Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

Supporting information

Electrochemical Mg^{2+} intercalation into a bimetallic CuFe Prussian blue analog with aqueous electrolytes

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Experimental

CuFe-PBA was prepared by a precipitation method. An aqueous solution of 0.15 M $CuSO_4 \cdot 5H_2O$ was added dropwise to an aqueous solution of 0.1 M $K_3Fe(CN)_6$. The precipitate was centrifuged, washed with distilled water, and then dried in vacuo for 24h.

The composition was determined by the standard micro-analytical method for C, H and N elements and the coupled plasma mass spectroscopy for K, Fe and Ni elements. Calcd. for $K_{0.1}Cu[Fe(CN)_6]_{0.7} \cdot 3.6H_2O$: K, 1.39; Cu, 22.6; Fe, 13.9; C, 17.97; N, 20.96 and H, 2.59. Found: K, 1.48; Cu, 21.9; Fe, 13.4; C, 18.20; N, 19.86 and H, 2.62.

Powder X-ray diffraction (XRD) measurement was carried out on a Bruker D8 Advance using Cu Kα radiation in steps of 0.01˚ over the 2θ range of 5 – 80˚. The unit cell parameters were calculated by the least square fitting with peak top values. SEM measurement was carried out on a Carl Zeiss Supra 35.

For the electrochemical measurements, three electrode glass cells were used. CuFe-PBA was mixed homogeneously with 20 wt% acetylene black and 10 wt% polyvinylidene fluoride (PVdF) in N-methyl-2-pyrrolidone (NMP) by using a sono-horn. The resulting slurry was cast on a carbon paper and dried in vacuo for 12h. For a reference electrode, an Ag/AgCl in 3 M NaCl was used. For an electrolyte, an aqueous solution of 1 M $Mg(NO_3)_2$ was used. For a counter electrode, the pretreated CuFe-PBA electrode was used as a reversible Mg^{2+} sink. For Mg^{2+} (de)intercalation, we used a galvanostat (SD-8, Hokuto Denko), and the cut-off voltages were 0.1 V and 1.0 V (vs. Ag/AgCl). The open-circuit voltages (OCVs) were measured by repeats of flowing

galvanostatic current (current density; 18 mA/g) for 10 minutes and the potential relaxation for 30 minutes under an open-circuit state.

For ^{57}Fe Mössbauer spectroscopy, ^{57}Co in Rh was used as a Mössbauer source. The spectra were measured in the transmission mode at room temperature. The spectra were calibrated by using six lines of α-Fe, the center of which was taken as zero isomer shifts.

The X-ray absorption spectroscopy was performed using synchrotron radiation on beamline BL-7C of the Photon Factory. The synchrotron X-ray absorption spectroscopy was conducted under the approval of the Photon Factory Program Advisory Committee (Proposal 2012G110). The quantitatively Mg^{2+} intercalated/deintercalated samples were prepared by GITT, washed with water, and then dried in vacuo. The spectra were recorded in the transmission mode at room temperature under an ambient atmosphere. The X-ray energy for each edge was calibrated by using a corresponding metal foil. The obtained experimental data were analyzed using Rigaku REX2000 software.

Table S1. The fitting parameters for the Mössbauer spectra for Mg_x(CuFe-PBA).

sample	state	*IS* (mm/s)	*QS* (mm/s)	Line width (mm/s)	Fraction(%)
CuFe-PBA	LS Fe^{3+}	-0.157(1)	0.506(2)	0.339(3)	100
$Mg_{0.3}$(CuFe-PBA)	LS Fe^{2+}	-0.058(6)	0	0.67(4)	69
	LS Fe^{3+}	-0.167(9)	0.97(2)	0.38(3)	31
Mg_0(CuFe-PBA)	LS Fe^{3+}	-0.180(3)	0.941(5)	0.467(6)	100