Electronic Supplementary Information (ESI)

A bis(terpyridine)iron network polymer on carbon for a potential energy storage material

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Materials

All reagents and materials were used directly without purification. 4'-Chloro-2,2':6',2"-terpyridine (4'-Cl-tpy, 99 %) was obtained from Acros Organics. Hydrazine monohydrate (98%), 2-methyl-1-propanol (98%), and HPLC grade acetonitrile (99.8%) were from Wako Pure Chemical Industries, Ltd. Iron(II) tetrafluoroborate hexahydrate ($Fe(BF_4)_2 \cdot 6H_2O$, 97 %) was from Sigma-Aldrich, and 3 mm diameter glassy carbon rods were purchased from Tokai Carbon Co., Ltd.

Instrument

Electrochemical experiments were conducted by an ALS 750A electrochemical analyzer (BAS. Co., Ltd.).

Experiments

Electrode preparations

The glassy carbon was sealed in a glass or Teflon tube and polished subsequently by 500, 1000, 2000 mesh sandpapers and 0.3 μm Al_2O_3. After that, the electrodes were washed by plenty of water, and then ultrasonicated by water and acetone. Finally, they were dried by air and used directly.

Synthesis of 4'-hyrazinylterpyridine:

The ligand was prepared according to a literature procedures with some alterations.[1] 4'-Chloro-2,2':6',2"-terpyridine (1.64 g, 6.2 mmol) and hydrazine monohydrate (8 mL) was dissolved in 12 mL isobutanol and heated to reflux overnight. The reaction was checked by TLC for completion. After 4'-chloroterpyridine completely reacted with hydrazine, the reaction was cooled to room temperature. 50 mL water was added, and the resulting mixture was extracted by CH_2Cl_2. The organic phase was washed by sat.

$NaCl_{(aq.)}$ and dried over $MgSO_4$. A white solid was obtained upon evaporation in 94 % yield (1.52 g).

Synthesis of bis(4'-hydrazinylterpyridine)iron(II) complex, 1:

4'-hydrazinylterpyridine (5.27 mg, 0.02 mmol) and $Fe(BF_4)\cdot 6H_2O$ (3.38 mg, 0.01 mmol) was stirred in 10 mL acetonitrile for 1 h at room temperature. The resulting purple solution is the desired complex and can be used in the following experiment without further treatment.

Electrochemical modification of the glassy carbon electrode by 1:

The solution for electromodification reaction was prepared by mixing the solution of **1** with Bu_4NBF_4 (0.33 g, 10 mmol). A glass carbon electrode was used as the working electrode, platinum electrode as counter electrode, and Ag^+/Ag electrode as reference electrode. The reaction was carried out by cyclic voltammetry from 1.5 V to −1.5 V at a scan rate of 0.2 Vs^{-1} under an air atmosphere with argon bubbling to stir the solution.

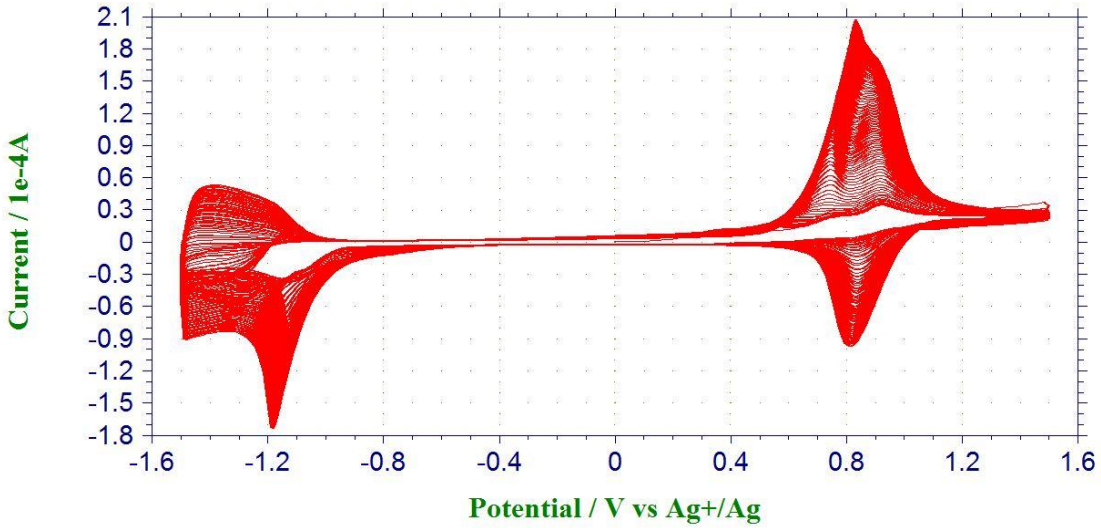

Fig. 1S. Cyclic voltammogram of electrochemical modification of the glassy carbon electrode by **1**.

Reference:

1 Z. Zhou, G. H. Sarova, S. Zhang, Z. Ou, F. T. Tat, K. M. Kadish, L. Echegoyen, D. M. Guldi, D. I. Schuster, S. R. Wilson, *Chem. Eur. J.* **2006**, *12*, 4241.