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Stability of the solid electrolyte Li_3OBr to common battery solvents

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ABSTRACT

Recently a new class of solid lithium ion conductors was reported based on the anti-perovskite structure, notably Li_3OCl and Li_3OBr. For many beyond lithium-ion battery uses, the solid electrolyte is envisioned to be in direct contact with liquid electrolytes and lithium metal. In this study we evaluated the stability of the Li_3OBr phase against common battery solvents electrolytes, including diethylcarbonate (DEC) and dimethylcarbonate (DMC), as well as a $LiPF_6$ containing commercial electrolyte. In contact with battery-grade organic solvents, Li_3OBr was typically found to be insoluble but lost its crystallinity and reacted with available protons and in some cases with the solvent. A low temperature heat treatment was able to restore crystallinity of the samples; however evidence of proton ion exchange was conserved.

1. Introduction

Lithium-ion conducting solid electrolytes for lithium-ion or lithium based batteries are under investigation again due to the growing interest in lithium–air (oxygen) and lithium–sulfur energy storage systems [1–3]. A key requirement to maximize energy density and system voltage for these high energy systems is the necessity to use lithium metal as the anode. However since lithium metal is unstable toward most of the common electrolyte solvents it requires a protection scheme that still allows it to function within the cell [4]. Previous barrier attempts used to shield lithium metal have included polymers [5,6], SEI additives [7], and use of lithiated Zintl phases [8,9]; however the most promising avenue appears to be solid electrolytes [10–13]. A significant limitation to their implementation has been either their poor intrinsic stability toward lithium metal (e.g. LATP), or their insufficient overall conductivity (e.g. LiPON). Recently, it was reported by Zhao and Daemen that the lithium-rich anti-perovskite compounds Li_3OX (X = Cl,Br) showed excellent room temperature lithium-ion conductivity ($\sim 10^{-2}$–10^{-3} S/cm) and should be stable against lithium metal [14]. Since many of the beyond-lithium ion applications of these materials involve being stable to not only to reduction by lithium metal but also to a variety of non-aqueous electrolytes, we have investigated the stability of Li_3OBr to a variety of commonly used electrolyte systems that have been proposed for lithium–air or lithium–sulfur energy storage systems.

In general the better electrolyte solvents should meet the following criteria: they should dissolve salts sufficiently to achieve conductivity above 10^{-3} S/cm; they have to have low viscosity, be inert to all cell components, and remain liquid over a wide temperature range. Ideally, they also need to be safe, non-toxic and economical. Since highly reducing and oxidizing materials are involved, they also should not have any active protons. The presence of polar groups however is typically required to achieve the needed salt solubility, typically 1 M. Based on those criteria, several solvents, mostly esters, carbonates, and ethers, have been selected; our stability study focuses on the most commonly used ones. Also included in our study is the extensively used electrolyte “Gen2” (1.2 M $LiPF_6$/70 wt% EMC/30 wt% EC), developed for high power systems.

2. Experimental

Li_3OBr was synthesized by the direct reaction of a stoichiometric ratio of $Li(OH)\cdot H_2O$ (Aldrich, >98% ACS Grade) and LiBr (Aldrich, >99%). As previously done by the authors in Ref. [14], the starting materials were ground together using a mortar and pestle and dried under an Argon atmosphere at 150 °C for 48 h. The sample was then heated to 400 °C over a 2-h period to liquefy the materials, held for 15 min, and quenched onto a copper block. It was noted that samples slow cooled in the furnace tended to be difficult to remove from the alumina crucible used. The sample was ground to a fine powder using a laboratory coffee-type grinder.

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The samples for the stability study were prepared by mixing of 0.15 g of Li_3OBr with 10 ml of the selected solvents or electrolytes. Chosen solvents were – water (DI), propylene carbonate (PC), diethylcarbonate (DEC), dimethylcarbonate (DMC), 1,2-dimethoxyethane (DME), and the electrolyte solution Gen2 (1.2 M $LiPF_6$ solution in 70 wt% ethylmethyl carbonate (EMC)–30 wt% ethylene carbonate (EC)). The battery grade electrolyte Gen2 (<10 ppm water) was purchased from Ube [15]. All anhydrous organic solvents were purchased from Sigma–Aldrich (>99%), stored in an inert atmosphere box, and used as received. The mixtures were placed in sealed glass vials and placed in an Ar-filled drybox (5–10 ppm H_2O), shaken for 1 minute and allowed to sit for 6 weeks. After the contact period, if present, residual solid was collected and dried at room temperature under vacuum.

Samples were analyzed for crystalline phases before and after heating to 75 °C for 24 h by powder X-ray diffraction using a Bruker D8 Powder Diffraction System. Samples were prepared for analysis and covered by tape during the data collection with some exposure to ambient air during the process. For the water-decomposed sample, data were also collected on a Rigaku MiniFlex 600 to determine phase purity. Elemental analysis of dried samples was performed using scanning electron microscopy (Quanta 400F ESEM) equipped with energy-dispersive X-ray spectrometry (EDS, Oxford INCA).

3. Results and discussion

For many of the evolving uses of lithium-based batteries, the high energy density imparted on a cell design by the use of lithium metal appears to be essential to meet goals. However, for these systems, including lithium–air or lithium–sulfur, the ability to protect the lithium surface from solvent attack (with associated loss of active lithium) is a critical need to ensure system life and stability. Li_3OBr is a promising solid electrolyte candidate for these types of systems because of its reported high ionic conductivity and stability to lithium metal. The structure is shown in Fig. 1. However, although it is a three-dimensional lattice compound, there was some question as to its stability toward common coordinating battery solvents that would be representative of the environments the solid electrolyte would be exposed. In this study we investigated the stability over time of Li_3OBr to commonly used energy storage system solvents. The solvents tested included water, several common organic solvents used in lithium-ion batteries, and Gen2 electrolyte. A summary of the observations made and the analysis of the results is presented in Table 1 and a summary of the various relevant solvent properties is presented in Table 2.

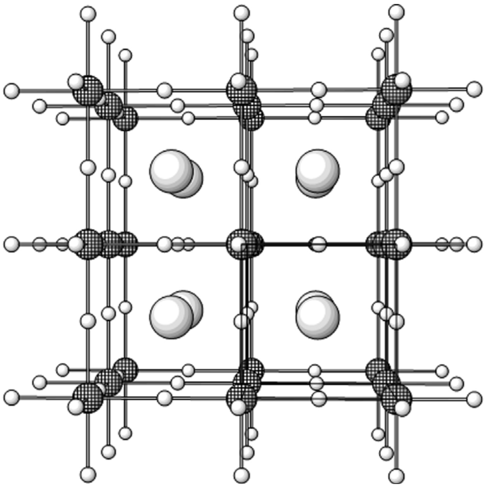

Fig. 1. The structure of Li_3OBr. The large gray sphere in the middle is the bromide anion, the oxide anion positions are at the corners of the cube and are represented as hatched mid-size spheres, the smallest gray spheres are lithium cations sit at the middle of each edge.

As can be seen in Table 1, the materials behaved in two distinct ways. For the solvents evaluated, visually, the Li_3OBr remained at the bottom of the tube and appeared insoluble. After six weeks, the solid residues were isolated and dried under vacuum. The XRD analysis of the collected samples only showed broad diffraction peaks, which is consistent with an amorphous or poorly crystalline phase. After heat treatment at 75 °C for 24 h, the samples were re-examined and evidence for ion exchange (proposed equation is shown below) was observed.

$$Li_3OBr + xH^+ \rightarrow Li_{3-x}H_xOBr + Li^+ (0 < x < 2)$$

Differentiation between the various $Li_{3-x}H_xOBr$ phases by powder X-ray diffraction is difficult owing to the very small differences in lattice constant reported (~0.02 Å over the whole range of stoichiometry) and the peak broadening observed due to the small particle sizes of the isolated products [16–18]. These solid solution ($Li_{3-x}H_x$)OBr phases most likely formed from ion exchange with protons present in the sample containers that came from sources including adventitious water in the solvents and side reactions with solvent that produce protons [19,20]. Fig. 2 shows the XRD pattern of Li_3OBr before and after contact with diethylcarbonate (DEC). This series is representative for the samples isolated from organic solvents. It appears that even at very low levels of water exposure the materials appear to favor ion exchange, possibly driven by the strong energy of solvation of lithium by the surrounding uncoordinated solvent.

It should be noted that the same stability was observed for Li_3OBr in all solvents tested despite significant differences in properties: cyclic esters (PC) are uniformly polar and rather viscous whereas acyclic esters (DMC, DEC) are weakly polar and fluid. As for ethers (DME), they are moderately polar and have a low viscosity.

It should also be noted that DME gradually turned brown over the time of the experiment. The color change is commonly observed and has been attributed to light degradation of the electrolyte components or by solvent decomposition reactions induced by slow reactions with the dissolved salt (from Li_3OBr) or combination thereof [15].

In water and Gen2, dissolution of Li_3OBr was observed. Whereas in water dissolution occurred within 30 min, it took several weeks to be completed in Gen2. The activity of Li_3OBr in the high salt molarity electrolyte was interesting in that with some of the solvent molecules already coordinated, the dissolution of the solid electrolyte appeared to be accelerated when compared to the simple solvents previously noted. Minimal attempts were made to vibrate or shake the sample so it may have dissolved faster if such actions were taken. For the water sample, the clear liquid was heated at 75 °C for several days to evaporate the water. The isolated crystalline products were identified by powder X-ray diffraction methods to contain mainly $LiBr{\cdot}H_2O$, $LiOH{\cdot}H_2O$, however several small additional peaks were not uniquely identified. The pattern is shown in Fig. 2d, compared to the starting Li_3OBr material. Since the glass container appeared discolored, additional EDS analysis identified the presence of sodium phases (from hydroxide attack on the glass) but no significant amounts of silica. The unknown XRD peaks were assigned as $NaHCO_3$.

From this data we can conclude that for several common non-aqueous organic solvents, Li_3OBr does not dissolve into solution, however it is not stable to the influence of solvation. Whereas, the