Solid State Lithium Cell

Development of NASICON based Solid State Electrolyte for Li-battery Application

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Demonstration of coin-type solid state lithium cell using synthesized LAGP glass ceramics.

ABSTRACT

All-Solid-State-Lithium Batteries (ASSLBs) are getting attentions because of their promising high energy density and safety characteristics. These batteries can provide better safety by preventing the internal short-circuit as compared to currently used liquid electrolyte in commercial batteries. Among others, inorganic oxide Solid State Electrolyte (SSE), such as, NASICON based Li₂O-Al₂O₃-GeO₂-P₂O₅ (LAGP) has certain advantages over others for use in ASSLBs. In this work LAGP glass was prepared using melt-quench technique and converted into glass-ceramics by controlled heat treatment. Phase formation was confirmed using XRD (X-ray diffraction) and ND (Neutron diffraction). Rietveld refinement analysis was used for structural analysis using both ND and XRD data. Bottleneck for Li⁺ migration. Impedance spectroscopy was used to evaluate the d.c. ionic conductivity and the value found was 2.48x10⁻⁴Scm⁻¹ at room temperature. Cells were fabricated with LiFePO₄(LFP) as cathode and Li metal as anode. The cell operated successfully giving capacity of 130mAhg⁺¹ with coulombic efficiency of 99% at 0.05C (1C=170mAg⁻¹) at the initial stage of Li-cells fabrication.

KEYWORDS: Solid state electrolyte, NASICON, Li-ion solid state battery

Introduction

Lithium ion batteries (LIBs) play important role in recent years for their applications as energy storage device in various electronic gadgets. However, LIBs suffer with various shortcomings: (a) internal short circuit (b) fire or explosion at high temperature because of the uses of the flammable liquid electrolyte etc[1]. To avoid all these issues pertaining to conventional LIBs, ASSLBs are considered as the safest alternative[2]. ASSLBs have mainly three components: cathode, anode and solid-state-electrolyte (SSE). The charging and discharging mechanism is same as LIBs. During the charging, lithium ion transferred from cathode to anode through SSE and during the discharge process exactly reverse phenomenon takes place[3]. SSEs are mainly two types: organic and inorganic. Despite of several advantages of organic SSE, it has few drawbacks like narrow temperature range and poor structural stability, whereas inorganic SSEs can have improved stability and safety over wide temperature range. A promising SSE should have high ionic conductivity, thermal and electrochemical stability. Lithium ions hop from one stable position to another inside the SSE. Therefore, the ion diffusion mainly related to the crystal lattice of the SSE. The ion migration channel can be widened by doping. Among other inorganic SSEs, oxide SSEs are more environment friendly and have ease of processing. These kind of materials are mainly polycrystalline, where the lithium ion migrates through two regions: grain and grain boundary. The movement is slow inside grain boundary as compared to the grain. Therefore, the oxide SSEs should have large and dense grains[4]. Among other oxides (i.e. perovskite, garnet etc.) Li-based NASICON (**NaS**uper-Ionic **Con**ductor) type materials $(LiM^{(V)}_{2}(PO_4)_3, M^{(V)})$: Ge, Ti, Zr etc.) show high ionic transport properties and find a potential application in ASSLBs as SSE[5]. In this work we report synthesis of Li₂O-Al₂O₃-GeO₂-P₂O₅(LAGP) glass ceramics with right amount of required phases and electrical conductivity value. The process parameters were optimised for synthesis of the LAGP glass ceramics and characterised for thermal, structural and electrical properties for use in Li battery.

Synthesis of Glass/Glass Ceramics

Glass sample with composition of Li_{1.5}Al_{0.5}Ge_{1.5}P_{2.9}Si_{0.1}O₁₂ (LAGP) was prepared by standard melt-quench technique. Each batch of 100g weight was prepared by taking initial constituents(Li₂CO₃, Al₂O₃, GeO₂, SiO₂, NH₄H₂PO₄), in the form of carbonate and di-ammonium hydrogen phosphate proportionately. The charge was calcined by holding the batch at decomposition temperature of each initial constituent for sufficient time. The calcination process was repeated to ensure complete decomposition after through mixing & grinding. The calcined charge was mixed and ground properly and melted in a Pt-Rh crucible at around 1450-1550°C. The melt was held at the melting temperature for 1-2 hrs for homogenization and poured on a metal plate. The glass was annealed at around 400-450°C for 4-6 hrs and cooled down to room temperature slowly.

Characterization

The annealed glasses were powdered, and differential thermal analysis measurements were carried out using a TGA/DTA instrument. Solid glass samples were taken for the DTA scan to avoid the dependency of crystallization on the particle size distribution. DTA scans were recorded at the

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Fig.1: DTA scans for LAGP glass sample at different heating rates.

heating rates of 5, 10, 15, 20 and 25K min⁻¹. The samples were scanned up to maximum 900°C. Based on the DTA data, the glass samples were heated at different temperatures: 600, 650, 700, 750 and 800°C for one hour to convert into glassceramics. Nature of glassy and crystalline phases formed in the base glass and glass ceramics (GC) samples were identified using powder X-ray diffractometric technique (XRD) with Cu K_{α} was used as radiation source. The impedance measurements were carried out in the frequency range of 1-10⁶Hz at room temperature. Conductivity studies showed that the sample heat treated at 700°C for one hour, exhibited highest value of d.c. ionic conductivity at room temperature among others. Therefore, further characterizations and cell testing were carried out on this sample only. For the detailed structural characterization, neutron diffraction data was collected with the linear 5-PSD based powder diffractometer at 100MW Dhruva Research Reactor in BARC Trombay in the twotheta range of 8-135°. Galvanostatic charge/discharge experiment was performed using automatic battery analyzer.

Results and Discussion

DTA analysis

Fig.1 shows the DTA scans of LAGP glass sample for different heating rate. Figure shows onset of a broad



Fig.3: Experimental (+) and calculated (-) neutron diffraction pattern. The difference profile is given at bottom. The Bragg positions are indicated by vertical marker below the observed pattern.



Fig.2: Simulated and experimental isotherms at 590°C.

endotherm at around 520°C indicating the glass transition temperature (T_g). The endotherm is followed by a sharp and intense exothermic peak called peak crystallization temperature (T_p) at around 600°C for 5Kmin⁻¹. In addition, a small loop was observed at the middle of the exothermic peak in the DTA scan which suggests a certain 'self-feeding' reaction, in this system. It suggests existence of some endothermic reaction along with the crystallization process[6]. Using the model free kinetics analysis an isotherm at 590°C was simulated using AKTS software and compared with the experimental data. Fig.2 shows the crystallized volume fraction (x) versus time (t) plot of the simulated and experimental isotherms. Simulated data obtained almost follow the experimental data within error.

Joint Rietveld Refinement

Joint Rietveld refinement was carried out with the collected XRD and ND data using Full Prof software. This gives us a structural model agreeing with both XRD and ND data giving us high confidence in the obtained model. Joint Rietveld refinement was carried out with the model based on the typical NASICON structure: space group *R*-3c and unit cell parameters given in ICSD file of pure $\text{LiGe}_2(\text{PO}_4)_3$. The observed and calculated neutron and X-ray diffraction patterns are shown in Fig.3 and Fig.4.



Fig.4: . Experimental (+) and calculated (-) X-ray diffraction pattern. The difference profile is given at bottom. The Bragg positions are indicated by vertical marker below the observed pattern.

Table 1	
Joint Refinement of ND and XRD	
Molecular formula	$Li_{1.5}AI_{0.5}Ge_{1.5}P_{2.9}Si_{0.1}O_{12}$
Molecular weight	417.47u
Spacegroup	R-3c
Unit cell parameters	
а	8.2682(9) Å
b	8.2682(9) Å
С	20.668(3) Å
Volume (unit cell) and Z	1412.14ų, 6
Density (Calculated)	3.42gm/cc
Profile	Pseudo-Voigt
Goodness of fit (X^2)	1.87
$R_{\scriptscriptstyle wp}, R_{\scriptscriptstyle exp}$	ND: 3.35%, 2.45%
	XRD: 8.56%, 4.41%

The details of various profile parameters and structural parameters obtained are shown in Table 1. A minor amount (0.63 wt%) of $\text{Li}_2\text{Ge}_4\text{O}_9$ impurity phase was detected in ND pattern only during the refinement, along with the major NASICON phase of 99.37% weight fraction. Simulated NASICON unit cell and its projection on b-c plane, using the joint Rietveld refinement, are shown in Fig.5(a) and Fig.5(b). Here GeO₆octahedra and PO₄ tetrahedra are linked to each other[7]. Li⁺ ions reside in two positions: M1 (0,0,0) site (6-fold co-ordination), which is directly located between two GeO₆octahedra and M2(0.07,0.34,0.08) site (8-fold co-ordination), which is located between two columns of GeO₆.

Ionic Conductivity Studies

Fig.6 shows the variation of electrical conductivity with frequency at room temperature. From the figure, it is observed that the a.c. conductivity value varies with frequency in three

different regimes. At lower frequency region, conductivity value is quite low and there is a gradual increase in conductivity value with frequency up to the order of 104Hz. Above this region the conductivity value is almost constant with frequency up to 106Hz. This frequency independent conductivity may bethought to be due to the long-range transport of existing mobile Li^{+} ion, and contributed as d.c. conductivity of the sample. In this region the conductivity is contributed primarily from the potential relaxation of ion, when the Li^{+} ion hops from one equilibrium position to a newposition[8].

Further, at higher frequency regime, above 106Hz, there is a dispersion and the conductivity again increases rather sharply with increase in frequency. In this region conductivity roughly increases in a power law fashion and eventually become almost linear at even higher frequencies. In low frequency region due to the accumulation of highly mobile lithium ions at the electrode surfaces, the conductivity is comparatively low. Considering the electrode polarization at low frequency region, the a.c. conductivity ($\sigma(\omega)$) can be expressed as [9]:

$$\sigma(\omega) = \sigma_{dc} - \frac{\sigma_{dc} - \sigma_0}{1 + \left(i\frac{\omega}{\omega_0}\right)^{\alpha}} + B\omega \tag{1}$$

The real part of the above equation is:

$$\sigma'(\omega) = \sigma_{dc} - (\sigma_{dc} - \sigma_0) \frac{1 + \left(\frac{\omega}{\omega_0}\right)^{\alpha} \cos\left(\frac{\alpha\pi}{2}\right)}{1 + 2\left(\frac{\omega}{\omega_0}\right)^{\alpha} \cos\left(\frac{\alpha\pi}{2}\right) + \left(\frac{\omega}{\omega_0}\right)^{2\alpha}} + B\omega$$
(2)

Where, σ_{dc} is d.c. ionic conductivity, $\sigma_0 = \sigma(0)$, ω_0 is the frequency at which full development of polarization occurs, α , B are constants. Experimental conductivity data was fitted with equation (2) and shown in Fig.6. The values of the different parameters, after fitting, are given in Table 2. The value of σ_{dc} is found 2.48×10⁻⁴Scm⁻¹ which is higher as compared to other SSE.



Fig.5: (a) Unit cell obtained from joint Rietveld refinement of ND and XRD for LAGP. Li1 atoms reside at the center of the pink polyhedral which is also known as trigonal antiprism and Li2 atoms situated at the center of the green polyhedra. Blue, violet, green and yellow atoms are Ge, P, O1 and O2 respectively. (b) Projection of the unit cell on bc plane. GeO_{c} -octahedra and PO_{4} -tetrahedra are shown in blue and grey colour respectively. Red, white, green and yellow atoms are Li1, Li2, O1 and O2 respectively.



Fig.6: Variation of A.C. electrical conductivity (σ ') with frequency at room temperature.



Fig. 7: In (σ T) versus 1/T plot.



Fig.8: LAGP glass ceramics disks of various dimensions (Diameter: 12mm, Thickness: 0.7mm).



Fig.9: Demonstration of coin-type solid state lithium cell using synthesised LAGP glass ceramics.

The d.c. ionic conductivities at different temperatures were also measured to evaluate the activation energy of ionic conduction (E_a). The temperature was varied from 300K to 373K. The relation between σ_{dc} and E_a is given below:

$$\sigma_{dc} (T) = \frac{A}{T} \exp\left(-\frac{E_a}{kT}\right)$$
(3)

Where, A is the pre-exponential factor and k is the Boltzmann constant. From the slope of in $(\sigma_{dc}T)$ versus 1/T plot the value of E_a (see Fig.7) was calculated.

Cell Fabrication and Testing

Coil cell was fabricated using, LiFePO₄ as cathode and lithium metal as anode. The loading of the active material on cathode was 9.47mgcm². LFP/LAGP/Li cell was assembled with 2032-coin cell inside argon filled glove-box. Fig.8 shows the photographic image of the LAGP SSEs in disc forms. The demonstration of cell testing using blue LED light is shown in Fig.9 in which the voltage shown in the multimeter is the 'closed circuit voltage' in Volt unit.

Fig.10 shows first three cycles of galvanostatic chargedischarge profiles of LFP/LAGP/Li cell in the voltage range of 2.6 to 4.0V at a constant current rate of 0.05C. The voltage plateau is nearly at 3.63V for charging and at 3.21V for discharging of the first cycle at 0.05C.



Fig.10: The galvanostatic charge and discharge curves of LFP/LAGP/Licellat 0.05C at room temperature.



Fig.11: Cyclic performance of specific discharge capacity and coulombic efficiency of the cell at 0.05C at room temperature.

At the first charging cycle, the specific capacity calculated is 154mAhg^1 which is approximately 90% of the theoretical capacity (170mAhg^1) and after that the charge and discharge capacities are almost fixed at nearly 130mAhg^1 (approximately 76% of theoretical capacity). Fig.11 depicts the values of discharge capacity and coulombic efficiency at different cycles. The capacity retention up to 20^{th} cycle is almost 100% which reveals that LAGP can be used in solid state Lithium ion batteries.

Conclusion

DTA study was used to predict the process parameters for conversion of glass to glass ceramics. Model free crystallization kinetics was performed to simulate isotherm of LAGP glass. This simulated isotherm almost matches with the experimental one. XRD and ND confirm the formation of Lithium Germanium Phosphate (LGP), NASICON phase in the Glass ceramic system. Joint Rietveld refinement of ND and XRD shows quite accurate structure of the crystal. The predicted amount of NASICON phase was 99.37% obtained from the refinement. For its higher ionic conductivity (2.48×10⁻⁴Scm⁻¹), it can be used as SSE in ASSLBs. The value of activation energy of ionic conduction (E_a) obtained is 0.43eV which is small enough to provide high ionic conduction in LAGP SSE. Performance of the solid state cell exhibited a good capacity retention (almost 100%) and coulombic efficiency. The cell showed a stable voltage of 3.42V.

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