Enhanced Li$_{1+x}$Al$_x$Ge$_{2-x}$(PO$_4$)$_3$ Anode-Protecting Membranes for Hybrid Lithium–Air Batteries by Spark Plasma Sintering

Guang Yang, Dorsasadat Safanama, Kia Chai Phuah, and Stefan Adams*

ABSTRACT: NASICON-type Li$_{1+x}$Al$_x$Ge$_{2-x}$(PO$_4$)$_3$ (LAGP) is a promising electrolyte with high ionic conductivity (>10$^{-4}$ S cm$^{-1}$), excellent oxidation stability, and moderate sintering temperature. However, preparing dense LAGP pellets with high ionic conductivity is still challenging because of the hazards of dopant loss and partial decomposition on conventional sintering. Here, spark plasma sintering (SPS) of LAGP membranes is explored as a promising ultrarapid manufacturing technique, yielding dense electrolyte membranes. Optimizing the SPS temperature is important to achieve desirable density and hence ionic conductance. Our results show that LAGP samples spark plasma-sintered at 750 °C exhibit the highest total ionic conductivity of 3.9 × 10$^{-4}$ S cm$^{-1}$ with a compactness of 97% and nearly single-crystalline particles. Our solid-state NMR results, X-ray diffraction studies, and scanning electron microscopy micrographs confirm that the achievable ionic conductivity is controlled by the retention of the Al dopant within the LAGP phase, necking between particles, and the minimization of grain boundaries between crystallites within a particle. To benchmark the performance of our spark plasma-sintered solid electrolyte membranes over conventionally prepared LAGP, we demonstrate their favorable performance in hybrid Li–air batteries. The highest energy efficiency is achieved for the fastest ion-conducting membrane sintered at 750 °C.

1. INTRODUCTION

Li–air batteries (LABs) are considered promising alternative energy storage systems for Li-ion batteries because of their huge energy density.1 Compared to conventional organic LABs, aqueous and hybrid LABs demonstrate improved cycle efficiency and volumetric energy density as the discharge products remain dissolved in the aqueous catholytes rather than clogging the air cathode surface.2,3

The key component typically controlling the performance of aqueous and hybrid LABs is the lithium-ion-conducting anode-protecting membrane, which not only has to transport Li$^+$ ions fast and exclusively but also has to maintain (kinetic) electrochemical stability when in contact with both lithium metal (or an organic anolyte) and the aqueous catholyte. The membrane acts both as a solid electrolyte and a mechanical separator that prevents lithium from reacting chemically with the catholyte or short-circuiting the cell by dendrite growth. Garnet-type oxides and LiSICON-type (i.e., Li$_{2+x}$Zn$_x$Ge$_{16}$O$_{39}$-related) ion-conducting electrolytes have been explored as anode-protecting membranes in organic electrolyte batteries because they have acceptable room temperature ionic conductivities and wide electrochemical windows.4−6 However, proton exchange in water renders them unstable when in contact with aqueous catholytes.7−9 Moreover, perovskite-type oxides have been investigated.10,11 Likewise, the perovskite-type solid electrolytes show relatively high bulk ionic conductivities but suffer from poor stability when in contact with lithium and low grain boundary conductivity.12

NASICON-type solid electrolytes such as Li$_{1+x}$Ti$_2$Al$_x$(PO$_4$)$_3$ (LTAP)$^{13−15}$ or Li$_{1+y}$Al$_x$Ge$_{2−y}$(PO$_4$)$_3$ (LAGP)$^{16−21}$ are the main class of solid electrolytes which have been successfully employed in aqueous and hybrid LABs.22 LTAP shows good stability in nearly neutral aqueous solutions such as aqueous LiCl but not in strongly acidic and basic solutions.23,24 In addition, Ti in LTAP is easily reduced progressively into a mixed conductor.25 NASICON-type LAGP also shows high ionic conductivity (bulk conductivities around 10$^{-3}$ S cm$^{-1}$ and total conductivities > 10$^{-3}$ S cm$^{-1}$), excellent stability at high potential, and relatively low sintering temperature.$^{26−30}$ In our previous work, the LAGP ceramic and Butvar-based hybrid membrane with LAGP as the ceramic filler have been successfully utilized as anode-protecting membranes in hybrid LABs.$^{31,32}$ The cells already demonstrate high energy efficiencies and cyclic stability. Although

Received: April 21, 2020
Accepted: June 15, 2020
Published: July 15, 2020
significant progress has been made for the application of LAGP in aqueous/hybrid LABs, it remains challenging to reliably prepare dense LAGP membranes with high ionic conductivity (as required for extending the range of current densities for which the membrane overpotential remains acceptably low). This is mostly caused by the proximity of sintering and decomposition temperatures and particularly the tendency of the material to segregate dopant-rich impurities on extended high-temperature sintering. Dense membranes not only maximize the membrane conductance but also reduce the rate of chemical attack by the catholyte (and the anolyte, in the case of a hybrid battery).

Spark plasma sintering (SPS) is emerging as a promising sintering technique for ultrarapid preparation of dense electrolyte pellets of NASICON, garnet, perovskite, sulfides, and lithium-ion-conducting solid electrolytes. Duan et al. recently reported that the total ionic conductivity of spark plasma-sintered LTAP is up to 2 orders of magnitude higher than that of conventionally sintered pellets, which is attributed by these authors to a fast-ion-conductive interphase between ceramic and glass phases. Kubanska et al. reported a total conductivity of $3.3 \times 10^{-5}$ S cm$^{-1}$ for LAGP pellets sintered at a relatively low temperature of 650 °C and a pressure of 75 MPa, yielding 87% dense pellets. In their study, the ceramic LAGP powder was obtained from glassy LAGP by heat treatment at 950 °C for 18 h. Our earlier detailed in situ synchrotron study of LAGP crystallization had, however, shown that such an extensive heat treatment is not necessary to ensure crystalline LAGP, as crystallization can be completed at just above 800 °C. Moreover, heating to temperatures above

Figure 1. Microstructures of (a) crystalline LAGP powder prepared by the solid-state sintering technique (sintered at 850 °C for 2 h) and the LAGP pellet prepared by the SPS technique at various sintering temperatures of (b−f) 600, 650, 700, 750, and 800 °C. SPS duration is 5 min with a heating rate of 100 °C/min from the precursor powder, shown in graph (a).

Figure 2. (a) Changes in XRD patterns of a cold-pressed pellet of the pristine LAGP powder (preannealed at 850 °C for 2 h) and spark plasma-sintered pellets in the temperature range of 600−800 °C; Rietveld refinement of the spark plasma-sintered pellet at (b) 750 and (c) 800 °C (wR$_p$ of 7 and 8%, respectively). Vertical bars correspond to different phases present in the structure, as indicated in the legend of the graphs.
900 °C will inevitably lead to partial decomposition (sometimes confused in the early literature on LAGP with the surviving amorphous phase) and substantial dopant losses, which might explain the moderate conductivity observed by these authors.

Recently, Zhu et al.\textsuperscript{40} have investigated the effect of SPS temperature on the compactness and ionic conductivity of LAGP pellets. The highest ionic conductivity was achieved in their study for pellets sintered at 650 °C for 10 min with a relatively high density of 97.6%, while for higher sintering temperatures, they report a drastic decrease in density. Apart from their electrochemical studies, however, no detailed analysis of the precursor powder and the effects of sintering conditions on the microstructure were reported in their work.

Here, we therefore aim for a more comprehensive rational optimization approach. Fully crystallized LAGP ceramic powder synthesized via melt quenching and subsequent crystallization by heat treatment is used as a starting material for SPS to produce dense pellets. Spark plasma-sintered LAGP pellets are prepared under well-controlled sintering pressure, time, and temperature conditions. The effect of sintering temperature on the relative density, ionic conductivity, and microstructure of the spark plasma-sintered pellets are investigated, and the relevance of the optimization of the LAGP membrane processing for enhancing the performance of LABs is demonstrated.

2. RESULTS AND DISCUSSION

The annealing procedure is of key importance to obtain LAGP ceramics with a desirable microstructure and thereby translate a material with high specific conductivity into an anode-protecting membrane with favorably high ionic conductance. According to scanning electron microscopy (SEM) micrographs of the LAGP pellet prepared by solid-state sintering (Figure 1a, i.e., the starting material for SPS processing), the average grain size is around 490 nm. Figure 1b–f then shows the effect of SPS on the surface topography of the LAGP pellet after SPS at 600, 650, 700, 750, or 800 °C for 5 min, respectively. The corresponding particle-size distributions and the homogeneous elemental distributions (for the 750 °C sample) are shown in Figures S1 and S2 in the Supporting Information.

As to be expected, the pellets grow denser on increasing the sintering temperature. The SPS samples sintered at 600 or 650 °C show insufficient necking, while for pellets sintered at 700 and 750 °C, it is evident that the structure is less porous, resulting from enhanced necking between particles. The pellet sintered at 800 °C differs from those sintered at lower temperatures by a marked increase in grain size. The primary particles obtained at 600 and 650 °C are of ~0.6–0.7 μm micron size but are only loosely connected. The particle size of pellets sintered at 700 and 750 °C increases gradually up to 1 μm. Pellets sintered at 800 °C feature a particle size of 2 μm along with obvious cracks between these larger particles.

The corresponding X-ray diffraction (XRD) patterns of the LAGP samples prepared by conventional cold pressing and SPS at different temperatures are shown in Figure 2a. To investigate the detailed structural effects of the different SPS treatments, XRD patterns are analyzed by Rietveld refinements. For all the samples, the rhombohedral high-temperature NASICON phase of LAGP (space group of R3c) remains the dominant crystalline phase. For pristine LAGP, ball milling prior to SPS results in partial loss of crystallinity. According to the Rietveld refined pattern shown in Figure 2c, for the sample spark plasma-sintered at 800 °C, the main phase of LAGP partially decomposes to Li₄P₂O₇ (space group P1). As discussed more in detail in our earlier work,\textsuperscript{16} the refined lattice parameter c of all LAGP samples can be used to estimate the Al dopant content. Based on the calibration curve of ref 16, the lattice parameter $c = 20.665(7)$ Å consistently found for the samples spark plasma-sintered up to 750 °C leads to an estimated Al content of $x \approx 0.57(2)$, in accordance with the corresponding estimate for the pristine LAGP and the nominal Al content $x \approx 0.5$ for the sample batch.

Overall, the XRD peaks become sharper, which is accompanied by a slight increase in the amount of the impurity phase GeO₂ (space group: P3₁21). The change in the Rietveld-refined Lorentzian XRD profile parameters with increasing SPS temperature was analyzed to semiquantitatively separate strain and size broadening effects for the LAGP main phase. As seen from Figure S3 in the Supporting Information, the strain in the precursor powder is negligible (because of the preceding annealing step), but it grows continuously with an SPS temperature of up to 750 °C. The reduced strain of the sample spark plasma-sintered at 800 °C is consistent with the observation of crack formation and beginning decomposition.

As seen from the Arrhenius plots in Figure 3, the crystallite size growth derived from the XRD analysis shows a thermally activated behavior with an activation energy of 0.82 eV in the temperature range up to 700 °C. This is a clearly faster increase than the growth of particles, as seen from the SEM micrographs, which corresponds to a thermal activation with an activation energy of ca. 0.2 eV. Combining the information from SEM and XRD, it becomes possible to estimate the number of crystallites within one particle. This number shrinks with increasing SPS temperature. In the 750 °C sample, a more...
pronounced crystallite growth is observed so that crystallite and particle sizes become undistinguishable. In other words, most particles in the 750 °C sample should correspond to single-crystalline grains in line with the visual impression from Figure 1e. The change in activation energy mentioned above for crystal growth above 700 °C obviously implies a change in the crystal growth mechanism, but the data available do not permit us to firmly conclude about the exact cause of the accelerated crystal growth at 750 °C (such as enhanced diffusion of the dopant, interface melting, and crystallite merging). Although the particles continue to grow with increasing SPS temperature further, the LAGP crystallites within the 800 °C sample seem to shrink again as LAGP starts to decompose, that is, the larger particles now again contain numerous crystallites.

Figure 4 shows 31P and 27Al magic-angle spinning (MAS) NMR spectra of LAGP pellets spark plasma-sintered at different temperatures. The presence of multiple signals in the observed NMR spectra confirms the efficient substitution of Al on the Ge site and the existence of various adjacent cation species surrounding the PO4 tetrahedron. These signals can be assigned to P4Ge2Al0, P3Ge1Al0, P2Ge2Al0, and P1Ge3Al0 from low to high chemical shift positions. For conciseness, we will indicate only the Al content in the subscripts from now onward, understanding that the number of Ge neighbors of the central P0 is always 4 minus the number of Al neighbors. Here, the superscript 0 refers to isolated 31P species with no P −O−P linkage. Similar to earlier reports, no P4Al0 (~23 ppm) is observed for our samples, ruling out the formation of lithium aluminum phosphate clusters. For the lowest sintering temperature of 600 °C, the broad peak at around ~8 ppm may be interpreted as an amorphous phase fraction (from the ball milling), which disappears on increasing the sintering temperature, in line with our interpretation of the corresponding XRD pattern. The small peak observed at around ~6 ppm for 750 and 800 °C can be assigned to a new impurity phase of (possibly amorphous) Li4P2O7, in good accordance with the chemical shift reported for this phase in the literature. Interestingly, this impurity phase is not observed in the XRD pattern of the pellet sintered at 750 °C. This highlights the advantage of solid MAS NMR in detecting both crystalline and amorphous phases present in a sample. The single peak observed in the 27Al MAS spectra (Figure 4c) can be assigned to AlO6 coordination in the LAGP structure. No other Al-rich impurity phase is observed at any of the SPS temperatures. This corroborates our conclusion from the XRD data that the Al dopant remains within the LAGP phase for all the studied SPS conditions. The amount of Al doping into the phase is estimated from the relative signal intensities in 31P MAS NMR spectra on the basis of the following equation:

\[ \text{Al}^{3+} = \frac{I_{3Al}}{I_{4Al} + 4I_{4Al}} \]

where I3Al and I4Al are the relative intensities of P4Al0, P3Al0, P2Al0, P1Al0, and P0Al0 fractions. Among these, I4Al is consistently found to be zero. Therefore, the relative intensities were obtained by deconvolution, and using the abovementioned equation, the dopant content x in crystalline Li1-xAlxGe2-x(PO4)3 is determined. For the samples with a nominal Al content of x = 0.5, we find in close harmony with the estimate x ≈ 0.57(2) from the lattice parameter calibration curve a value of x = 0.56 for the samples sintered at 600 and 700 °C and a slightly higher value (x ≈ 0.58) for pellets sintered at 750 and 800 °C. Again, the proximity of the values after SPS to the nominal composition demonstrates that LAGP heat treatment prior to

![Figure 4](https://dx.doi.org/10.1021/acsomega.0c01826)
SPS ensured the full incorporation of the dopant Al into the LAGP structure. The apparent slight increase in dopant concentration at higher temperatures might be linked to the fact that all the Al remains in the LAGP phase, while a part of the phosphorus forms the new impurity phase of Li4P2O7.

The room temperature ionic conductivities for melt-quench-prepared LAGP before and after SPS at 600, 650, 700, 750 and 800 °C are extracted from the respective impedance spectra and summarized in Figure 5. The bulk conductivities for all the samples remain almost the same with only a slight local maximum for the LAGP pellet spark plasma-sintered at 750 °C (1.02 × 10⁻³ S cm⁻¹). This harmonizes with the finding that SPS preserves the dopant concentration. More importantly, the sample spark plasma-sintered at 750 °C exhibits clearly the highest grain boundary and total conductivities of 6.25 × 10⁻⁴ and 3.9 × 10⁻⁴ S cm⁻¹. This can be understood based on the absence of grain boundaries within the nearly single-crystalline particles (cf. Figure 3) and a high relative density of 97% observed for this sintering temperature (see Figure 5b). For the pellet sintered at 800 °C, the extensive phase decomposition and crack formation due to the rapid grain growth result in a marked drop in ionic conductivity. The strong influence of the grain boundaries within the particles on the overall ion transport properties is clarified by Figure 6, which relates the logarithm of the crystallite size to the grain boundary resistivity and to the total resistivity. As seen from Figure S4 in the Supporting Information, this correlation to the crystallite size is clearly stronger than the correlations to particle size and density, although both will of course also contribute to the overall effect. Hence, it should be noted that for the high-performance LAGP membrane, it is not sufficient to achieve a dense particle morphology, but the particles should also contain as few as possible intraparticle grain boundaries.

The practical efficiency of lithium transfer across the membranes was investigated by galvanostatic deposition/stripping cycles of symmetrical Li/solid electrolyte/Li cells. The results for both spark plasma-sintered membranes and conventional cold-pressed LAGP pellets are shown in Figure 7a. Spark plasma-sintered LAGP membranes show lower overpotentials than the cold-pressed pellets under comparable conditions (for this comparison, we chose current densities of 6 μA/cm² for the cold-pressed pellet and a slightly higher value...
of 10 μA/cm² for the somewhat thinner SPS membrane to compensate for differences in geometry). In this process, the overpotential is mostly governed by the iR drop and higher total conductance of the SPS pellet directly translates into lower overpotential. The (in both cases) somewhat higher initial overpotential might be due to the formation of an electrically and ionically conductive interphase between the pellet and the lithium anode, which on prolonged contact acts as a protective layer for the pellet. The voltage profile of spark plasma-sintered samples stabilizes somewhat faster than that of the cold-pressed pellet. This may be tentatively attributed to the more uniform local current density in the spark plasma-sintered samples.

The main requirements determining the performance of the anode-protecting LAGP membrane in hybrid LABs are high chemical and electrochemical stability along with fast ion conductivity. The compactness of the pellet will directly lower the overpotential of the cell and reduce the solid/liquid interfacial area for chemical attack by the catholyte. Figure 7b compares the cell overpotentials for hybrid LABs using spark plasma-sintered or cold-pressed LAGP pellets as their anode protecting membranes in combination with Fe-doped CNT/CNF catalysts in the air cathodes.43 The enhanced ionic conductivity of the pellets spark plasma-sintered at 700 and 750 °C directly translates into a drop in overpotential of the cell from 0.44 V for the conventional cell to 0.34 eV for the 700 °C sample and to 0.27 V for the 750 °C sample, all at a moderate current density of 0.08 mA cm⁻². Thereby, the energy efficiency of the cell is increased from 86% for the cell employing the conventional membrane to 90 and 92% for the cell employing the anode protecting membrane spark plasma-sintered at 700 and 750 °C, respectively. The Coulombic efficiency for all these devices is >99% under this operation mode.

3. CONCLUSIONS

LAGP pellets were prepared by the SPS method at various temperatures from powdered LAGP ceramic prepared via a melt quenching method. Optimizing SPS temperature is necessary to achieve the desired density and ion conductivity of the solid electrolyte. A close look into the microstructure evolution of the pellets as a function of the sintering conditions by NMR, SEM, and XRD shows that on increasing the SPS temperature, the crystallite size increases faster than the particle size, resulting in dense pellets with a reduced density of both inter- and intraparticle grain boundaries. The sample sintered at 750 °C reaches a relative density of 97% and with its nearly single-crystalline, well-connected particles exhibits the highest total ionic conductivity of 3.9 × 10⁻⁴ S cm⁻¹. The SPS experimental results show that the highly dense LAGP solid electrolytes with desirable ionic conductivities can be prepared reliably and with a short sintering time of 5 min at a low processing temperature of 750 °C (compared to 850 °C for 2 h for the conventional samples). For conventional high-temperature sintering, a segregation of Al-rich phases is often observed, which requires a compromise between densification to enhance grain boundary conductivity and retaining a high bulk conductivity. Because of the shorter sintering time, the Al⁺⁺ dopant content remained practically unchanged, allowing for higher densification with unchanged (or even slightly enhanced) bulk conductivity. It is demonstrated both in symmetric cells and in hybrid LABs that the higher total ionic conductivity for spark plasma-sintered samples under optimization processing conditions directly translates into lower cell polarization and hence higher energy efficiency.

4. EXPERIMENTAL SECTION

4.1. Preparation of the Material. Preparation of LAGP powder by melt quenching and subsequent crystallization: LAGP glass with a nominal Al content x = 0.5 was prepared using stoichiometric amounts of Li₂CO₃ (Alfa Aesar, Ward Hill, MA), Al₂O₃ (Sigma-Aldrich, Milwaukee, WI), GeO₂ (Alfa Aesar, Ward Hill, MA), and NH₄H₂PO₄ (Merck). The ball-milled precursor mixture was initially heated in air to 700 °C and kept at this temperature for 2 h to remove volatile components. Thereafter, the temperature was increased to 1450 °C and kept at this value for 1 h to produce and homogenize the melt. The melt was then quenched on a copper plate, yielding a transparent glass, which was subsequently powdered. Finally, the glass powder was annealed at 850 °C for 2 h to ensure the formation of crystalline LAGP.

Preparation of dense LAGP pellets by SPS: A carbon mold was used to prepare the LAGP pellets in a Dr. Sinter Lab Jr. Series 632L× SPS system. To this end, typically 0.33 g of LAGP powder was packed into the carbon mold and uniaxially precompressed to 0.3 kN to increase the packing density before SPS. A carbon punch with a diameter of 13 mm was used, and a static pressure of 40 MPa was applied during the SPS process. The samples were held under vacuum for 5 min at the specified temperature (in the temperature range 600–800 °C). Voltage and current used in the process were controlled under the automatic operation mode. The temperature increase rate was set to 100 K min⁻¹.

4.2. Materials Characterization. XRD patterns of LAGP were collected using a high-resolution X-ray powder diffractometer (Bruker D8) with Cu Kα radiation (λ = 1.5406 Å). Generalized Structure Analysis System (GSAS) software along with the graphical user interface, EXPGUI, was applied to conduct Rietveld refinements of the X-ray patterns.44 Besides a quantitative phase analysis, this allows to semiquantitatively distinguish the effect of SPS processing on crystallite size and strain in the resulting membranes. Instrumental broadening effects are described by a Caglioti-type Gaussian broadening function and kept constant among all samples, while size and strain broadening are described by individually refined Lorentzian broadening functions with different angular dependences. The microscopic structure and particle size distribution of the samples were examined using SEM (Zeiss Supra 40 VP). Solid-state NMR spectra were recorded at a magnetic field of 9.4 T on a Bruker AVANCE NEO instrument. Electrochemical impedance spectroscopy measurements were conducted using an impedance spectrometer (Solartron SI1260, Schlumberger) in the frequency range of 0.1 Hz to 5 MHz inside a Swagelok cell (X2 Labwares Pte Ltd). MAS experiments were performed in ZrO₂ rotors at a spinning speed of 10 kHz using a Bruker 4 mm probe.

4.3. Electrochemical Characterization. The use of spark plasma-sintered ceramic pellets as anode-protecting membranes in hybrid LABs was demonstrated. Rechargeable LABs are assembled by sandwiching spark plasma-sintered LAGP ceramic membranes between the anode chamber (lithium metal, Honjo Metal Co., Ltd, filled with LiPF₆ in the ethylene carbonate/dimethyl carbonate electrolyte) and the 1 M LiOH aqueous catholyte in a custom-built LAB cell. Oxygen reduction and evolution in the cell were catalyzed by transition metal oxide-based air cathodes with an active area of 0.6 cm².
analogous to the ones described in our recent work. Room temperature electrochemical performance of the cells was investigated using a potentiostat/galvanostat (Arbin BT2000) under open-air conditions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c01826.

Statistical size distribution of pristine LAGP powder and spark plasma-sintered LAGP at 600, 650, 700, 750, and 800 °C, as determined from SEM micrographs; SEM image of spark plasma-sintered LAGP at 750 °C and elemental mapping of Ge, P, and O; variation of the relative inhomogeneous crystallite strain of the LAGP main phase with the SPS temperature as extracted from Rietveld refinements of RDX powder pattern; and correlation of resistivity to crystallite size, particle size, and relative density (PDF)

AUTHOR INFORMATION

Corresponding Author

Stefan Adams — Materials Science and Engineering, National University of Singapore, Singapore 117576 Singapore; orcid.org/0000-0003-0710-135X; Email: msea@nus.edu.sg

Guang Yang — Materials Science and Engineering, National University of Singapore, Singapore 117576 Singapore

Dorsasadat Safanama — Materials Science and Engineering, National University of Singapore, Singapore 117576 Singapore; orcid.org/0000-0001-9632-3901

Kia Chai Phuah — Materials Science and Engineering, National University of Singapore, Singapore 117576 Singapore

Complete contact information is available at: https://pubs.acs.org/doi/10.1021/acsomega.0c01826

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors are grateful to Singapore Ministry of Education for financial support in the frame of the AcRF project “Mesoporous hierarchically structured materials for clean energy technologies” and to NUS for the “Centre for Energy Research” strategic seed grant.

REFERENCES

(1) Balaish, M.; Kratysberg, A.; Ein-Eli, Y. A critical review on lithium-air battery electrolytes. Phys. Chem. Chem. Phys. 2014, 16, 2801–2822.

(2) Lu, Y.-C.; Xu, Z.; Gasteiger, H. A.; Chen, S.; Hamad-Schifferli, K.; Shao-Horn, Y. Platinum−gold nanoparticles: a highly active bifunctional electrocatalyst for rechargeable lithium−air batteries. J. Am. Chem. Soc. 2010, 132, 12170−12171.

(3) Manthiram, A.; Li, L. Hybrid and Aqueous Lithium-Air Batteries. Adv. Energy Mater. 2015, 5, 1401302.

(4) Thangadurai, V.; Kaack, H.; Weppner, W. J. F. Novel fast lithium ion conduction in garnet-type Li5La3M2O12 (M= Nb, Ta). J. Am. Ceram. Soc. 2003, 86, 437−440.

(5) Thangadurai, V.; Adams, S.; Weppner, W. Crystal structure revision and identification of Li+ ion migration pathways in the garnet-like Li5La3M2O12 (M= Nb, Ta) oxides. Chem. Mater. 2004, 16, 2998−3006.

(6) Murugan, R.; Thangadurai, V.; Weppner, W. Fast lithium ion conduction in garnet-type Li5La3Zr2O12. Angew. Chem. Int. Ed. 2007, 46, 7778−7781.

(7) Nyman, M.; Alam, T. M.; McIntyre, S. K.; Bleier, G. C.; Ingersoll, D. Alternative approach to increasing Li mobility in Li-La-Nb/Ta garnet electrolytes. Chem. Mater. 2010, 22, 5401−5410.

(8) Yow, Z. F.; Oh, Y. L.; Gu, W.; Rao, R. P.; Adams, S. Effect of Li+/H+ exchange in water treated Ta-doped Li5La3Zr2O12. Solid State Ionics 2016, 292, 122−129.

(9) Truong, L.; Thangadurai, V. Soft-Chemistry of Garnet-Type Li5−xBaxLa3−yNbxO12 (x= 0, 0.5, 1): Reversible H+↔Li+ Ion-Exchange Reaction and Their X-ray, 7Li MAS NMR, IR, and AC Impedance Spectroscopy Characterization. Chem. Mater. 2011, 23, 3970−3977.

(10) Stramare, S.; Thangadurai, V.; Weppner, W. Lithium lanthanum titanates: a review. Chem. Mater. 2003, 15, 3974−3990.

(11) Geng, H.; Lan, J.; Mei, A.; Lin, Y.; Nan, C. W. Effect of sintering temperature on microstructure and transport properties of Li5La3−x−yTiO2 with different lithium contents. Electrochim. Acta 2011, 56, 3406−3414.

(12) Wolfenstine, J. Stability predictions of solid Li-ion conducting membranes in aqueous solutions. J. Mater. Sci. 2010, 45, 3954−3956.

(13) Fu, J. Superionic conductivity of glass-ceramics in the system Li1−xO−xAl2O3−xTiO2−xP2O5. Solid State Ionics 1997, 96, 195−200.

(14) Thokchom, J. S.; Kumar, B. Ionically conducting composite membranes from the Li1−xO−xAl2O3−xTiO2−xP2O5 glass−ceramic. J. Am. Ceram. Soc. 2007, 90, 462−466.

(15) Aono, H.; Imanaka, N.; Adachi, G.-y. High Li+ conducting ceramics. Acc. Chem. Res. 1994, 27, 265−270.

(16) Safanama, D.; Sharma, N.; Rao, R. P.; Brand, H. E. A.; Adams, S. Structural evolution of NASICON-type Li1+xAlxGe2(PO4)3 using in situ synchrotron X-ray powder diffraction. J. Mater. Chem. A 2016, 4, 7718−7726.

(17) Xu, X.; Wen, Z.; Wu, X.; Yang, X.; Gu, Z. Lithium Ion-Conducting Glass−Ceramics of Li1+xAlxGe1.5(PO4)3−xLi2O (x= 0.0−0.20) with Good Electrical and Electrochemical Properties. J. Am. Ceram. Soc. 2007, 90, 2802−2806.

(18) Thokchom, J. S.; Gupta, N.; Kumar, B. Superionic conductivity in a lithium aluminum germanium phosphate glass−ceramic. J. Electrochem. Soc. 2008, 155, A915−A920.

(19) Kumar, B.; Thomas, D.; Kumar, J. Space-Charge-Mediated Superionic Transport in Lithium Ion Conducting Glass−Ceramics. J. Electrochem. Soc. 2009, 156, A506−A513.

(20) Fu, J. Fast Li+ ion conducting glass-ceramics in the system Li1−xO−xAl2O3−xGeO2−xP2O5. Solid State Ionics 1997, 104, 191−194.

(21) Mariappan, C. R.; Yada, C.; Rosciano, F.; Roling, B. Correlation between micro-structural properties and ionic conductivity of Li5AlxGe1.5(PO4)3 ceramics. J. Power Sources 2011, 196, 6456−6464.

(22) Visco, S. J.; De Jonghe, L. C.; Nimon, Y. S. Composite solid electrolyte for protection of active metal anodes. U.S. Patent 8,182,943 B2, December 19, 2006.

(23) Imanishi, N.; Hasegawa, S.; Zhang, T.; Hirano, A.; Takeda, Y.; Yamamoto, O. Lithium anode for lithium-air secondary batteries. J. Power Sources 2008, 185, 1392−1397.

(24) Zhang, T.; Imanishi, N.; Hasegawa, S.; Hirano, A.; Xie, J.; Takeda, Y.; Yamamoto, O.; Sannes, N. Water-stable lithium anode with the three-layer construction for aqueous lithium−air secondary batteries. Electrochem. Solid-State Lett. 2009, 12, A132−A135.

(25) Zhang, T.; Imanishi, N.; Shimonoishi, Y.; Hirano, A.; Takeda, Y.; Yamamoto, O.; Sannes, N. A novel high energy density rechargeable lithium/air battery. Chem. Commun. 2010, 46, 1661−1663.

(26) Aboulaich, A.; Bouchet, R.; Mathias, G.; Doss, Y.; Sacc, V.; Tortet, L.; Morcrette, M.; Rozier, P.; Tarascon, J.-M.; Viallet, V.; Drolle, M. A New Approach to Develop Safe All-Inorganic Monolithic Lith-Ion Batteries. Adv. Energy Mater. 2011, 1, 179−183.

(27) Adachi, G.-y.; Imanaka, N.; Aono, H. Fast Li+ conducting ceramic electrolytes. Adv. Mater. 1996, 8, 127−135.
(28) Aono, H.; Sugimoto, E.; Sadaoka, Y.; Imanaka, N.; Adachi, G. y. Ionic conductivity of solid electrolytes based on lithium titanium phosphate. J. Electrochem. Soc. 1990, 137, 1023−1027.

(29) Aono, H.; Sugimoto, E.; Sadaoka, Y.; Imanaka, N.; Adachi, G. Ionic conductivity of the lithium titanium phosphate (Li1+xMxTi2−x(PO4)3, M= Al, Sc, Y, and La) systems. J. Electrochem. Soc. 1989, 136, 590.

(30) Cretin, M.; Fabry, P. Comparative study of lithium ion conductors in the system Li1+xAlxIV(PO4)3 with AIV= Ti or Ge and 0≤ x≤ 0.7 for use as Li+ sensitive membranes. J. Eur. Ceram. Soc. 1999, 19, 2931−2940.

(31) Safanama, D.; Adams, S. High efficiency aqueous and hybrid lithium-air batteries enabled by Li1.5Al0.5Ge1.5(PO4)3 ceramic anode-protecting membranes. J. Power Sources 2017, 340, 294−301.

(32) Safanama, D.; Adams, S. Flexible light-weight lithium-ion-conducting inorganic−organic composite electrolyte membrane. ACS Energy Lett. 2017, 2, 1130−1136.

(33) Zhu, H.; Liu, J. Emerging applications of spark plasma sintering in all solid-state lithium-ion batteries and beyond. J. Power Sources 2018, 391, 10−25.

(34) Wang, L.; Zhang, J.; Jiang, W. Recent development in reactive synthesis of nanostructured bulk materials by spark plasma sintering. Int. J. Refract. Met. Hard Mater. 2013, 39, 103−112.

(35) Guillon, O.; Gonzalez-Julian, J.; Dargatz, B.; Kessel, T.; Schiering, G.; Räthel, J.; Herrmann, M. Field-assisted sintering technology/spark plasma sintering: mechanisms, materials, and technology developments. Adv. Eng. Mater. 2014, 16, 830−849.

(36) Du, M.; Liao, K.; Lu, Q.; Shao, Z. Recent advances in the interface engineering of solid-state Li-ion batteries with artificial buffer layers: challenges, materials, construction, and characterization. Energy Environ. Sci. 2019, 12, 1780−1804.

(37) Azarniya, A.; Azarniya, A.; Safavi, M. S.; Farshab Ahmadipour, M.; Esmaeili Seraji, M.; Sovizi, S.; Saraei, M.; Yamanoglu, R.; Soltaninejad, M.; Madaah Hosseini, H. R.; Ramakrishna, S.; Kawasaki, A.; Adams, S.; Reddy, M. V. Physicochemical properties of porous materials by spark plasma sintering. Crit. Rev. Solid State Mater. Sci. 2020, 45, 22−65.

(38) Duan, S.; Jin, H.; Yu, J.; Esfahani, E. N.; Yang, B.; Liu, J.; Ren, Y.; Chen, Y.; Lu, L.; Tian, X.; Hou, S.; Li, J. Non-equilibrium microstructure of Li1.5Al0.5Ge1.5(PO4)3 superionic conductor by spark plasma sintering for enhanced ionic conductivity. Nano Energy 2018, 51, 19−25.

(39) Kubanska, A.; Castro, L.; Tortlet, L.; Schäß, O.; Dollé, M.; Bouchet, R. Elaboration of controlled size Li1.5Al0.5Ge1.5(PO4)3 crystallites from glass-ceramics. Solid State Ionics 2014, 266, 44−50.

(40) Zhu, H.; Prasad, A.; Doja, S.; Bichler, L.; Liu, J. Spark Plasma Sintering of Lithium Aluminum Germanium Phosphate Solid Electrolyte and its Electrochemical Properties. Nanomaterials 2019, 9, 1086.

(41) Liu, Z.; Venkataraman, S.; Kirchhain, H.; van Wüllen, L. Study of the glass-to-crystal transformation of the NASICON-type solid electrolyte Li1.5AlGe2−x(PO4)3. Solid State Ionics 2016, 295, 32−40.

(42) Schröder, C.; Ren, J.; Rodrigues, A. C. M.; Eckert, H. Glass-to-Crystal Transition in Li1.5AlGe2−x(PO4)3: Structural Aspects Studied by Solid State NMR. J. Phys. Chem. C 2014, 118, 9400−9411.

(43) Ji, L.; Peng, S.; Safanama, D.; Yu, H.; Li, L.; Yang, G.; Qin, X.; Srinivasan, M.; Adams, S.; Ramakrishna, S. Design of 3-dimensional hierarchical architectures of carbon and highly active transition metals (Fe, Co, Ni) as bifunctional oxygen catalysts for hybrid lithium−air batteries. Chem. Mater. 2017, 29, 1665−1675.

(44) Larson, A.; Von Dreele, R. General Structure Analysis System (GSAS), Los Alamos National Laboratory Report LAUR 86-748; Los Alamos National Laboratory: Los Alamos, NM, 2004.