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# Environmentally Benign, Intrinsically Coordinated Lithium-Based Solid Electrolyte with Modified Purine as a Supporting Ligand

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**Abstract:** Bioinspired materials have become increasingly competitive for electronic applications in the recent years owing to environment-friendly alternatives they offer. The notion of biocompatible solid organic electrolytes addresses the issues concerning potential leakage of corrosive liquids, volatility and flammability of electrolyte solvents. This study presents a new intrinsically coordinated Li<sup>1</sup>-adenine complex, which exhibits electrical conductivity behaviour as a solid electrolyte capable of self-sustained supply of Li<sup>1</sup> ions. It exhibited conductivity via moisture-assisted Li<sup>1</sup> ion motion up to 373 K, and possibly via ionhopping mechanism beyond 373 K. This purine-derived solid electrolyte displays enhanced conductivity and transference number demonstrating the potential of purine-based ligands and their coordination complexes in interesting material applications.

### Introduction

Rechargeable Li-ion batteries (LIBs) serve as one of the promising approaches to address issues concerning depleting energy resources. Notably, LIBs have become an essential part of our daily-use products and devices. Over the time, LIBs have contributed substantially to portable devices, electric vehicles, flexible and lightweight electronics and many more. However, volatile and flammable nature of liquid electrolytes, usually organic, renders the end-use product unsafe and risky, especially when operated at higher temperatures. Another drawback concerns the growth of Li dendrites at electrolyteelectrode interface, which leads to reduced battery life. One of the most effective solutions to this problem involves replacement of liquid electrolyte by a solid electrolyte.<sup>[1-3]</sup> Solid electrolytes are safe, leakage-proof, compact, can be used at higher temperatures and suppress growth of lithium dendrites to ensure homogenous ionic distribution and faster Li<sup>+</sup> diffusion. Although the solid electrolytes possess lower conductivity, this disadvantage is outweighed by their significant safety and

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operational advantages over liquid electrolytes.

A wide variety of solid electrolytes such as inorganic ceramic materials.<sup>[4]</sup> organic polymers<sup>[5]</sup> and hybrid/composite electrolytes<sup>[6]</sup> have been developed in the past years to improve safety, performance and durability of LIBs. Li7La3Zr2O12 nanofibers integrated with a composite polymer electrolyte led to suppressed growth of Li dendrites along with improved mechanical properties and conductivity.<sup>[7]</sup> Cross-linked solid polymer electrolytes ensure safety owing to their thermal stability and mechanical robustness.<sup>[8]</sup> The choice of fillers in composite solid electrolytes also affects the performance of the battery and results in improved transference number, ionic conductivity and enhanced interfacial contact with electrodes.<sup>[9]</sup> Hence, different aspects of a battery can be targeted by prudent alteration of the solid electrolytes used in them.

Since the prime motivation behind the development of solid state LIBs was the conservation of energy resources and circumvention of environmental hazards and risks associated with the previously used batteries, we considered that utilization of bioinspired motifs for the development of electrolytes would further add to the purpose. Bioinspired motifs have gained attention owing to their excellent features like high tunability, versatility, safety, biodegradability and biocompatibility opening up a whole new realm of applications, when melded with organic electronics.<sup>[10,11]</sup> With significant advancements in the field of organic biomaterials<sup>[12]</sup> and bioelectronics,<sup>[13]</sup> newer electrolytes could be easily and effectively altered and processed according to requirements, thus paving way for superior and highperformance LIBs. Materials of biological origin have been successfully employed as electrodes, binders and separators in LIBs.<sup>[14-16]</sup> For example, Xia et. al reported use of porous carbon microspheres, derived from microalgae, in Li-S batteries.<sup>[17]</sup>

DNA, carrier of genetic information, is known to possess conductivity of the order of  $10^{-15} \Omega^{-1}$ cm<sup>-1</sup>, at 400 K and a vacuum of 10<sup>-6</sup> mm of Hg. This was attributed to  $\pi$ -electron overlap in the nucleic acid base pairs present in the double-helical structure of DNA.<sup>[18]</sup> Conductivity measurements and electronic studies have been carried out for short DNA sequences (12-base-pair), nucleosides, nucleotides, nucleic acid base homopolymers and salts.[19-22] their Computational studies have verified experimental results.<sup>[23]</sup> But there are limited reports exploring direct application of nucleic acids or their fragments in the field of electronics and batteries.<sup>[24-27]</sup> We have also reported a Liguanine complex previously, as an electrolyte displaying high Li ion transference number and conductivity.<sup>[27]</sup>

Earlier reports have highlighted the significance of nucleobases in electronic conductivity owing to their  $\pi$ -electron overlap. The nucleobases being a constituent of nucleic acids are expected to further achieve a 'green' approach towards the development of electrolytes/electrodes for electrochemical applications, given



**Figure 1.** (a) Schematic representation of 1 along with its asymmetric unit; (b) part of lattice depicting zig-zag arrangement of Li<sup>I</sup> ions and  $\pi...\pi$  stacking interactions between the six membered rings of the two adjacent purines.

the biocompatibility and biodegradability offered by biological fragments.  $\ensuremath{^{[28]}}$ 

With this background, we decided to probe functionalised purine for the development of better and efficient bioinspired electrolytes for high-performance batteries. Fascinated by the promising Li<sup>1</sup> electrolytes in literature as well as in practical applications, we made Li<sup>1</sup> complex of derivatised adenine. Such a chemical design ensures that Li<sup>1</sup> ions were inherent in the complex and no additives were required to have a sustained supply of Li<sup>1</sup>.

### **Results and Discussion**

The crystalline Li<sup>I</sup> complex, **1** was synthesised (Scheme S1) and diffraction quality colourless block-shaped crystals were grown from acidic water (HCI in water at pH 3) layered with ethanol. **1** crystallised in a monoclinic system within the space group *P* 1  $2_1/c$  1 as established by careful analysis of the crystal data. The asymmetric unit comprised of a single ligand molecule bound to Li<sup>I</sup> through carboxylate O atom of the N9 substituent, which was further coordinated to a water molecule. In addition, a free lithium hydroxide molecule was also present in the lattice space of the asymmetric unit (Fig. 1a).

Further analysis of the crystal lattice suggested tetrahedral geometry of coordinated Li<sup>1</sup> ion where it is bound to two carbonyl O, one carboxylate O and one O atom from water. Notably, the lattice demonstrated a chain-like arrangement of purine units along the *b*-axis with tetracoordinate Li<sup>1</sup> ions facing each other along the entire length of the chain (Fig. 1b).



Figure 2. XRD pattern: Experimental, refined and difference profile obtained after Rietveld refinement of XRD data of 1 (powder).

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Figure 3. Thermogravimetry profile of 1 (32-300 °C) in nitrogen atmosphere.

These Li<sup>I</sup> ions were aligned in a zig-zag manner throughout the chain giving rise to channel-like formations. These chain-like entities were held together by parallelly displaced  $\pi$ ... $\pi$  stacking interactions between the six membered rings of two purines from two adjacent chains (4.099 Å), leading to a stable 2D lattice structure.<sup>[29]</sup> The interstitial spaces were occupied by lithium hydroxide molecules. Diagonally the Li<sup>I</sup> ions are separated by a distance of 3.034 Å from each other which is slightly less than their sum Van der Waal radii (3.64 Å). Curiously, the channels display an infinite array of Li<sup>I</sup> ions when viewed along *b*-axis making it a suitable candidate for evaluation as an electrolyte. Since 1 possesses an array of Li<sup>1</sup> ions in the lattice which are reminiscent of ion channels, it is expected that 1 would afford an intrinsic supply of Li ions for conduction purpose. Thus, it would provide a sustained Li ion transport without any external supply of Li ions. Moreover, closer arrangement of Li<sup>1</sup> ions (3.034 Å) in 1 as compared to the guanine-Li complex (6.991 Å)<sup>[27]</sup> might further aid conduction. This reduced distance might be attributed to the participation of two carbonyl O atoms binding Li<sup>1</sup> thereby bringing them in closer proximity. Interaction of O atoms with Li is a common phenomenon observed in case of Li<sup>I</sup> complexes of diacids/triacids.[30]

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Figure 4. (a) Nyquist plots for 1 from RT-473 K temperatures; Inset: equivalent circuit used; (b) Nyquist plots for 1 from 498-573 K temperatures; Inset: Arrhenius plot of ionic conductivity (In) versus temperature (1000/T) for 1.

PXRD graph for 1 was obtained and it showed high crystallinity with intense diffraction peaks. Rietveld refinement of X-ray diffraction pattern of 1 was performed by using Fullprof software.<sup>[31]</sup> The initial parameters used for Rietveld refinements such as atom coordinates, space group and cell parameters have been taken from matching reference pattern of crystallography open database (COD). The crystal of Li<sup>1</sup>-complex, 1 with space group  $P 1 2_1/c 1$  was used as a starting model for 1 (powder). Fourier series with polynomial function six refinable coefficients was used for refining background. Pseudo-Voigt function was modelled for refinements of XRD peaks shape. It is advantageous to use Pseudo-Voigt function for refinements, as it is a combination of Lorentzian and Gaussian functions. At the start, the background coefficients were refined. Consequently, structural parameters such as scale and structure factor, position parameters, occupancy and unit cell parameters were refined one after the other. It is clearly illustrated in Fig. 2 that Rietveld fitting is almost replica of observed XRD pattern and confirmed the formation of 1.

TGA analyses of **1** revealed an initial weight loss of about 10% at 100 °C which corresponds to loss of a water molecule (Fig. 3). It showed another cusp at 150 °C corresponding to loss (12%) of a LiOH molecule, followed by stability up to 300 °C, and hence all the electrochemical studies have been carried out till this temperature.

Electrochemical Impedance Spectroscopy (EIS) results are used to obtain information related to bulk electrolyte conductivity and other electrochemical processes such as charge-transfer resistance. The variable-temperature EIS is used to calculate the activation energy. The data acquired from electrochemical impedance spectroscopy for **1** was fitted using equivalent circuit

shown in the inset in Fig. 4a where R0 is the resistance of the bulk electrolyte, R1 is the resistance at the electrode/electrolyte interface, CPE1 is the capacitance corresponding to electrode/electrolyte interface and CPE2 is the capacitance of the electrolyte material. In the low conductivity regime, impedance data typically shows a single depressed semicircle. In the temperature range of 498–573 K and at room temperature, which are high conductivity regions, the impedance data shows depressed semicircle at high frequency region and a "spike-like" region at low frequency region (Fig. 4b). The impedance data was fitted well with 'n' in the range of 0.8-0.9, resulting in bulk capacitance values ~10<sup>-10</sup>-10<sup>-11</sup> F. The impedance response of 1 which is similar to G7Li as reported earlier is very similar to a solid polymer electrolyte with the additional advantage of in-built lithium ions without the requirement of addition of any external Li salts.[27]

lonic conductivity of 7.17 × 10<sup>-5</sup>  $\Omega^{-1}$ cm<sup>-1</sup> was calculated for 1 at room temperature. At 373 K, conductivity dropped down to 4.50 × 10<sup>-5</sup>  $\Omega^{-1}$ cm<sup>-1</sup>. Beyond that, a linear increase in the conductivity was observed with an increase in temperature till 573 K as shown in the Arrhenius plot in the inset of Fig. 4b. At 573 K, ionic conductivity reached 6.23 × 10<sup>-5</sup>  $\Omega^{-1}$ cm<sup>-1</sup>. The standard deviation of EIS measurements is ~0.53 x 10<sup>-5</sup> siemens.cm<sup>-1</sup> for a sample.

The data were fitted using the Arrhenius equation ( $\sigma = A \exp(-E_a/kT)$ ) for the temperature range of 373–573 K, where A is a pre-exponential factor, k is Boltzmann constant, T is absolute temperature and  $E_a$  is the activation energy. The activation energy for **1** was calculated and found to be 0.029 eV. Similar to what was reported by Dutta *et. al* in their study of guanine-lithium based bioinspired organic electrolyte,<sup>[27]</sup> water-assisted lithium ion motion is possibly the reason for room temperature

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Figure 5. (a) Schematic for assembly made for the measurement of transference number; (b) polarization curve (current vs time) and Nyquist plot before and after polarization (inset) for 1.

ionic conductivity as revealed by the Nyquist plot, while a decrease in conductivity till 373 K could be attributed to the removal of water molecules from the complex. At temperatures above 373 K, in the absence of water molecules, ion hopping mechanism contributes to the observed ionic conductivity.

The enhanced conductivity could also be ascribed to channellike arrangement of Li<sup>1</sup> ions in the crystal lattice of **1**. A close insight into crystallographic lattices of **1** and G7Li<sup>[27]</sup> reveal that the separation between the Li<sup>1</sup> ions in case of G7Li is 6.991 Å, whereas that in case of **1** is 3.034 Å. Thus, a dramatic difference in Li<sup>1</sup> ion separation clearly establishes a better Li ion conduction in **1**.

DC polarisation technique was used for the estimation of lithium ion transference number. For this measurement, lithium metal foils were employed as non-blocking electrode to make a cell configuration of Li-metal/organic-electrolyte/Li-metal (Fig. 5a). Nyquist plot 'before' and 'after' polarisation and polarisation curves for 1 were acquired as shown in Fig. 5b. In Fig. 5b, the polarization curve shows the amount of current carried by Li+ ions with respect to time. This curve gives us two values of current i.e. initial and saturated. EIS measurements were done in two steps, first before polarization and second after polarization. These measurements give us two values of charge transfer resistance, one initial resistance and second saturated resistance. Using these initial and saturated values of current and resistances into Bruce-Vincent method, we calculated the transference number. The transference number obtained was 0.547  $\pm$  0.044, which suggested that 54.7% of the current is carried by Li+ ionic species. The attained value of transference number is towards the higher side as compared to reported solid organic lithium electrolytes.<sup>[1,8,32,33]</sup> The details of transference number, ionic conductivity and activation energy for 1 are shown in Table 1. All the measurements were done at least twice to check the data and measurement setup repeatability. It is notable that we have achieved this transference number with a purine-based ligand, as it is a crucial quantity to improve energy density and charge/discharge rates of lithium ion batteries.<sup>[33–35]</sup>

 Table 1. Conductivity, activation energy and transference number data for 1 and some reported compounds.

	(		
Sample	Conductivity at RT $\Omega^{-1}$ cm <sup>-1</sup>	Activation Energy eV	Transference Number
1	7.17 × 10 <sup>-5</sup>	0.029	0.547 ± 0.044
G7Li <sup>[27]</sup>	~1.0 × 10 <sup>-7</sup>	0.8	0.75
LiO <sup>t</sup> Bu- grafted UiO- 66 <sup>[36]</sup>	3.3 × 10 <sup>-6</sup>	0.18	
ICOFs <sup>[37]</sup>	3.05 × 10 <sup>-5</sup>	0.24	$0.80 \pm 0.02$
Li- IL@MOF <sup>[38]</sup>	3.0 × 10 <sup>-4</sup>		0.36

### Conclusions

To summarise, we synthesised a crystalline Li-adenine complex and explored its potential as a solid-state electrolyte using conductivity studies. The complex offers an intrinsic supply of Li ions and hence proves beneficial over the existing ones where Li additives are required to achieve a sustained supply of Li ions for conduction. Adenine-based electrolyte is structurally tunable and the initial conductivity data indicates that it offers substantial promise and can be modified further to achieve electrolytes with enhanced efficiency in order to afford high performance, ecofriendly batteries. Further, performance gain in these bioinspired

motifs,<sup>[39-41]</sup> coupled with newer processing approaches, would offer interesting insights and add value to research in electrolytes for solid state LIBs.

### **Experimental Section**

#### Materials and Reagents

Analytically pure chemicals were purchased from commercial sources and used without further purification. All the crystals were obtained by slow evaporation process. High resolution (ESI+ mode) mass spectra were obtained on Waters, Q-Tof Premier Micro mass HAB 213 mass spectrometer. Solartron 1260A impedance analyser was used for the impedance measurements. Transference number measurements were done using CH Instruments electrochemical analyser.

#### Synthesis of 2-(6-amino-9H-purin-9-yl) acetic acid (9A1)

Synthesis of the ligand was carried out in two steps using a literature procedure (Scheme S1).  $^{\left[ 42\right] }$ 

#### Synthesis of 1

The reaction of **9A1** (0.4 g, 1 eq.) and LiOH.H<sub>2</sub>O (0.35 g, 4 eq.) in 25 mL methanol/water (1:4) mixture was carried out at room temperature for 1 h. After the completion of the reaction, the solvent was evaporated to obtain **1**(0.690 g) as a white solid. Next, 0.006 g of this solid was dissolved in 3 mL water by addition of HCl to it while maintaining a pH of 3. Crystals of **1** (0.003 g)were obtained in a month by layering it with 3 mL ethanol.

#### Crystal structure determination and refinement

Single crystal of 1 coated with light hydrocarbon oil was mounted in the 100 K dinitrogen stream of a Bruker SMART APEX CCD diffractometer equipped with CRYO industries low-temperature apparatus and intensity data were collected using graphite-monochromated Mo  $\ensuremath{\mathsf{K}\alpha}$  radiation. The data integration and reduction were processed using the SAINT software. An absorption correction was applied. Structures were solved by direct methods using SHELXS-97 and refined on P<sup>2</sup> by a full matrix least squares technique using the SHELXL-97 program package. Nonhydrogen atoms were refined anisotropically. In the refinement, hydrogens were treated as riding atoms using the SHELXL default parameters. Crystal structure refinement parameters are listed in the Table S1. All of these software packages were the integrated WINGX software package. CCDC No. 1972809 contains the supplementary crystallographic data for this paper. Copies of this information can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (fax +44-1223/336-033; e-mail deposit@ccdc.cam.ac.uk).

#### Electrochemical characterization

AC electrochemical impedance spectroscopy (EIS) was used to determine the ionic conductivity of the bio-inspired solid organic electrolytes. Synthesised organic white powder of **1** was compressed in a die to form a pellet of diameter 1.2 cm. Pellet was sandwiched between the two-blocking electrodes of stainless steel (SS) to form symmetric cell of configuration SS/Organic-electrolyte/SS. The measurements were taken from room temperature to 300 °C at a temperature interval of 25 °C.

The chamber temperature was controlled within  $\pm$  1-3 °C of the set point. Frequency range for EIS was 1 MHz to 100 Hz with excitation signal of 50 mV. Impedance data was analysed for bulk resistance with suitable equivalent circuit using Z-View software by Scribner Associates Inc. Ionic conductivity was calculated using following equation:



Here,  $\sigma$  is the ionic conductivity of the electrolyte; R is the bulk resistance calculated from the data fitting; L is the thickness of the electrolyte and A is the area of stainless-steel blocking electrode. Conductivity data was further used to carry out activation energy calculations.

'Bruce and Vincent' method was used to determine the cationic (Li+) transference number of the electrolyte.[43] For measurements electrolyte was sandwiched between blocking electrodes of lithium metal foils to obtain the stacking of Li/organic-electrolyte/Li. The whole assembly and measurement of the symmetric cell for transference number was done inside the glove box at controlled O2 and H2O levels. The cell was heated at 90 °C for the duration of 4 h to ensure good contact between the Li metal foil and solid electrolyte. Transference number measurements using 'Bruce and Vincent' method consist of a combination of AC impedance spectroscopy and chronoamperometry technique. Symmetric cell of Li/organic-electrolyte/Li is first subjected to impedance measurements followed by chronoamperometry which is again followed by one more impedance measurement. All these measurements were taken at room temperature. For impedance measurements frequency range of 100 kHz to 50 Hz was applied with the excitation signal of 500 mV. During chronoamperometry the cell was subjected to potential difference,  $\Delta V$  of 50 mV, change in current from initial value, i<sub>0</sub> with time was monitored until the steady state current, is was reached. Steady state was reached after 4 h of DC biasing. During DC biasing anions move away from the anode and get accumulated at the anode which create concentration gradient. As the steady state current is achieved, net anion motion goes to zero with total overall current carried by cation (Li<sup>+</sup>) only. The resistance due to the passivating layer (R') is also taken into consideration.<sup>[40]</sup> Steady state resistance is obtained by making the impedance measurements immediately after removing the DC potential difference. Transference number equation as per Bruce and Vincent method is

$$t_{+} = \frac{i_{s}(\Delta V - i_{0}R'_{0})}{i_{0}(\Delta V - i_{s}R'_{s})}$$

Here, the subscripts 0 and s represent the initial and steady state values respectively. In the above equation, t<sub>+</sub> is the transference number, R'<sub>0</sub> and R'<sub>s</sub> are the resistances of the passivating layer during initial and steady state conditions respectively,  $\Delta V$  is the value of DC bias applied, i<sub>0</sub> and i<sub>s</sub> are the current values of initial and steady state current obtained from chronoamperometry.

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An environment-friendly approach towards the development of a self-sustained, purinebased solid state Li-electrolyte. Ilesha Avasthi, Gaganjot, Monica Katiyar and Sandeep Verma\*

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Environmentally Benign, Intrinsically Coordinated Lithium-Based Solid Electrolyte with Modified Purine as a Supporting Ligand