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Electronic Supplementary Information

A nonaqueous all organic semisolid flow battery

Xueqi Xing,[a,b] Qinghua Liu,[a] Jiang Li,[c] Zhihua Han,[a] Baoguo Wang,[b] and John P. Lemmon*[a]

[a]National Institute of Clean-and-Low-Carbon Energy, Beijing 102211, China

[b]Department of Chemical Engineering, Tsinghua University, Beijing 100084, China

[c]SUNCAT Center for Interface Science and Catalysis, Department of Chemical Engineering, Stanford University, Stanford, CA 94305, USA

Corresponding author. E-mail: John.Lemmon@chnenergy.com.cn (J. L.)

1. Experimental

1.1. Materials

10-methylphenothiazine (MPT) and thioxanthone (THA) were purchased from TCI (Shanghai) Development Co., Ltd. Conductive additive Ketjet (KB) was obtained from Suzhou Yilong Sheng Energy Technology Co., Ltd. Acetonitrile (MeCN) was obtained from Alfa Aesar. DMC, 1,3-dioxolane (DOL), ethyl methyl carbonate (EMC), and 1,2-dimethoxyethane (DME) were obtained from Beijing Institute of Chemical Reagents Co., Ltd. Tetraethylammonium hexafluorophosphate ($TEAPF_6$) was prepared following a previously reported synthetic process.[1] MPT, THA, and KB were dried in a vacuum oven at 60 °C for 12 h to remove trace moisture. All the chemicals were used as received without further purification.

1.2. Cyclic voltammetry

All electrochemical measurements were conducted in an argon-filled glovebox (Shanghai Mikrouna Technology Co., Ltd.) with a level of less than 1 ppm H_2O and O_2 at room temperature.

Cyclic voltammetry (CV) was carried out in a three-electrode test cell with an Electrochemical Workstation (CHI 660D, Shanghai Chenhua Instruments Co., Ltd., China). A 3-mm-diameter glassy carbon was used as the working electrode; a platinum strip served as the counter electrode; a nonaqueous Ag/Ag^+ electrode was used as the reference electrode.

The diffusion coefficient was calculated using the Randle–Sevcik equation: [2]

$$\left|i_p\right| = 0.4463nFAC\sqrt{\frac{nFvD}{RT}} \qquad (1)$$

In equation (1), i_p is the peak current (A); F is Faraday constant (96485 C mol^{-1}); n is the electron-transfer number in the redox reaction (n = 1); T is the absolute temperature (K); R is the universal gas constant (8.314 J K^{-1} mol^{-1}); A is the area of electrode (cm^2); v is the sweep rate (V s^{-1}); C is the concentration of redox species (mol cm^{-3}); D is the diffusion coefficient (cm^2 s^{-1}).

1.3. Solubility measurements

The solubility of MPT and THA in different organic solvents was measured using the volume–mass method. The solid active materials were added to a certain volume of solvents partially. Then, the solution was shaken until no solid was observed.

1.4. Preparation of MPT@KB and THA@KB semisolid electrolyte

MPT@KB and THA@KB were prepared by mixing dried MPT and THA with KB at a 95:5 mass ratio, respectively. The mixtures were placed in a ball mill to grind them homogenously for 1 h under Ar atmosphere. Then, a certain amount of homogeneous mixture was transferred to a 0.5 M $TEAPF_6$/MeCN solution in a glove box. Under Ar atmosphere, the homogeneous-suspension electrolytes were prepared by stirring the suspension for 12 h and sonicating for 2 h in an ice–water bath.

1.5. Density functional theory (DFT) calculation

DFT calculations were performed using Gaussian 09W software package.[3] The geometries of redox states of MPT and THA were optimized at the B3LYP/6-31G(d) level of theory by considering the solvation effect of water. The molecular orbital plots were obtained using Gaussian View Version 5.[4]

1.6. Flow cell tests

The charge/discharge performance was tested in a flow mode cell with a BTS-4000 battery tester (Shenzhen Neware Electronics, China). Two stacked three pieces of 0.1-mm-thickness PTFE were used to adjust the electrode space. Two polar plates with serpentine flow field (active area 4 cm^2) were used as the positive and negative electrodes. A porous CG 2500 (Celgard LLC, USA) was used as a separator. The suspension electrolytes were pumped through the electrodes space using a BT100-2J peristaltic pump (Longer Precision Pump Co., Ltd, China) at a flow rate of 20 mL min^{-1}. At the same time, the suspension electrolytes were stirred in an electrolyte tank. The volume of electrolyte was 10 mL at each side for all the flow cell tests.

2. Supporting table and figure

Table S1 Solubility of MPT and THA in MeCN, DMC, EMC, DME, and DOL solvents.

Compounds	$S_{(MeCN)}$	$S_{(DMC)}$	$S_{(EMC)}$	$S_{(DME)}$	$S_{(DOL)}$
MPT	0.158	0.226	0.599	1.139	1.430
THA	0.010	0.027	0.027	0.071	0.094

S is the solubility, and the unit is M.

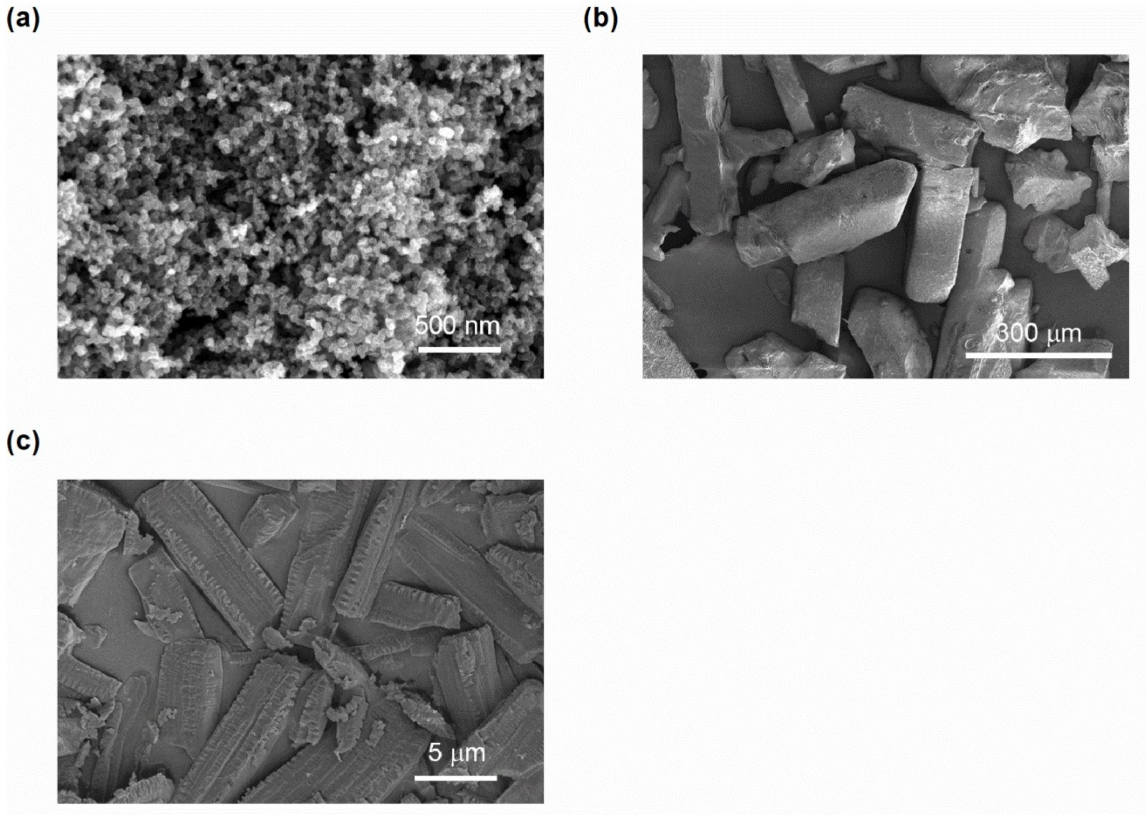

Fig. S1 The SEM images of (a) KB, (b) MPT and (c) THA.

References

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