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# Supporting Information

## Ultra-small Sulfur Nanoparticles Configured Inside a Flexible Organic Mixed Conducting Network as Cathode for Lithium-Sulfur Battery

Sudeshna Sen, Dipak Dutta, Aninda J Bhattacharyya

Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore-560012, India

**Materials and Methods:**

All chemicals are of analytical grade and used as received without further purification. Aniline is distilled twice before use and tetrahydrofuran (THF) is dried prior to use. Mili-Q water (resistivity~ 18.2 MΩ.cm) is used all throughout for synthesis purposes. The conductive carbon paint is obtained from Bare Conductive Ltd.

*Synthesis of mixed conducting (ionic and electronic) sulfur electrode (S-MIEC)*: S-MIEC is synthesized in three steps: (a) synthesis of triton X-100 (TX-100) tethered sulfur nanoparticles (SNP-TX), (b) lithiation of SNP-TX (SNP-TX-Li) and wrapping up of the SNP-TX-Li with polyaniline.

*Synthesis of SNP-TX*: SNP-TX is synthesized using a modified procedure reported elsewhere by Dai *et al* in ref. [21]. In a typical procedure, requisite amount of sodium thiosulphate is dissolved in water followed by addition of 1% aqueous solution of TX-100. This solution is then heated at 70 $^{o}$C and stirred for 15 min. 12 ml of concentrated hydrochloric acid (HCl) is added to the above reaction mixture followed by stirring for 30-40 min at the same temperature. This results in the formation of a yellow suspension of sulfur nanoparticles. For better performance of the electrochemical cell, acetylene carbon black (20% w/w of sulfur) is also added to the above suspension followed by stirring for 15-20 min, washing with distilled water and finally drying at 70 $^{o}$C.

*Lithiation of SNP-TX*: Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) is dissolved in dry THF solvent to prepare 0.1MLiTFSI-THF solution followed by the addition of SNP-TX particles and stirred for 4-5 h at room temperature in argon atmosphere. The SNP-TX-Li particles are washed by ethanol to remove excess unbound lithium salt and finally dried at room temperature in Argon atmosphere.

*Synthesis of S-MIEC:* To a mixture containing requisite amount of aniline in water, concentrated HCl is added dropwise to form a saturated solution of anilinium hydrochloride in water, followed by dispersion of the SNP-TX-Li particles into it and drying the mass at room temperature for 24 h. A few drops of hydrogen peroxide ($H_2O_2$ 30% v/v) were then added to the dried sample resulting in a greenish coloration within few minutes. This is finally dried at room temperature inside an argon filled glove box.

*Synthesis of SNP-TX-PAni*: The SNP-TX-PAni sample was synthesized following the same procedure of synthesis of S-MIEC but with SNP-TX sample. SNP-TX sample is dispersed in saturated solution of anilinium hydrochloride in water and dried it for 24 h. Then the dried product was soaked with few drops of hydrogen peroxide ($H_2O_2$ 30% v/v) and dried in argon filled glove box.

*Sample preparation for electrical and electrochemical measurements:* The dc I-V and ac impedance spectroscopy measurements are recorded using 1.5 mm thick pellet of the S-MIEC. The electrochemical stability and battery performance studies are studied using Swagelok$^{TM}$ cells with lithium foil (Aldrich) as the counter and reference electrode, Whatman glass fiber based separator and1M LiTFSI indioxolane (DOL) : dimethylether (DME) (1:1 v/v) as the electrolyte.

The battery configuration used is as follows S-MIEC│1M LiTFSI (DOL:DME 1:1 v/v)│Li. For electrochemical measurements, slurry of the active material (S-MIEC)(SNP : C= 80:20 w/w)is prepared with acetylene carbon black (Alfa Aesar) and polyvinylidene fluoride (PVDF, Kynarflex) in a weight ratio of 80:10:10 in cyclopentanone. The slurry is cast on a carbon coated aluminium foil (thickness = 20 μm, Ranga Techno Impex) and dried in Argon atmosphere for 24 h. The preparation of slurry and casting of electrode are done inside the Argon filled glove box (pressure: 3 mbar, $H_2O < 0.5$ ppm, $O_2 < 0.5$ ppm). The specific capacity reported here is based on the active mass of sulfur only.

*Structural and electrochemical characterization*: The powder X-ray diffraction (XRD) data is collected on a Philips X'Pert Pro diffractometer; Cu $K_\alpha$ radiation, $\lambda$= 1.542 Å, voltage = 40 kV; current= 30 mA, in the $2\theta$ range of 5°-90°. Fourier transform infrared (FTIR) spectra are recorded on a Perkin Elmer Spectrum 2000Spectrometer at a spectral resolution of 4 $cm^{-1}$ in the transmission mode on a KBr pellet of the sample. X-ray photo electron spectroscopy (XPS) data are recorded on the AXIS-Ultra, instrument of Kratos using monochromatic $AlK_\alpha$ radiation (225 W, 15 mA, 15 kV). Prior to the electrode casting, the aluminium foil is coated with carbon paint (Bare Conductive Ltd) by using the Elcometer Doctor Blade Film Applicator 4340. The dc current-voltage (I-V) is measured using a Keithley source measure unit (2635A SYSTEM Source meter) instrument at applied voltages in the range -5V to +10V. Ac impedance spectroscopy is performed on a Novocontrol Alpha-A instrument in the range 1 MHz-1 Hz. The cyclic voltammetry experiment is performed using a CH Instruments (CH608C) in the voltage range (1.3–3) V at a scan rate of 0.25 $mVs^{-1}$). The galvanostatic charge/discharge cycling measurements are performed using an Arbin Instruments (BT 2000 Corp., USA) at different C-rates in the voltage range of (1.3- 3.0) V (versus $Li^+/Li$). The galvanostatic intermittent titration technique (GITT) measurements are carried out using Arbin Instrument (Model BT 2000, Arbin Instruments Corp., USA). This consists of a series of current pulses applied to the Swagelok*TM* cells at a current rate of 0.1 C in voltage ranges from 3.0 to 1.3 V. The battery is cycled up to 20 steps, each step consisting of 17.1 min open circuit stand relaxing the battery to steady state potential ($E_s$) for 5 h. Amount of sulfur in the S-MIEC sample is evaluated from the thermogravimetric analysis (fig S1) (TGA/SDTA851, Mettler Toledo) and revalidated using CHNS elemental analysis (Thermo Finnigan FLASH EA 1112 CHNS analyzer).

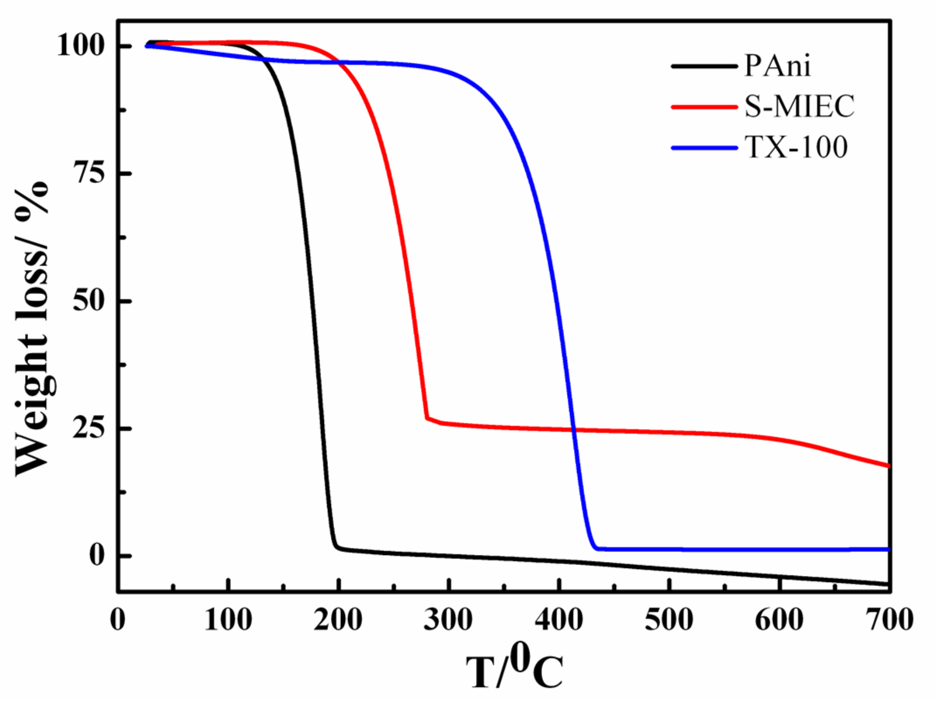

Fig. S1: Thermo gravimetric (TGA) analysis of S-MIEC.

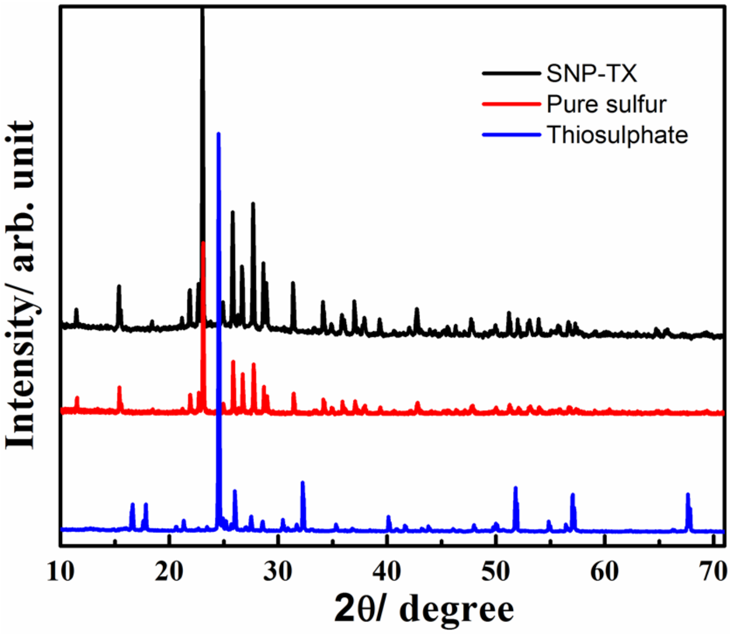

Fig. S2 (a): PXRD patterns of SNP –TX, thiosulfate and elemental sulfur.

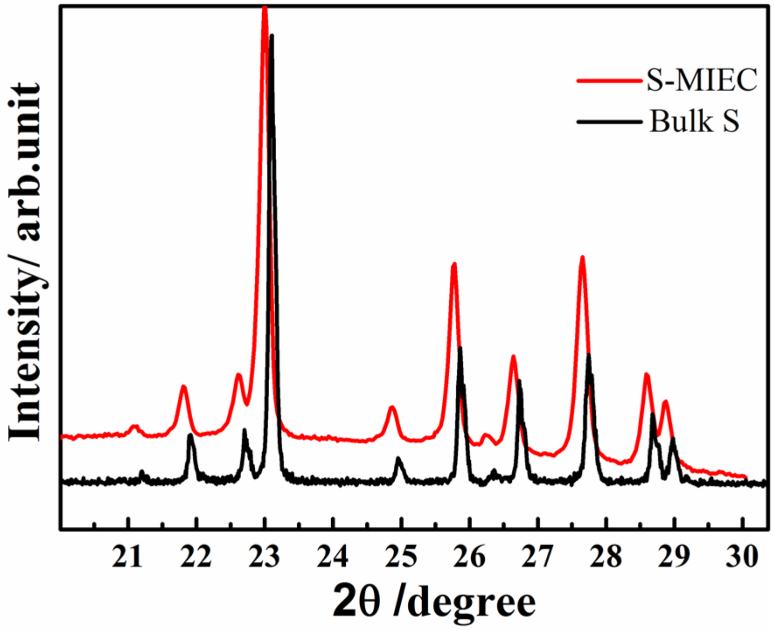

Fig. S2 (b): PXRD patterns of S-MIEC and bulk Sulfur.

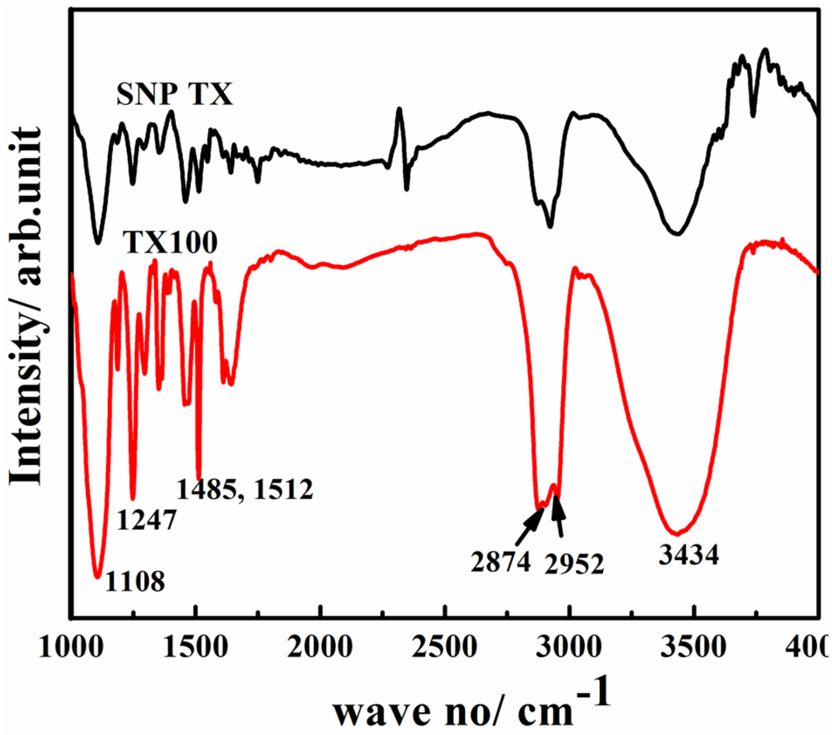

Fig. S3:  FTIR spectra of SNP-TX and TX-100.

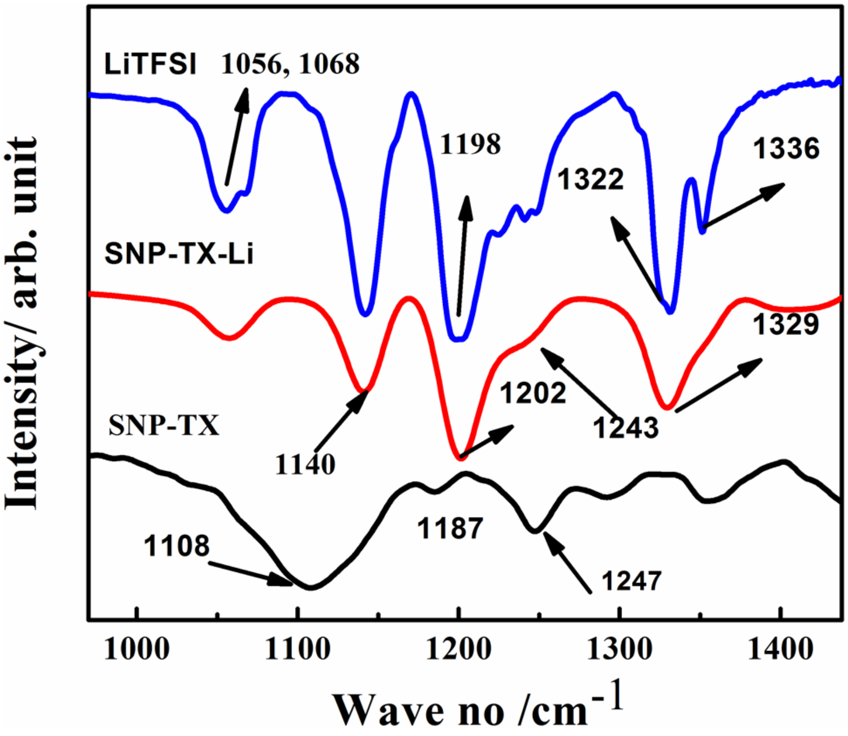

Fig. S4: FTIR spectra of SNP-TX, SNP-TX- Li and LiTFSI.

Table ST 1: Infrared band positions and assignments for SNP-TX.

| Triton | | SNP-TX |
|---|---|---|
| Peak positions | Assignment | Peak positions |
| 3434 | $\nu_{\text{O-H}}$ | 3434 |
| 2951, 2922 | $\nu_a$ $CH_2$ of ether | 2922 |
| 2874 | $\nu_s$ $CH_2$ | 2872 |
| 1611 | $\nu_{\text{C-C}}$ benzenoid | 1610 |
| 1353, 1364, | $\Delta$ Umbrella methyl doublet | 1358, broad |
| 1465 | $\nu_{\text{C-C}}$ benzenoid | 1459 |
| 1512 | $\nu_{\text{C-C}}$ benzenoid | 1513 |
| 1247 | $\nu$ (Ar-o-CH2) | 1247 |
| 1105 | $\nu_a$ arom. ether c-o-c | 1108 |
| 1186 | $\nu_a$ aliph. ether c-o-c | 1188 w |

Table ST2 : Infrared band positions and assignments for SNP-TX-Li.

| Region | LiTFSI | Assignment | SNP-TX | Assignment | SNP-TX-Li |
|---|---|---|---|---|---|
| **800-1000** | | | | | |
| | | | | | 463 new |
| | 514 | $\delta_a(CF_3)$ | | | 514 |
| | 574 | $\delta_a(CF_3)$ | | | 574 |
| | | | 576 | | - |
| | 596 | $\delta_a(CF_3)$ | | | 596 |
| | 609 | | | | 609 |
| | | | 620 | | 620 appear |
| | 650 | $\delta_a$ in plane $SO_2$ ) | | | |
| | | | | | 667 new peak |
| | | | 680 | Ph-O | Appear broadening |
| | 742 | $\delta_s$ CF3 | | | 742 |
| | 798 | $\nu$ (C-S) | | | 798 |
| | | | | | |
| | | | **833** | $\nu_{a(\text{C-O-C})}$ aliph ether | 820, 841 weak broad |

| | | | | | |
|---|---|---|---|---|---|
| **1000-1400** | | | | | |
| | 1056, 1068 | $\nu_a$ **(SNS)** | | | 1056 |
| | 1142 | $\nu_s$ ($SO_2$ ) | | No peak from TX100 | 1142 |
| | 1198, 1242 | $\nu_a$ ($CF_3$) | | | 1198 |
| | 1336,1331 | $\nu_a$ ($SO_2$ in plane) | | | 1329 |
| **1400-1600** | | | | | |
| | | | 1457 | $\nu_{C\text{-}C}$ benzenoid | 1447 |
| | | | 1513 | $\nu_{C\text{-}C}$ benzenoid | 1488 |
| | | | 1546 | $\nu_{C\text{-}C}$ benzenoid | 1508 |
| | | | | | |
| **2800-3000** | | | | | |
| | | | 2867 | $\nu_a$ ($CH_2$ of ether) | 2846, split |
| | | | 2923 | $\nu_a$ ($CH_2$ of ether) | 2915. 2885 split |
| | | | 2954 | $\nu_s$($CH_2$ of ether) | 2950 |

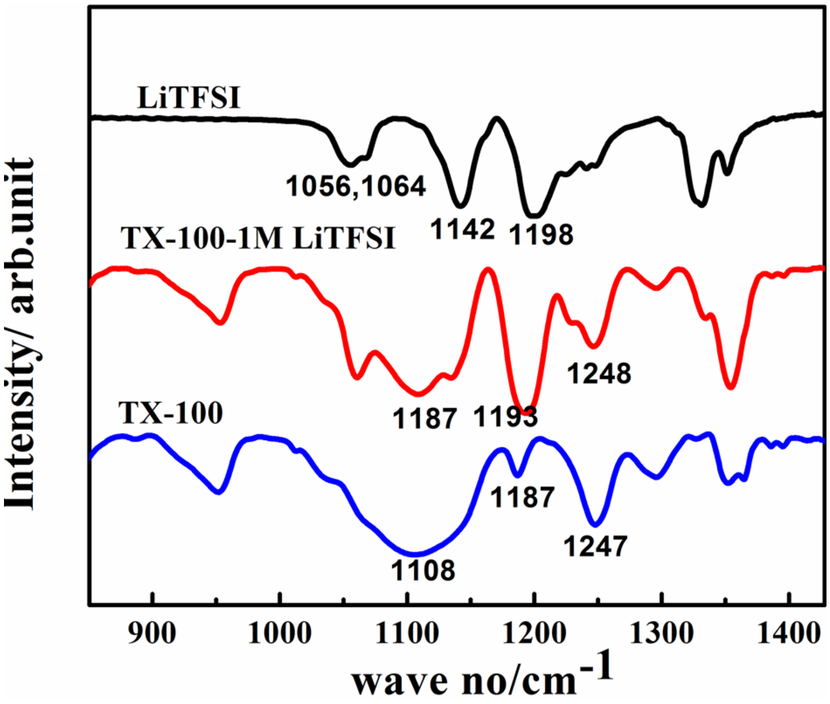

Fig. S5: IR spectrum of TX-100-LiTFSI (1 M).

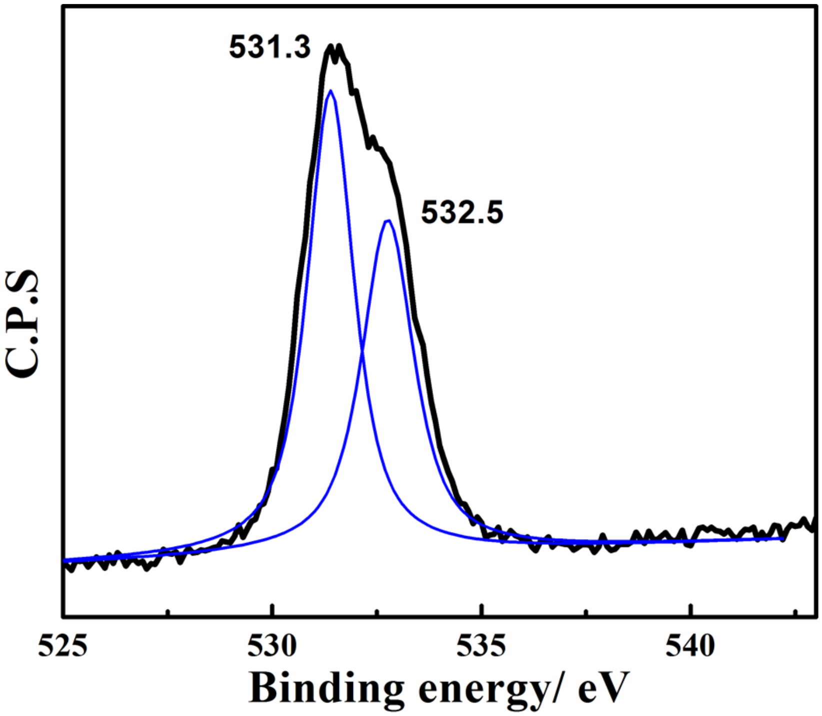

Fig. S6: XPS O1s spectrum of SNP-TX.

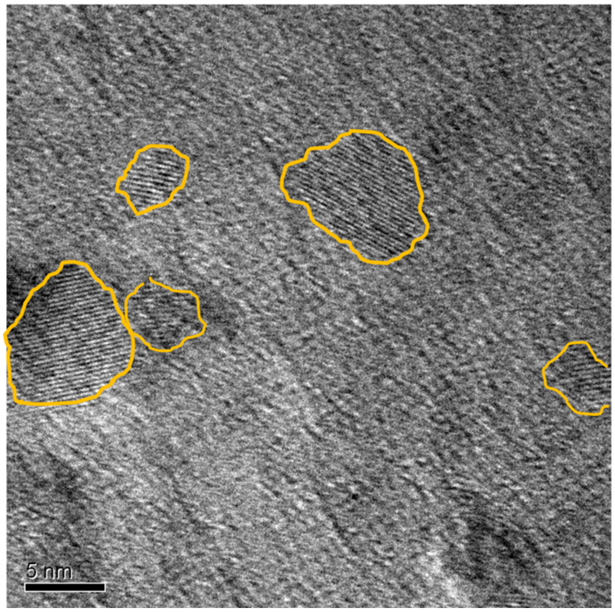

Fig. S7 : HRTEM image of bare SNP-TX.

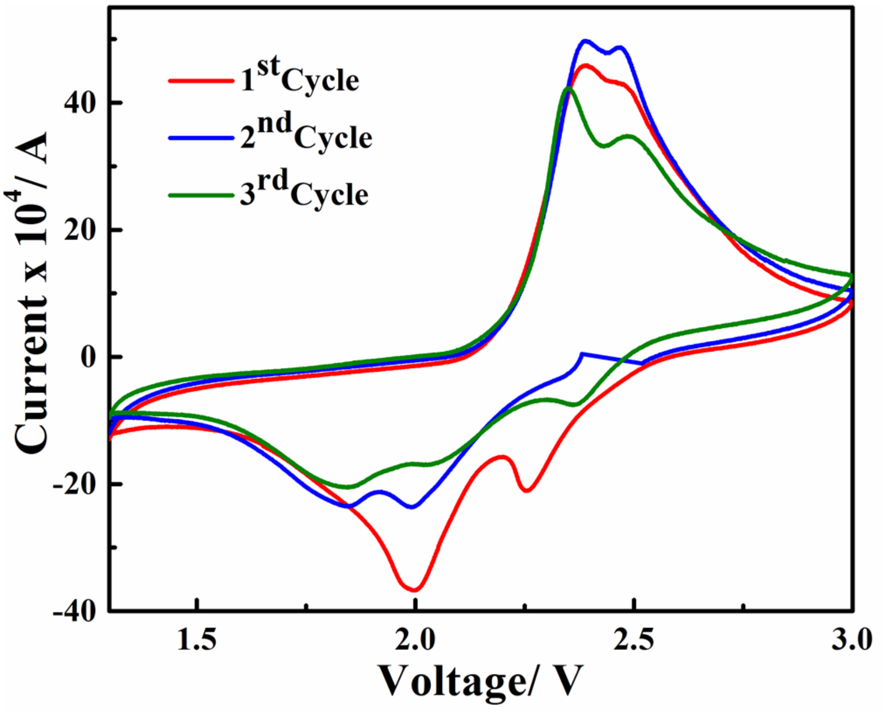

Fig. S8: Cyclic voltammogram of SNP-TX-PANI (at 0.25 mV s$^{-1}$).

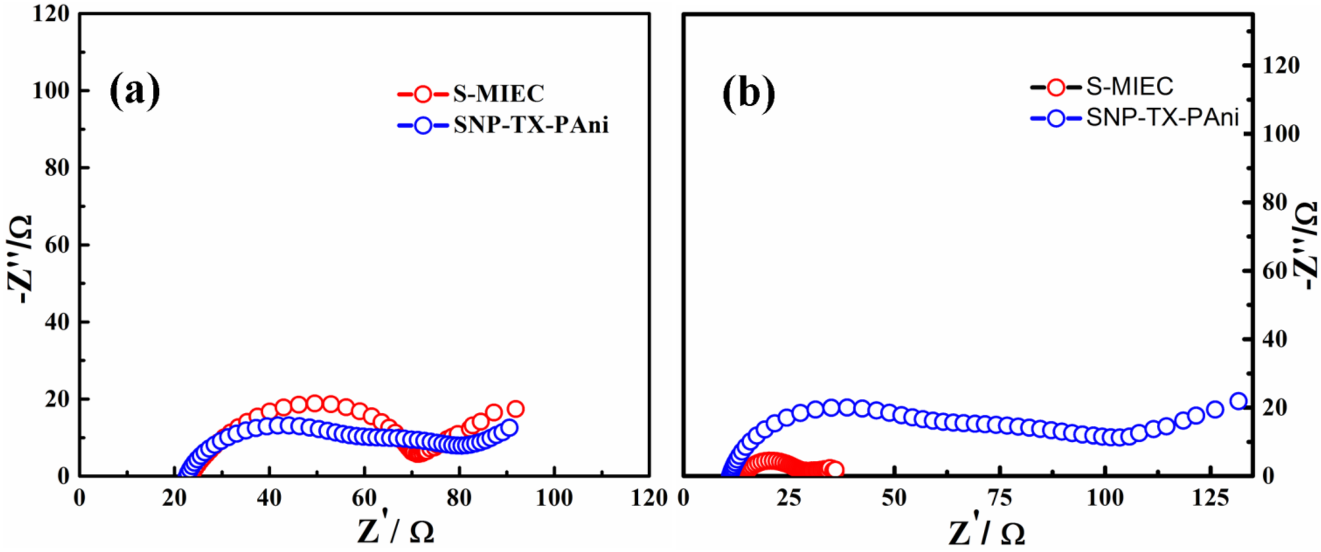

Fig. S9: EIS of Li-S-MIEC cell (a) before and (b) after 10th galvanostatic cycles.

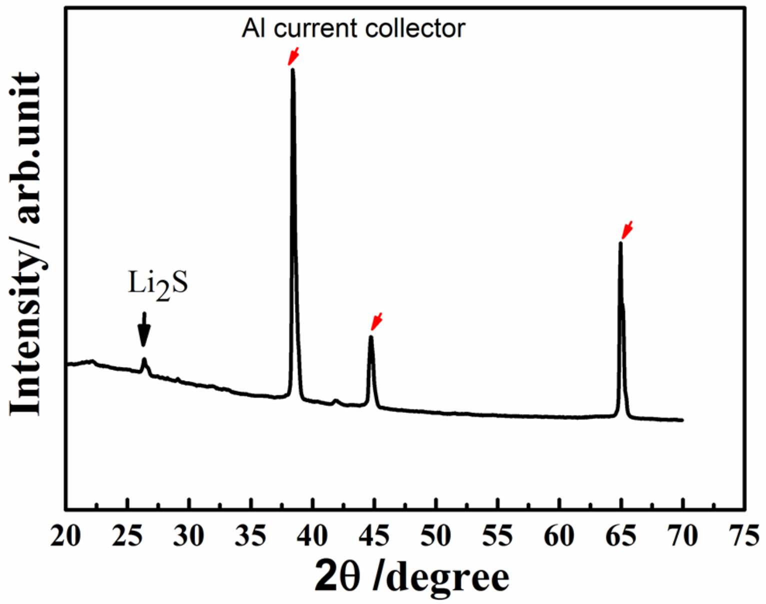

Fig. S10: Ex-situ XRD of S-MIEC after 10th cycle.