Supporting Information

All Solid-state Rechargeable Lithium-Iodine Thin Film Battery Using LiI(3-hydroxypropionitrile)₂ as I⁻ Ion Electrolyte

Fang-Chao Liu¹, Wei-Ming Liu¹, Mo-Han Zhang¹, Zheng-Wen Fu¹,*, Hong Li²,*

[*] Mr. Fang-Chao Liu, Mr. Wei-Ming Liu, Mr. Mo-Han Zhang, Prof. Zheng-Wen Fu Laser Chemistry Institute and Department of Chemistry, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, Shanghai 200433, P.R China Fax: (+86)-21-65642522 E-mail: zwfu@fudan.edu.cn

Prof. H. Li, Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences Beijing 100190, China Fax: (+86)-10-82649046 E-mail: hli@aphy.iphy.ac.cn
Figure S1. a) Cross-sectional backscattered electron images of Li/LiI(HPN)₂/LiI(HPN)₂-I₂ cell, and the corresponding energy-dispersive X-ray spectrometry mappings of b) N; c) I; d) C and (e) O; (f) the average molar concentration ratio of I/C/N/O from corresponding EDX spectra in two selected regions (1 and 2).

The electrolytes of LiI(HPN)₂ preparation method is similar to report previously elsewhere (B. Xue, Z. W. Fu, H. Li, X. Z. Liu, S. C. Cheng, J. Yao, D. M. Li, L. Q. Chen, Q. B. Meng, J. Am. Soc. Chem. 2006, 128, 8720-8721). The LiI(HPN)₂-ethylacetate saturated solution was prepared by adding 0.1 g LiI(HPN)₂ into 2 ml ethylacetate (a few LiI(HPN)₂ was salted out) in the glove box for the film fabrication of LiI(HPN)₂. In a typical process, this solution was firstly coated on the surface of the lithium foil (purity 99.999%) at 50 °C. After drying, the surface of LiI(HPN)₂ film was exposed to the I₂ vapor that sublimed from I₂ crystals in a vial at room temperature. The distance between the substrate and the I₂ crystals was about 6 cm. After exposure to I₂ vapor for 8 seconds, a battery consisting of Li/LiI(HPN)₂-I₂-LiI(HPN)₂ was formed. As shown in Figure S1, the fresh cell includes two layers: the lithium foil is at the right side of the dotted line. The
LiI(HPN)$_2$ electrolyte and a complex mixture of iodine and LiI(HPN)$_2$ consisting of N, C, I, O elements as cathode is at the left side of the dotted line. The thickness of solid electrolyte and parts of reacted produce with iodine is about ~100 μm. Existence of trace amount of oxygen and nitrogen in the lithium foil should be attributed to the oxidation and nitridation of lithium contacted with air during sample transfer. The chemical reaction of I$_2$ vapor with LiI(HPN)$_2$ can be investigated by measuring EDX spectra in selected area. As shown in Figure S1 (f), the average molar concentration ratios of I/C/N/O are 10:37:29:23 and 8:38:22:32 in two selected regions 1 and 2. Apparently, the iodine concentration in selected region 1 is higher than that in region 2. The composition of I$_2$-LiI(HPN)$_2$ in region 1 is estimated to be 0.33:1 using I/C=10:37.
Figure S2 XRD patterns of a complex mixture of iodine and LiI(HPN)$_2$ with different molar ratio of I$_2$/LiI(HPN)$_2$. XRD pattern of the pure electrolyte LiI(HPN)$_2$ is included for comparison.

Several peaks at $13.1^\circ$, $18.4^\circ$, $21.1^\circ$, $23.3^\circ$, $25.9^\circ$, $27.0^\circ$, $29.0^\circ$, $29.3^\circ$, $30.7^\circ$, $36.3^\circ$, $36.8^\circ$, $41.4^\circ$, and $42.1^\circ$ are in good agreement with the diffraction peaks of single crystal LiI(HPN)$_2$. (See Ref. [8], H. X. Wang, Z. X. Wang, H. Li, Q. B. Meng, L. Q. Chen, Electrochimica Acta 52 (2007) 2039-2044). The new diffraction peaks (marked with star) appear after addition of iodine. The crystal structure of new phase will be resolved in future.
Fig. S3 Raman spectra of the pure iodine, pure electrolyte LiI(HPN)\textsubscript{2} and a complex mixture of iodine and LiI(HPN)\textsubscript{2} with different molar ratio of I\textsubscript{2}/LiI(HPN)\textsubscript{2}.


It is found that no any peaks from the Raman shift of I\textsubscript{2} is observed for the mixture of iodine and Li(HPN)\textsubscript{2}. This indicates clearly that a mixture of LiI(HPN)\textsubscript{2} with iodine is not a physical mixture and iodine should react with Li(HPN)\textsubscript{2}. Previous studies showed that the weak band at 107 cm\textsuperscript{-1} and a strongly band at 163 cm\textsuperscript{-1} in (trimesic acid H\textsubscript{2}O)\textsubscript{10}HI\textsubscript{5} can be attributed to be that characteristic of a I\textsuperscript{3}\textsuperscript{-}ν\textsubscript{1} and I\textsuperscript{5}\textsuperscript{-}ν\textsubscript{1} vibrations, respectively (See Masagi Mizuno, Jiro Tanaka, Issei Harada, *J. Phys. Chem.* 1981, 85, 1789-1794). In the PVP-I\textsubscript{a} complex, the peak at 115 cm\textsuperscript{-1} and 173 cm\textsuperscript{-1} are assigned to I\textsuperscript{3}\textsuperscript{-}ν\textsubscript{1} and I\textsuperscript{5}\textsuperscript{-}ν\textsubscript{1} vibrations (See L. Weinstein, W. Yourey, J. Gural, and G. G. Amatucci, *Journal of The Electrochemical Society*, 2008, 155, A590-A598). The I\textsuperscript{3}\textsuperscript{-} ν\textsubscript{3} band at 144 cm\textsuperscript{-1} is clearly observed as a shoulder on the main I\textsuperscript{5}\textsuperscript{-} peak, which can be deconvoluted as shown in Figure. A clear assignment of Raman bands in Figure S4 need clear information of the coordination of iodine in LiI(HPN)\textsubscript{2} and possible crystal structure, which will be studied further. Above preliminary results indicate clearly the formation of certain LiI(HPN)\textsubscript{2}-I\textsubscript{a} complex.
Figure S4. The discharging curves of an Li/I_2-LiI(HPN)_2 battery using a 20 kΩ and 40 kΩ loading.

The primary batteries of Li/I_2-LiI(HPN)_2 were constructed as following. Li plate (purity 99.999%) with a thickness of 0.5 mm (1.0 cm²) was used as an anode directly. The finely ground powders of iodine (purity 99.99%) and LiI(HPN)_2 with a molar ratio of 0.5:1 were mixed mechanically and pressed into a columnar electrode (diameter=11.3 mm, thickness= 0.5 mm) as cathode. The cells were assembled and measured in an Ar-filled dry glove box. No separator or electrolyte was used in this case. The operating voltage is relative flat at the 40 kΩ discharge curve until the cathode is depleted in iodine. The operation of this battery indicates that the I_2-LiI(HPN)_2 can be used as cathode material for lithium-iodine batteries, similar as I_2-P_2VP cathode. It has to be mentioned that this battery cannot be discharged galvanostatically at a current density of 1 μAcm⁻² using CHI660A electrochemical workstation.
Figure S5 Conductivity of a complex mixture of iodine and Li(HPN)$_2$ with different molar ratio of I$_2$/Li(HPN)$_2$.

Conductivity measurement was carried out by using the sandwiching with two carbon electrodes and one columnar electrode of I$_2$:Li(HPN)$_2$, which were obtained by cold pressing iodine (purity 99.99%) and Li(HPN)$_2$ with different molar ratio. The conductivity of I$_2$:Li(HPN)$_2$ was calculated by the known area and the thickness as well as the examined resistance of C/I$_2$:Li(HPN)$_2$/C by a CHI660A electrochemical workstation. It can be found that the conductivity drastically decrease from $10^{-2}$ S/cm$^{-1}$ to $10^{-5}$ S/cm$^{-1}$ with the value of I$_2$:Li(HPN)$_2$ from 1.0 to 0.1