High Voltage Aqueous Sodium-ion Battery with Prussian Blue-type Open Framework Electrodes

IMCE

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Introduction

●Advantages of aqueous sodium-ion battery

Table 1. Candidates for post lithium-ion batteries.

Electrolyte	Aqueous	Non-aqueous	Solid
Commercialized Advantage /disadvantage	Nickel metal hydride(OH⁻) High power Memory effect	Lithium-ion (Li^+) High energy density Flammable Expensive Low ionic conduction	Sodium-sulfur (Na^+) No minor metal High temperature operation (300 ºC)
Research stage	Aqueous lithium-ion (Li^+) Non-flammable High power Low energy density (low voltage)	Sodium-ion (Na^+) Room temperature operation Inexpensive Low power	
Target of this work	Aqueous sodium-ion (Na^+) Non-flammable High power Inexpensive Low energy density (low voltage)		

●Stability window of water

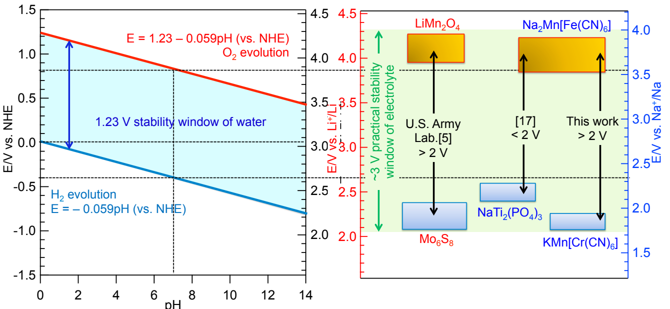

Fig. 1. Stability window of water and candidates of materials for aqueous alkali metal ion batteries.

●Reported aqueous alkali metal ion batteries

Table 2. Reported aqueous alkali metal ion batteries.

Cathode	Anode	Electrolyte	Capacity/mAh g⁻¹	Voltage/V	Ref.
$LiMn_2O_4$	VO_2	5 mol/l $LiNO_3$ aq.	50 (electrodes)	1.5	1
$LiMn_2O_4$	$LiTi_2(PO_4)_3$	1 mol/l Li_2SO_4 aq.	40 (electrodes)	1.5	2
$LiFePO_4$	$LiTi_2(PO_4)_3$	1 mol/l Li_2SO_4 aq.	55 (electrodes)	0.9	3
$LiCoO_2$	Polyimide	5 mol/l $LiNO_3$ aq.	71 (electrodes)	1.1	4
$LiMn_2O_4$	Mo_6S_8	21 mol/kg LiTFSA aq.	47 (electrodes)	2.0	5
$LiMn_2O_4$	TiO_2	21 mol/kg LiTFSA + 7 mol/kg LiOTf aq.	48 (electrodes)	2.1	6
$LiCoO_2$	$Li_4Ti_5O_{12}$	20 mol/kg LiTFSA + 8 mol/kg LiBETA aq.	55 (electrodes)	2.4	7
$LiNi_{0.5}Mn_{1.5}O_4$			30 (electrodes)	3.0	
$LiMn_2O_4$	S_8	21 mol/kg LiTFSA + 7 mol/kg LiOTf aq. + 10 wt% PVA	84 (electrodes) 1327 (anode)	1.6	8
λ-MnO_2	Active carbon	1 mol/l Na_2SO_4 aq.	50 (electrolyte)	1.2	9
$NaVPO_4F$	Polyimide	5 mol/l $NaNO_3$ aq.	40 (electrodes)	1.1	4
$Na_3V_2O(PO_4)_2F$	$NaTi_2(PO_4)_3$	10 mol/l $NaClO_4$ aq.	40 (cathode)	1.4	10
$Na_4Mn_9O_{18}$	$NaTi_2(PO_4)_3$	1 mol/l Na_2SO_4 aq.	100 (anode)	1.0	11
$Na_2FeP_2O_7$	$NaTi_2(PO_4)_3$	4 mol/l $NaClO_4$ aq.	48 (cathode)	0.9	12
$Na_2Ni[Fe(CN)_6]$	$NaTi_2(PO_4)_3$	1 mol/l Na_2SO_4 aq.	100 (anode)	1.3	13
$Na_2Cu[Fe(CN)_6]$	$NaTi_2(PO_4)_3$	1 mol/l Na_2SO_4 aq.	102 (anode)	1.4	14
$NaCr[Mn(CN)_6]$	$Na_2Mn[Mn(CN)_6]$	10 mol/l $NaClO_4$ aq.	28 (electrodes)	1.0	15
$Na_2Co[Fe(CN)_6]$	$NaTi_2(PO_4)_3$	1 mol/l Na_2SO_4 aq.	120 (cathode)	1.6	16
$Na_2Mn[Fe(CN)_6]$	$NaTi_2(PO_4)_3$	17 mol/kg $NaClO_4$ aq.	117 (cathode)	1.4	17
$Na_3(VOPO_4)_2F$	$NaTi_2(PO_4)_3$	35 mol/kg NaFSA aq.	ND	1.5	18
$Na_2[Mn_3Ti]O_6$	$NaTi_2(PO_4)_3$	9 mol/kg NaOTf aq.	31 (electrodes)	1.0	19
$Na_2Mn[Fe(CN)_6]$	$KMn[Cr(CN)_6]$	17 mol/kg $NaClO_4$ aq.	111 (cathode)	> 2	This work

Aqueous sodium-ion battery with $Na_2Mn[Fe(CN)_6]$ (sodium manganese hexacyanoferrate; NMHCF) cathode, $KMn[Cr(CN)_6]$ (potassium manganese hexacyanochromate; KMHCC) anode, and highly concentrated $NaClO_4$ aqueous electrolyte may realize high voltage operation and high cost effectiveness.

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Experimental

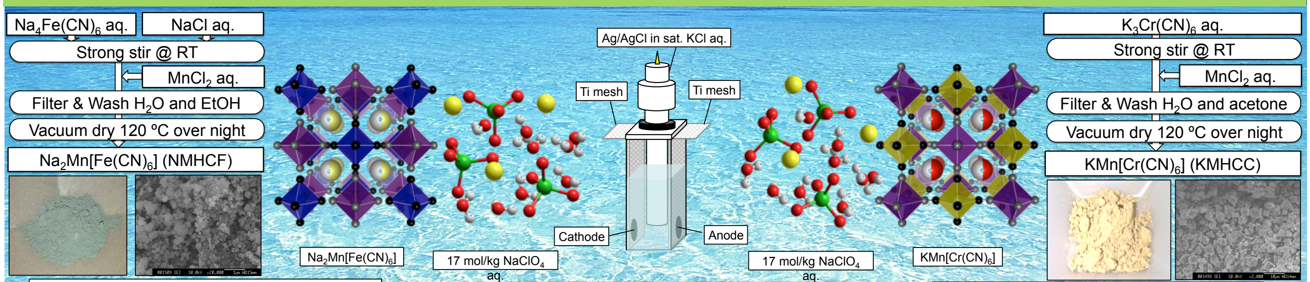

Fig. 2. Synthesis route, photo, SEM and crystal structure images of $Na_2Mn[Fe(CN)_6]$ cathode material.

Fig. 3. Configuration of 3/2 electrodes beaker-type cell with/without Ag/AgCl reference electrolode.

Fig. 4. Synthesis route, photo, SEM and crystal structure images of $KMn[Cr(CN)_6]$ anode material.

Result & Discussion

●FT-IR (ATR)

●Ionic conductivity

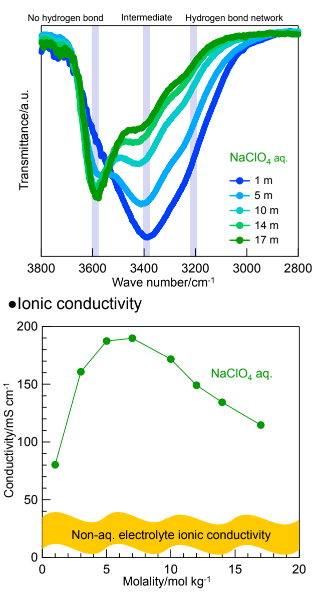

Fig. 5. (upper) FT-IR/ATR spectra and (lower) ionic conductivities of $NaClO_4$ aq. dependence on concentration.

●CV of Ti current collector

●CV of active materials

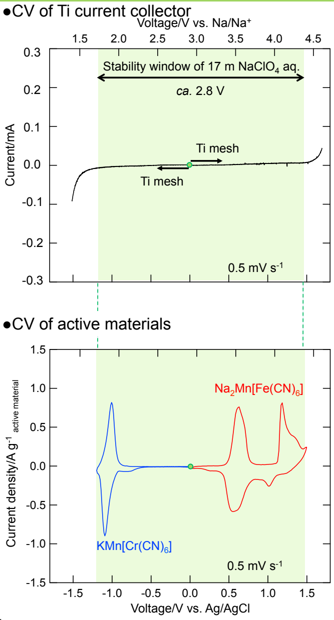

Fig. 6. Cyclicvoltammogram of (upper) Ti mesh current collector, (lower) NMHCF cathode, and KMHCC anode.

●Half cell

●Full cell

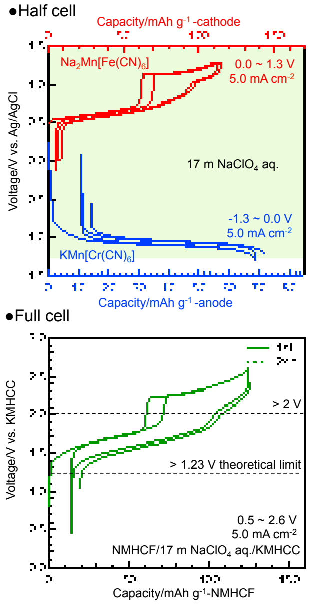

Fig. 7. Charge/discharge curves of (upper) NMHCF cathode, KMHCC anode half cells, and (lower) its full cell.

●Cyclability

●Rate capability

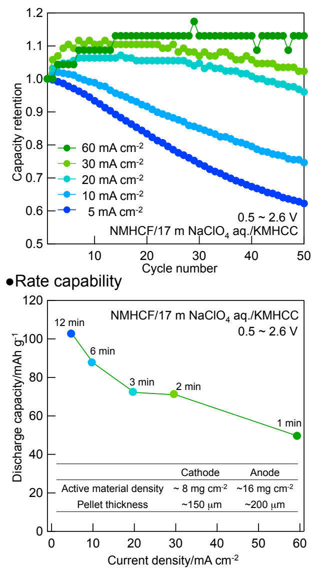

Fig. 6. (upper) Cyclabilities and (lower) rate capability of NMHCF/17 mol kg⁻¹ $NaClO_4$ aq./KMHCC full cell.

Highly concentrated $NaClO_4$ aqueous electrolyte differs from diluted in terms of interaction between Na^+ and H_2O, ionic conductivity, and electrochemical stability.

NMHCF/17 m $NaClO_4$ aq./KMHCC aqueous sodium-ion battery operated at high voltate over 2 V with remarkable high rate performance.

Conclusion

A combination of Prussian blue-type $Na_2Mn[Fe(CN)_6]$ cathode and $KMn[Cr(CN)_6]$ anode was examined as aqueous sodium-ion battery. The battery displayed high operation voltage over 2 V and remarkable high rate performance assisted by open-framework electrodes and concentrated but high ionic conductive electrolyte.