Electronic Supplementary Information

Li-Se battery: absence of lithium polyselenides in carbonate based electrolyte

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1. Electrochemical characterization The electrochemical performance of the selenium-carbon composites was assessed by fabricating CR2032 coin cells. Metallic Li foil was used as the negative electrode. The positive electrode was prepared by first mixing a slurry containing 70 wt.% composite material, 10 wt.% carbon black, and 20 wt.% polyvinylidene fluoride (PVDF) or sodium alginate (SA) binder previously dissolved in N-methyl-2-pyrrolidinone (NMP) and water, and the proper amount of NMP and water as dispersant, respectively. Then, the slurry was then coated on aluminum foil using a doctor blade. The solvent were removed by first drying the electrode at 75 °C for 2 h, then further drying the electrode in a vacuum oven at 100 °C overnight. A half-cell was constructed in an argon-filled glove box. The cells were tested with a MACCOR Electrochemical Analyzer at a current density of 50 mA/g between 0.8 and 3/3.5 V. Electrochemical tests were conducted at room temperature and duplicated to check reproducibility. The capacity was calculated based on the active material mass, which corresponds to 49 wt.% of the electrode weight.

Pouch cells for in-situ XAS measurements were fabricated using the Cell Fabrication Facility at the Argonne National Laboratory with Li metal as the negative electrode.

2. X-ray diffraction The HEXRD measurements were carried out at Beamline 11-ID-C of the APS. The X-ray wavelength was 0.111538 Å. In-situ HEXRD patterns were collected with custom-designed coin cells cycled with a MACCOR cycler at a constant rate between 0.8 and 3.5 V. During the charging and discharging, the XRD patterns were collected for 1 minute, with 15-26 minute intervals, using a Perkin Elmer 2D X-ray detector. 2D images were converted into 1D plot of 2θ versus intensity by using the FIT2D program calibrated against a CeO_2 standard.

3. X-ray absorption spectroscopy The XAS measurements for the Se K-edge (12,658 eV) were made in transmission mode on the bending-magnet beamline of the APS (20-BM-B). The incident beam was monochromatized by using a Si (111) fixed-exit, double-crystal monochromator. In-situ XAS experiments were made on the pouch cells cycled with a MACCOR cycler. Standard materials were mixed with boron nitride and then pressed into a self-supported pellet sealed in 50-µm-thick Kapton tape. X-ray absorption near edge structure (XANES) data reduction followed standard methods using the ATHENA software package.

4. Raman spectroscopy Raman spectra were taken in the Center for Nanoscale Materials (CNM) at ANL on the inVia Raman microscope using 785 nm excitation. Powdered specimens and electrodes were placed in Teflon cells equipped with a CaF_2 window to prevent exposure to ambient atmosphere. The Raman spectra were recorded through the CaF_2 window. The liquid Raman spectra were obtained using a quartz cuvette.

5. Li_2Se_n preparation and solubility test: Four Li-Se cells assembled with 1 M lithium bis(trifluoromethanesulphonyl)imide (LiTFSI) in 1,3-dioxolane (DOL): 1,2-dimethoxyethane (DME) (1:1 v/v ratio) electrolyte were cycled for about 3 hrs. at a rate of 50 mA/g, then stopped and disassembled in the argon filled glove box. The voltage profiles Se1-4 were shown in Fig. 1S (a) as compared with a fully discharge Li-Se cell in DOL/DME electrolyte. The components of opened cells were rinsed with DOL/DME solvent, which was tested by liquid Raman spectroscopy. Features between 220 and 340 cm^{-1} not attributable to Se or Li_2Se could be associated with one or more polyselenide anions according to theoretical calculation and experimental results reported.[1] The distinct Raman band at 293 cm^{-1} is in the range of frequency expected for polyselenides. In the work of Goldbach et al, theoretical calculation indicate three fairly intense Raman bands at 277, 293 and 312 cm^{-1} for Se_4^{2-} (C2) molecule, and they experimentally observed a band at 269 cm^{-1} for Se_4^{2-} in aqueous solution. Due to the hindered motion of molecules in liquid, the translational and rotational degrees of freedom of gas phase molecules become restricted translations and librational modes, respectively, which contribute to the Raman spectra.[1] Therefore, it is reasonable to ascribe the band at 293 cm^{-1} to Se_4^{2-} in the DOL/DME solvent. This is consistent with our earlier studies show that the major component of this discharge state is lithium polyselenides as demonstrated by the dark brown colour as well.[2]

The cell rinse solution were separates into two glass bottles as shown in Fig. 2S (a, b). Then the solvent was evaporated Fig. 1S (c, d) with the solids deposited at the bottom of the bottles, finally EC/EMC and DOL/DME solvent were added into the two bottles respectively. As shown in Fig. 1S (e, f), the solid deposit is not soluble in the EC/EMC solvent and dissolved in the DOL/DME solvent.

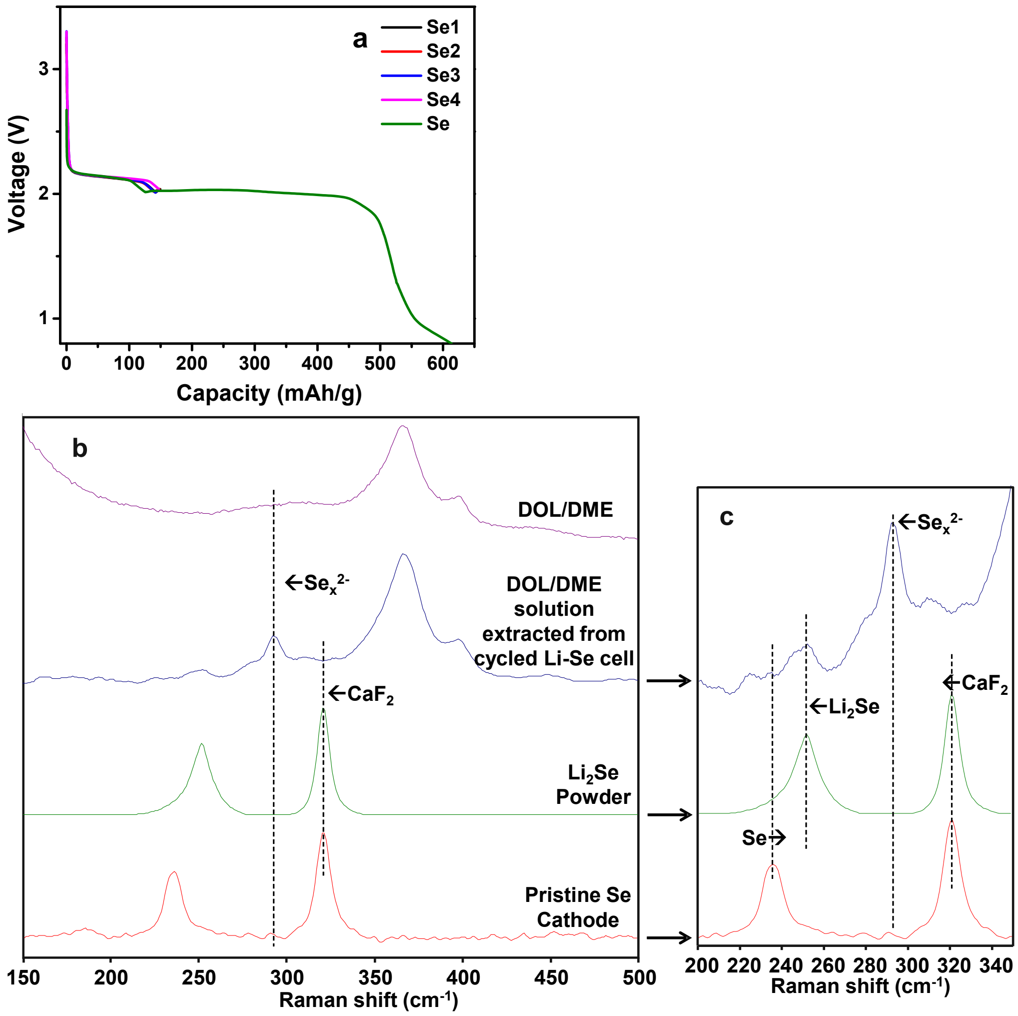

Fig. 1S Voltage profile of the cells cycled with ether-based electrolyte to prepare Li$_2$Se$_n$.(a), Raman spectroscopy of DOL/DME solvent, the Li-Se cell rinsing solution, Li$_2$Se powder and pristine Se cathode for comparison.

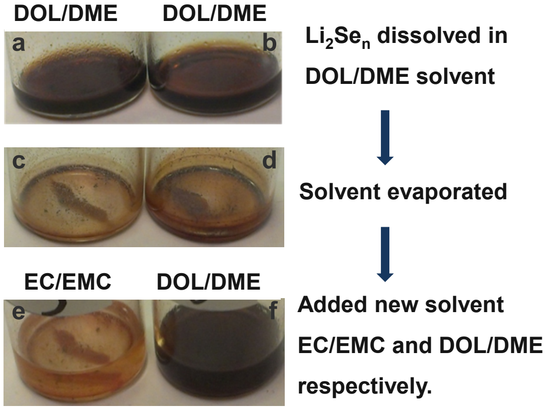

Fig. 2S Li$_2$Se$_n$ solubility test in different electrolyte solvents.

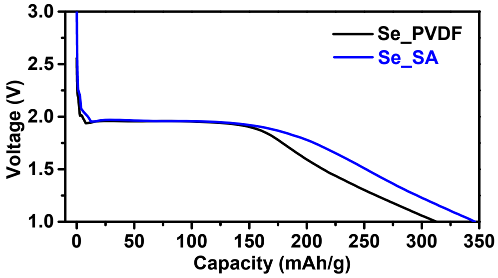

Fig. 3S First discharge voltage profile of Se cathode prepared with SA and PVDF binder, respectively.

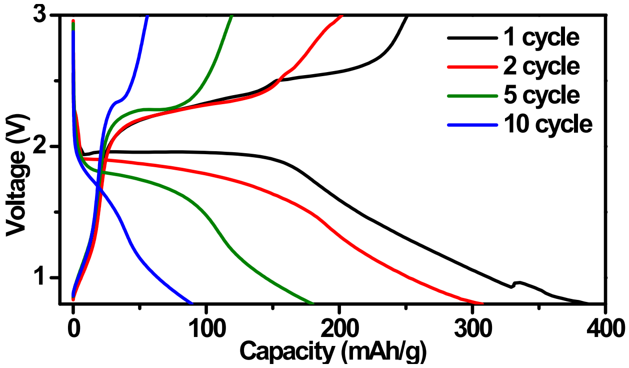

Fig. 4S Voltage profile of Li-Se cells cycled with carbonate based electrolyte.

References:

1. A. Goldbach, J. Johnson, D. Meisel, L. A. Curtiss and M. L. Saboungi, *J. Am. Chem. Soc.* , 1999, **121**, 4461-4467.
2. Y. Cui, A. Abouimrane, J. Lu, T. Bolin, Y. Ren, W. Weng, C. Sun, V. A. Maroni, S. M. Heald and K. Amine, *J. Am. Chem. Soc.*, 2013, **135**, 8047-8056.