discharge the slower OH$^-$ diffusion.

Conclusions

This brief review of old and new solid electrolytes, including gel-polymer/oxide composites in which the liquid electrolyte may be immobilized, give promise of efficient, low-cost electrochemical cells for the storage of electrical energy from sources other than fossil fuels provided the alkali-metal-anode/solid-electrolyte interface problem can be solved. The concept of a glass/amorphous electrolyte containing solvated water deserves further exploration.

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