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A novel small molecule compound of Lithium Iodine and 3-Hydroxypropionitrile as Solid-state Electrolyte for Lithium-Air Batteries

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Abstract: A novel small molecule compound of LiI 3-hydroxypropionitrile (HPN) has been successfully synthesized. Our combined experimental and theoretical studies indicated that LiIHPN is a Li-ion conductor, which is utterly different from the I⁻ anion conductor of LiI(HPN)₂ reported previously. Solid-state lithium-air batteries based on LiIHPN as the electrolyte exhibit a reversible discharge capacity of more than 2100 mAh g⁻¹ with cyclic performance over 10 cycles. Our findings provide a new way for the design new solid-state electrolytes towards high performance lithium-air batteries.

Keywords: Solid-state electrolyte; Small molecule; Lithium-air battery

1. Introduction

The extensive attention has been focused on the development of solid electrolytes for all-solid-state high energy lithium-air batteries due to their chemical /electrochemical stabilities and their non-permeability of oxygen, carbon dioxide and moisture in air [1-4]. Considering the critical role of the solid-state electrolyte for Li ion migration across the all-solid-state cell, and the electrochemical reaction only takes place at a three-phase zone composed of oxygen gas/air electrode/solid electrolyte, the development of a high-quality interface between the solid electrolyte and air electrode is very important for high performance all-solid-state lithium-air batteries. So far, two general classes of solid electrolytes for all-solid-state lithium-air batteries have been developed: inorganic ceramics [5-6] and organic polymers [7-9]. However, the ceramic electrolytes are hard solids, and the polymer electrolytes have chain entanglement and limited polydispersity. Therefore, their contact areas in the interface between solid electrolytes and air electrodes are much smaller than that between liquid electrolyte and air electrode. Here, we reported a new solid-state Li-ion conductor –LiI 3-hydroxypropionitrile (HPN), which is made up of organic and inorganic molecules. In this small molecule electrolyte, lithium ions are coordinated by discrete low molecular weight ligands such as nitrile group (-CN), hydroxyl group (-OH) and I atoms. Such a new solid electrolyte has the feature of high monodispersity and is expected to improve the performance of the solid-state rechargeable lithium-air battery because of good interfacial contact between electrolyte and electrodes. Previous study suggested that the small molecule compound of LiI (HPN)₂ is an I⁻ anions conductor [10-13]. In this work, a novel class of Li⁺ cation conductor -LiIHPN is used in all-solid-state lithium-air batteries for the first time.

2. Experimental and theoretical methods

2.1 Synthesis

Preparation of materials and electrodes: LiI(HPN)₂ (Single crystal synthesized by reference [10]) and highly pure LiI crystal (99.999% metals basis, Alfa Aesar) are prepared

for the synthesis of single crystal LiHPN. LiI(HPN)₂ (5.5204(5) g, 20.001(2)) mmol and LiI (2.6672(5)g, 20.002(4) mmol) are mixed and stirred at 130°C for 48h into homogeneous liquid in an argon-filled glove box. Obtained LiHPN liquid is stored in an oven at the designed temperatures from 90 °C to 80 °C with the decreasing step 0.5°C/day. After three weeks, single crystal LiHPN is obtained. The LiHPN powder can be simply synthesized by annealing the mixture of LiI and LiI(HPN)₂ at 130 °C for 48h.

Three-dimensional graphene: Three-dimensional graphene (3D-G) is prepared by a chemical reduction-induced self-assembly method [14] with a hydroiodic acid (HI) as the reducing agents. In brief, 2.2 mL with a concentration of 46.5 mg mL⁻¹ HI are added to the graphene oxide suspension (2.8 mL with a concentration of 3.0 mg mL⁻¹) to form the mixture. Then, such a mixture is sonicated for 10 min and transferred to an oil bath at 90 °C for 12 hours without stirring. The obtained black plate of graphene hydrogel is washed with ethanol and water in a Soxhlet extractor for 24 h to remove residual impurities and then the wet hydrogels are freeze dried for 2 days to obtain 3D-G.

LiHPN-LiI@3D-G electrode: After heating the finely ground powders of LiI and LiHPN with a molar ratio of 1:1 onto the surface of 3D-G electrode (weight of 300 µg, diameter = 7mm, and h=1.2 mm) at 130°C for one hour, these mixture powders (total weight of 8 mg) are melted into 3D-G electrode. LiHPN-LiI@3D-G electrode can be easily formed after subsequently cooling to the room temperature.

2.2 Measurements

All-solid-state cell: All-solid-state batteries of Li/LiHPN-LiI/LiHPN-LiI@3D-G are constructed as following: Li plate (purity 99.999%) with a thickness of 0.5 mm (2.0 cm²) is used as an anode directly. Then, LiHPN-LiI films (~100 µm) were coated onto the Li plate. LiHPN-LiI@3D-G electrode (diameter=7 mm) is used as air electrode. Ni foam with a pore size of several hundred micrometers was used as the current collector. All-solid-state Li/LiHPN-LiI/LiHPN-LiI@3D-G battery can be assembled by simply pressing one Li/LiHPN-LiI plate onto LiHPN-LiI@3D-G electrode with the substrate of Ni foam in an Ar-filled dry glove box.

Single crystal test of LiHPN: A suitable single-crystal particle with dimension of 0.250 x 0.200 x 0.130 mm³ is selected for X-ray diffraction. The crystal is sealed in a capillary to protect the sample from moisture. Diffraction data are collected on a Bruker AXS APEX

CCD diffractometer equipped with a rotating anode using graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). Diffraction data are collected over the full sphere and corrected for absorption. The structures are solved by direct methods using SHELXS and refined against F2 on all data by full-matrix least squares with SHELXL-97. Details of the data collection and refinement are summarized in Table S1-4.

Conductivity measurement: The ionic conductivities are measured by electrochemical impedance spectroscopy (EIS). Conductivity measurement is carried out by using the sandwiching with two carbon electrodes and one columnar electrode of LiI: LiHPN, which are obtained by cold pressing iodine lithium (purity 99.999%) and LiHPN with different molar ratio. Impedance data are obtained with an electrochemical working station CHI660C (Chenhua, China) in the frequency range 10Hz–100 kHz between 298K and 355K. The conductivity of LiI: LiHPN was calculated from Eq. (1) by the known area and the thickness as well as the examined resistance of C/ LiI: LiHPN /C by a CHI660A electrochemical workstation.

$$\sigma = d / R_b S \quad (1)$$

where R_b is the bulk resistance; d is the thickness of the LiHPN electrolyte, and S is the area of the carbon electrode.

Transference numbers measurement: The electrolyte films of LiHPN (diameter=11.3 mm, thickness= 0.12 mm) are sandwiched between two carbon electrodes as a blocking type cells. LiHPN electrolyte films are sandwiched between two lithium metal electrodes as the non-blocking type cells. The total number of ion transference is calculated based on Eq. (2):

$$t_{\text{ion}} = 1 - I_e / I_t \quad (2)$$

Where I_t and I_e are the total and residual currents, respectively. The lithium ion transference numbers of LiHPN electrolyte films were estimated by using an a.c. impedance combined with a d.c. polarization technique [15]. The a.c. impedance and the d.c. polarization curve of non-blocking-type cells (Li/LiHPN/Li) are measured by a CHI660A electrochemical workstation. The step potential is 100 mV. The value of t_{Li^+} is calculated from Eq. (3):

$$t_{\text{Li}^+} = I_s (\Delta V - R_0 I_0) / I_0 (\Delta V - R_s I_s) \quad (3)$$

Where I_0 and I_s are the initial and final currents, respectively, and R_0 and R_s are the cell resistances before and after the polarization, respectively.

Charge-discharge measurements: Charge-discharge measurements are performed at 355K with a Land BT 1-40 battery test system. The current densities and capacities of electrodes are calculated based on the total mass of 3D-G materials.

Physical characterization: Scanning electron microscopy (SEM, Cambridge S-360) is employed to study the morphology of 3D-G and LiHPN-LiI@3D-G electrode. Powder X-ray diffraction patterns were collected at beamline X7B of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. The wavelength used was 0.3196 Å. The morphology of 3D-G are investigated by battery backscattered electron imaging and energy-dispersive X-ray (EDX) spectra are captured using a FEI field-emission scanning electron microscope (Sirion XL) operated at an accelerating voltage of 20 kV. TEM and SAED measurements were carried out in a 200 kV side entry JEOL 2010 TEM with an energy dispersive X-ray (EDX) analysers.

2.3 Density function theory (DFT) calculations

To understand microscopic ion transport mechanism in the LiI(HPN)_n ($n=0,1,2$) system, we carried out first-principles calculations adopting the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) [16] and projector augmented waves (PAW)[17] pseudopotential as implemented in the Vienna ab initio simulation package (VASP) [18]. Intermolecular Forces of HPN (3-Hydroxypropionitrile) are not negligible, so we chose DFT-D2 method of Grimme in LiHPN calculation [19]. We used a plane-wave cutoff energy of 520 eV and $1\times3\times1$ Monkhorst-Pack k-point grid with Gaussian smearing of 0.20 eV to relax the electronic energies and nuclear degrees of freedom. The calculations were performed in a monoclinic 8-f.u. $\text{LiIC}_3\text{H}_5\text{NO}$ and all internal parameters were fully relaxed with the force convergence criterion of less than 0.02 eV/Å, while the lattice parameters are optimized with a total energy convergence within 10^{-4} eV/unit cell. The densities of states are obtained with a Γ -centered $2\times5\times2$ meshes. The ion hopping barriers are obtained using the climbing image nudged elastic band (CINEB) method [20] with a total energy convergence within 10^{-4} eV/unit cell and force convergence within 0.05 eV/Å. By comparison, FCC 4-f.u. LiI are calculated with a plane-wave cutoff energy of 230 eV and $5\times5\times5$ Monkhorst-Pack k-point grid based on DFT method. A supercell consisting of $2\times2\times1$ primitive unit cells for LiI is selected in our CINEB calculations. The convergence criterions are the same as LiHPN. The lattice parameters of a unit cell LiI, LiHPN and LiI(HPN)_2 before and after optimize and the computational band gap are list in Table S1. The calculated average bond length for LiHPN

and LiI(HPN)_2 and the bond length for related inorganic compounds [21-23] are listed in Table S3.

3. Results and discussions

The crystal structure of $\text{LiI:HPN}=1:1$ is shown in Figure 1(1). According to single-crystal structure analysis (Table 1), the molecular formula of the compound is $\text{LiIC}_3\text{H}_5\text{NO}$ (LiHPN) and the molecular weight is 204.92. It belongs to the C2/c space group with the monoclinic parameters $a=15.750(5)$ Å, $b=5.5760(18)$ Å, $c=16.139(7)$ Å, and $\beta=117.405(3)^\circ$. There are eight molecules in a unit cell. One lithium ion is coordinated with four atoms in the single-crystal structure of LiHPN . For example, Li1 is coordinated with $\text{N1\#1}$ of the nitrile group, O1 of the hydroxyl group, two iodide atoms I1 and $\text{I1\#2}$. Two lithium ions are connected via two HPN molecules to form a closed 12-membered ring. Two neighboring rings are connected via iodide atom to form a 3-dimensional net-like structure. The bond length of $\text{Li1-N1\#1}$ is $1.982(2)$ Å, Li1-O1 is $1.904(7)$ Å, Li1-I1 is $2.742(7)$ Å and $\text{Li1-I1\#2}$ is $2.739(7)$ Å. It is known that the bond lengths of Li-O and Li-N in inorganic compounds are in the range of 1.9-2.1 and 1.94-2.3 Å, respectively. The above data indicates that strong chemical bonds between Li and O and N atoms exist in the LiHPN . It should be noticed that each HPN molecule has two possible positions, which are shown as H1-O1-C1-C2-C3-N1 and $\text{H1-O1-C1'-C2'-C3-N1}$.

The structure of LiHPN along a -, b - and c -axes are shown in Figure 1(2) respectively. The hydrogen bond, C1' and C2' are omitted for clarity. It is observed that each Li ion is almost in the central site of the tetrahedron surrounded by four atoms, i.e., one N atom in the nitrile group ($-\text{CN}$), one O atom in the hydroxyl group ($-\text{OH}$) and two I atoms. Two sequent Li anions are connected via two organic molecules to form a closed twelve-membered ring. Different from iodide anion in LiI(HPN)_2 , iodide anion in LiHPN is restrained by two Li ion and two hydrogen bonds of hydroxyl groups. As shown in the Table 2, the bond length of $\text{H1}\cdots\text{I1}$ is $2.69(5)$ Å. Details of other bond lengths, bond angles, and atomic coordinates for the single-crystal structure are listed in the Supporting Information Tables S1, S2.

In order to figure out the ion-conductor type of single crystal LiHPN and the ion transport mechanism in LiHPN crystal structure, we have calculated the ion hopping barrier for LiHPN and LiI by using CINEB method, which can efficiently determine the pathway for

structural changes and ion transport [24-26]. Through rotating the model of the crystal structure LiHPN in Material Studio (MS), we found the space around each Li and I ion are very open along three directions. The distance between the two nearest neighboring Li or I ions in LiHPN is 4.079 or 4.609 Å and the ion radius of Li or I ion is 0.76 or 2.2 Å, respectively. We calculated the ion hopping barriers of LiHPN by moving a Li or I ion to their nearest neighboring sites which had been removed ions beforehand to avoid blocking the way.

The energy barriers for LiHPN are illustrated in Figure 2. The data from LiI are included for comparison. The energy barrier of Li ion in LiI (0.39 eV) and LiHPN (0.57 eV) are lower than the case of I (1.13 eV, 0.81 eV), which indicate that the LiHPN and LiI are Li ion conductors. Meanwhile, the difference of the energy barrier between Li and I ion in LiI (0.74 eV) is larger than that in LiHPN (0.24 eV), but smaller than that in LiI(HPN)₂ (-7.66 eV) [11]. These results indicate that the ion-conductor type of LiHPN is Li ion, which is utterly different from LiI(HPN)₂ as an I ion conductor. Apparently, the crystal structure change of synthesized LiHPN after the mixture of LiI and LiI(HPN)₂ annealing 130°C for 48 h results in the different ion-conductor type from LiI(HPN)₂.

XRD of LiHPN powder is shown in Figure 3 and the simulation result is included for comparison. Apparently, all peaks from pure LiHPN are in good agreement with the simulation of single crystal LiHPN. It indicates that the LiHPN can be synthesized without any impurity phase.

The dependence of ionic conductivity of LiHPN on the temperature is shown in Figure 4. The values from LiI(HPN)₂ and references are included for comparison. Both electrolytes of LiHPN and LiI(HPN)₂ exhibit a typical Arrhenius behavior. Significantly, LiI(HPN)₂ is an I ion conductor while LiHPN is a Li ion conductor. Their ionic conductivities were about 1.8×10^{-6} and 2.3×10^{-8} S/cm at 25°C, respectively. The experimental values of LiI(HPN)₂ are well consistent with references. However, the data from LiHPN synthesized in this work is utterly different from previous work[10], in which LiHPN is synthesized by simply mixing LiI and LiI(HPN)₂ with molar ratio of 1:1. Apparently the crystal structure of synthesized LiHPN change after the mixture of LiI and LiI(HPN)₂ annealing 130 °C for 48h.

The temperature dependence of the ionic conductivity of LiHPN with the various LiI concentrations is shown in Figure 5. All of the composite electrolytes exhibit a well linear fit of an Arrhenius plots. Significantly, the enhancement of the ionic conductivity of LiHPN with

the addition of LiI is found. The ionic conductivity at LiI/LiHPN=1 is 1.4×10^{-4} S/cm in 328 K and is over two orders of magnitude higher than that of pure LiHPN (4.9×10^{-7} S/cm). The highest conductivity of 1.8×10^{-3} S/cm for the electrolyte from LiI/LiHPN=1 can be achieved in 355K. The increasing concentration of Li ions with the introduction of LiI into LiHPN should also be responsible for the enhancing ionic conductivity. In addition, it is known that the boundary region in composite material (As shown in the Figure S1, a physical mixture of LiHPN with LiI is confirmed) is much larger than that in single system, which makes the transport of lithium easily. These reasons are beneficial to enhancing ionic conductivity with the addition of LiI into LiHPN.

In order to study the electrochemical window of LiHPN, a linear sweep polarization was performed at 355 K. As shown in Figure 6, a wide electrochemical window of at least 5.5 V for the solid LiHPN electrolyte is achieved. Such a wide window can be used for lithium-air batteries. The current responses of Li/LiHPN/Li and C/LiHPN/C as a function of time during voltage stepping from 0 to 0.1V were examined to clarify the ion transference feature of LiHPN as shown in Figure 7. When the potential is applied across C/LiHPN/C, ionic and electronic conduction can be separated because Li ions are blocked by carbon contacts. The total (I_t) and residual currents (I_e) are 11.8 and 0.02 μ A, respectively. The value of the total ionic transference number evaluated from Eq. (2) (in the Experimental section) is calculated to be 0.996, suggesting that the charge transport in the LiHPN is ionic. The lithium ion transference number (t_{Li+}) has been evaluated by combining a.c. and d.c. techniques. The current evolution of Li/LiHPN/Li with longer time is caused by the migration of Li ions in the LiHPN. D.C. polarization curve of symmetric cells Li/LiI(HPN)/Li indicates that the initial (I_0) and final currents (I_s) are 3.49 and 3.33 μ A, respectively. As shown in the insert of Figure 4, the cell resistances before (R_0) and after the polarization (R_s) for Li/LiI(HPN)/Li are 2314 and 2328 Ω , respectively. According to Eq. (3) in the Experimental section, t_{Li+} is evaluated to be 0.96 for the LiHPN electrolyte. These results strongly support that LiHPN is a Li ion conductor.

Three-dimensional graphene (3D-G) materials were used for air electrodes due to their unique mechanical characteristics, excellent electrical conductivity and large surface area. As shown in Figure 8, the graphene electrode obtained by freeze-drying the graphene hydrogels exhibits similar 3D network structures composed of a large amount of interconnected macropores. Many ripples and wrinkles on the graphene electrode form the highly

macroporous structure of the graphene, which enables small molecule electrolytes to be readily infiltrated, leading to 3D-G network-based conducting composites. In order to investigate the composition and morphology of LiIHPN-LiI@3D-G electrode, backscattered electron images of 3D-G electrode after the mixture powder of LiIHPN and LiI melted into 3D-G electrode were examined. The EDX results of LiIHPN-LiI@3D-G electrode are shown in Figure 9. It is clearly found that N, C, I, O elements are highly dispersed into the surface of LiIHPN-LiI@3D-G electrode. LiIHPN-LiI particles/clusters could closely anchor on the 3D-G and had intimate contact with 3D-G matrix. The LiIHPN-LiI@3D-G electrode offers a much larger contact area between 3D-G and solid-state electrolyte, which reduces the inner resistance of the electrode and facilitates electron and ion transportations to/from active sites during discharge/charge process, therefore may help in improving performance of lithium-air batteries.

Figure 10 shows the galvanostatic cycling profiles of the Li/LiIHPN-LiI/LiIHPN-LiI@3D-G cell in air ambient at the current densities of 67 mA g^{-1} . In order to ensure the high value of Coulombic efficiency, the charge capacity is limited to 2740 mAh g^{-1} . The cell is discharged at a fixed voltage of 1.9 V to achieve the good cyclic performance. The open circuit voltage (OCV) of the cell was about 2.8 V . The first and second discharge capacities of the cell are about 1470 and 2100 mAh g^{-1} , respectively. These measurements can be carried out up to 10 cycles. This performance is close to that of previously reported all-solid-state Li-air battery (1000 mAh g^{-1} , cycle number of 10) [27], but needs further improvement. In order to further confirm the air electrode character, the charge-discharge performances of the Li/LiIHPN-LiI/LiIHPN-LiI@3D-G cell in Ar ambient for comparison are carried out (the red curves in the first cycle). In argon ambient, the discharge curve is almost a drop line and the initial discharge capacity is less than 30 mAh g^{-1} , indicating that there is no Faraday process during the discharge process. The discharge curve of the cell is significantly different from that in air ambient, indicating that LiIHPN-LiI@3D-G in air ambient is an air cathode. In addition, it can be found that the discharge capacity of Li/LiIHPN-LiI/LiIHPN-LiI@3D-G cell in Ar ambient is much lower than charge capacity, indicating the possibility of decomposition from the solid electrolyte. The decomposition of

LiI from a physical mixture of LiHPN-LiI electrolyte (Figure S1) was electrochemically driven by the graphene as an efficient catalyst.

In order to further grasp for the feature of air cathode, SEM and TEM images of 3D-G electrode after the discharging to 1.8 V are measured. As shown in Figure 11(a), many particles with the sizes about 150 nm are observed on the surface of the electrode at the discharged state. These particles are uniformly distributed in 3D-Gelectrode and closely anchored on graphene. Because of the existence of the LiHPN-LiI thin film (less than 50 nm) on the surface of graphene, the electrochemical reaction of O_2 in air with lithium ions is limited to a local space between LiHPN and graphene films, resulting in the coated nano-particles of the products with LiHPN. The composition of discharged product was identified by TEM after the lithiated 3D-G electrodes are rinsed in an acetone to eliminate LiHPN. Two-dimension lattices can be seen clearly in this image as shown in Figure 11(b). After measuring the d-space in two directions, they can be attributed to (200) of Li_2O_2 . The SAED pattern in this phase shown in the insert of Figure 11(b) exhibits some rings made up of discrete spots, indicating the nanosized polycrystalline nature of the discharged product. All d-spacings derived from the SAED spectrum could be unambiguously indexed by the Li_2O_2 phase (JCPDS Card No. 73-1640, Li_2O_2).

It should be noted that the OCV of the Li/ LiHPN-LiI/LiHPN-LiI@3D-G cell in air ambient (2.8V) is lower than previous reported values of lithium-air batteries [7-9], which might be associated with the decomposed potential of LiI at 2.79 V. On standing stage of the Li/ LiHPN-LiI/LiHPN-LiI@3D-G cell in air, the OCV of the Li/LiHPN-LiI/LiHPN-LiI@3D-G cell will be larger than 2.8 V if the active sites on air cathode are fully covered by O_2 in air, this will result in the directly decomposition of LiI from LiHPN-LiI@3D-G and the formation of I_2 on the surface of air electrode. It is reasonable assumed that I_2 instead of O_2 is covered on surface of the air electrode at the primary state of the Li/LiHPN-LiI/LiHPN-LiI@3D-G cell. Thus, the electrochemical reaction mechanisms of the Li/LiHPN-LiI/LiHPN-LiI@3D-G cell at air electrode side are proposed as follows:

During discharging:

During charging

Li ions will react with I_2 from the decomposition of LiI on the air electrode to form LiI during the initial period of discharge process and can be expressed by equ. (4). After the I_2 at surface of air electrode is exhausted, the O_2 in air will enrich on the air electrode instead of I_2 , the discharge process proceed with the electrochemical reaction of O_2 as expressed by equ. (5). This could be used to explain for the feature of the discharge curve, in which a shorter sloping voltage plateau from 2.7 to 2.5 V (less than 250 mAh g^{-1} , less than 10% of total discharge capacity) and a sloping voltage plateau from 2.3 to 1.9 V are observed. They should correspond to discharge reactions of I_2 and O_2 on the air electrode with lithium, respectively. The discharge plateau from 2.3 to 1.9 V is lower than those of the previous reported Li-air batteries[5-6]. This may be due to the passivation after the reduction reaction process at 2.7 to 2.5 V. The charge capacity of 2740 mAh g^{-1} is observed when the Li/LiHPN-LiI/LiHPN-LiI@3D-G cell in the Ar ambient. The initial charge peak centered at 2.74 V versus Li corresponds to the electrochemical decomposition of LiI electrochemically driven by the graphene as an efficient catalyst as described as equ. (6), which can be confirmed by Raman measurements (Figure S2). The charge potential vs. Li^+/Li is less than that in a recently report[28]. The difference is mainly ascribed to the fact that the charge reaction of LiI occurs at high temperature of 355 K in the present work instead of at room temperature in Liu' s work. The reverse charge process of Li/LiHPN-LiI/LiHPN-LiI@3D-G cell in air ambient should mainly involves the electrochemistry of LiI (equ. (6)) as Li/LiHPN-LiI/LiHPN-LiI@3D-G cell in Ar ambient and chemical reaction of Li_2O_2 with I_3^-

(supported by Raman data (Figure S2)), in which the oxidized product of I_3^- will spontaneously react with Li_2O_2 formed after the discharge process to re-generate LiI and release O_2 at the air electrode side (equ. (7)). Obviously, Li/LiHPN-LiI/LiHPN-LiI@3D-G cell in air ambient is a typical lithium-air battery with LiHPN as solid-state electrolyte and both LiI and graphene as catalysts.

4. Conclusion

The chemistry of small molecular compounds based on LiI and HPN is revealed, the manipulation of the ratio of LiI to HPN can design the different structural parameters and band energy of small molecular compounds. Interestingly, LiHPN is a Li ion conductor, which is utterly different from previously reported $LiI(HPN)_2$ as a I ion conductor. Furthermore, the all-solid-state lithium-air batteries could be achieved by using a perfect combination of LiHPN electrolyte and LiHPN-LiI@3D-G cathode. Our findings have demonstrated that a small molecular solid-state electrolyte based on organic and inorganic molecules can be employed for high performance lithium-air batteries for the first time.

Supporting Information

The supporting information is available free of charge via the Internet at <http://pubs.acs.org>. XRD patterns of a complex mixture of LiI and LiHPN with different molar ratio of LiI/LiHPN (Figure S1), Raman spectra of LiHPN-LiI@3D-G air electrodes (Figure S2). The galvanostatic cycling profiles of the Li/ LiHPN-LiI/LiHPN-LiI@3D-G cell in air at the current density of 100 mA g^{-1} (Figure S3) , SEM images of LiHPN-LiI@3D-G aerogels (Figure S4), crystal data and structure parameters (Table S1-4).

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Table Captions:

Table 1 Crystal Data and Structure Refinement for LiHPN

Table 2 Bond Lengths and Angles of Hydrogen Bonds for LiHPN^b

Figure Captions:

Figure 1 (1) Li^+ cation coordination environment in the single-crystal structure of LiHPN. Symmetry transformations used to generate equivalent atoms: #1 $-x+1/2, -y-3/2, -z+1$; #2 $-x+1/2, y+1/2, -z+1/2$; #3 $-x+1/2, y-1/2, -z+1/2$. (2) X-ray structure plot for LiHPN viewed along a, b and c axes. Two possible positions are shown as H1-O1-C1-C2-C3-N1 and H1-O1-C1'-C2'-C3-N1.

Figure 2 Calculated Li and I migration barriers for (a) LiHPN and (b) LiI along selected paths

Figure 3 XRD patterns of the pure LiHPN and its simulation are included for comparison

Figure 4 Arrhenius plots of LiHPN and LiI(HPN)_2 ionic conductivity

Figure 5 The temperature dependence of the ionic conductivity of on the LiI concentration in LiHPN.

Figure 6 Linear sweep voltammogram at a scan rate of 1 mVs^{-1} for the LiHPN electrolyte

Figure 7 Current responses of Li/LiHPN/Li and C/LiHPN/C when the potential was stepped from 0 to 0.1 V at 355K

Figure 8 SEM images of the 3D graphene with magnification of (a) $5000\times$ and (b) $20000\times$.

Figure 9 (a) Backscattered electron images of LiHPN-LiI@3D-G aerogels electrode and the corresponding energy-dispersive X-ray spectrometry mappings of (b) all elements; (c) C; (d) N; (e) O and (f) I elements.

Figure 10 The galvanostatic cycling profiles of the Li/ LiHPN-LiI/LiHPN-LiI@3D-G cell in air at the current densities of 67 mA g^{-1} (the charge capacity was limited to 2740 mAh g^{-1})

Figure 11 (a) SEM images and (b) TEM images (its corresponding SAED pattern in the inset) of 3D-G electrode after the discharging to 1.8 V.

Table 1

Empirical formula	C ₃ H ₅ I Li N O
Formula weight	204.92
Crystal system	Monoclinic
Space group	C2/c
Crystal color	colorless, transparent
Lattice params	
<i>a</i> (Å)	15.750(5)
<i>b</i> (Å)	5.5760(18)
<i>c</i> (Å)	16.139(7)
<i>β</i> (deg)	<i>β</i> = 117.405(3) °.
Volume(Å ³)	1258.2(8)
<i>Z</i>	8
Density (calculated)	2.163 kg/m ³
Absorption coefficient (mm ⁻¹)	4.973
<i>F</i> (000)	752
Temperature (K)	293(2)
Reflections collected	3195
Refinement method	Full-matrix least-squares on <i>F</i> ₂

Table 2

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O1-H1...I1#4	0.88(5)	2.69(5)	3.497(3)	152(4)

^b Symmetry transformations used to generate equivalent atoms: #1 $-x+1/2, -y-3/2, -z+1$; #2 $-x+1/2, y+1/2, -z+1/2$; #3 $-x+1/2, y-1/2, -z+1/2$; #4 $x, y+1, z$

Figure 1 illustrates the crystal structure of LiI. (1) A 1D chain structure of LiI is shown, with Li atoms (blue spheres) and I atoms (pink spheres) forming the backbone. The structure is labeled with various atoms and bonds, including Li^{1#3}, I^{1#2}, O^{1#3}, H^{1#3}, C¹, C², C³, N^{1#1}, and N¹. (2) The 3D crystal structure is shown, with the a, b, and c axes indicated. The structure is composed of LiI units (Li atoms in blue, I atoms in pink) and organic ligands (C atoms in white, N atoms in green, O atoms in yellow). The legend indicates: Li (blue sphere), I (pink sphere), C (white sphere), N (green sphere), and O (yellow sphere).

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

For Table of Contents Only

A new solid-state Li-ion conductor of LiHPN has been successfully synthesized and was used for solid-state lithium-air batteries. Our results provide a new way for the design of solid-state electrolytes based on small organic and inorganic molecules towards high performance lithium-air batteries