

Electrolyte

Commercialized

/disadvantage

Research stage

1.5

1.0

0.5

뿔

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ģ 0.0

-0.5

-10

-1.5

Transmittance/a.u

3800

200

150

100 ja

50

0 **`** 

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Condue

0

## High Voltage Aqueous Sodium-ion Battery with Prussian Blue-type Open Framework Electrodes Kosuke Nakamoto<sup>1</sup>, Yuki Sawada<sup>2</sup>, Ryo Sakamoto<sup>2</sup>, Masato Ito<sup>1</sup>, Shigeto Okada<sup>1</sup>

Solid

Sodium-sulfur (Na+)

High temperature operation (300 °C)

No minor n

Sodium-ion (Na<sup>+</sup>)

rature o pensive

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Cathode

LiMn<sub>2</sub>O<sub>4</sub>

LiMn<sub>2</sub>O

LiFePO,

LiCoO,

LiMn<sub>2</sub>O<sub>4</sub>

LiMn<sub>2</sub>O<sub>4</sub>

Reported aqueous alkali metal ion batteries
Table 2. Reported aqueous alkali metal ion batteries.

Electrolyte

5 mol/l LiNO3 aq.

1 mol/l Li<sub>2</sub>SO<sub>4</sub> aq.

1 mol/l Li2SO4 aq.

5 mol/l LiNO<sub>2</sub> ag

21 mol/kg LiTFSA aq.

21 mol/kg LiTESA

Anode

VO<sub>2</sub>

LiTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>

LiTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>

Polyimide

MosS

TiO<sub>2</sub>



Ref

2

3

4

5

6

7

8

9

4

10

11

12

13

14

15

16

17

18

19

This

work

40 50

~200 µm

50 60

1.5

1.5

0.9

1.1

2.0

2.1

Capacity/mAh g-1 Voltage/V

50 (electrodes)

40 (electrodes)

55 (electrodes)

71 (electrodes)

47 (electrodes)

48 (electrodes)



Table 1. Candidates for post lithium-ion batteries.

Non-aqueous

Lithium-ion (Li+)

High energy density

Flammable

Low ionic conduction

Bor

Aqueous

Nickel metal hydride(OH-)

High power Memory effect

Aqueous lithium-ion (Li+)

Non-flam

## + 7 mol/kg LiOTf aq Low energy density (low voltage) Low power LiCoO<sub>2</sub> 20 mol/kg LiTFSA 55 (electrodes) 2.4 Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> Aqueous sodium-ion (Na+) LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> 8 mol/kg LiBETA aq 3.0 30 (electrodes) Non-flammable Target of this work 21 mol/kg LiTFSA High power 84 (electrodes) 1327 (anode) LiMn<sub>2</sub>O<sub>4</sub> S, + 7 mol/kg LiOTf aq. 1.6 Low energy density (low voltage) + 10 wt% PVA Stability window of water 1.2 λ-MnO Active carbon 1 mol/l Na<sub>2</sub>SO<sub>4</sub> ag 50 (electrolyte) 4.5 NaVPO<sub>4</sub>F 5 mol/l NaNO3 aq. 1.1 LiMn<sub>2</sub>O Na<sub>2</sub>Mn[Fe(CN)<sub>6</sub>] Polyimide 40 (electrodes) 9pH (vs. NHE) O<sub>2</sub> evolution 1 NaTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> 10 mol/l NaClO<sub>4</sub> aq. Na<sub>3</sub>V<sub>2</sub>O(PO<sub>4</sub>)<sub>2</sub>F 40 (cathode) 1.4 40 Na4Mn9O18 NaTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> 1 mol/l Na2SO4 aq. 100 (anode) 1.0 Na<sub>2</sub>FeP<sub>2</sub>O<sub>7</sub> NaTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> 4 mol/l NaClO<sub>4</sub> aq. 48 (cathode) 0.9 3.5\_1 1.23 V stabili indow of wate This 1 mol/l Na<sub>2</sub>SO<sub>4</sub> ag. U.S. Army [17] < 2 V Na<sub>2</sub>Ni[Fe(CN)<sub>6</sub>] NaTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> 100 (anode) 1.3 Lab.[5] 3.083.0 1 mol/l Na<sub>2</sub>SO<sub>4</sub> aq. Na<sub>2</sub>Cu[Fe(CN)<sub>6</sub>] NaTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> 102 (anode) 1.4 > 2 V NaCr[Mn(CN)<sub>6</sub>] Na<sub>2</sub>Mn[Mn(CN)<sub>6</sub>] 10 mol/l NaClO4 ag. 28 (electrodes) 1.0 2.5 2.5 NaTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> 1 mol/l Na2SO4 aq. Na2Co[Fe(CN)6] 120 (cathode) 1.6 0.059pH (vs. N 20 NaTi<sub>2</sub>(PO<sub>4</sub>) 117 (cathode) Na2Mn[Fe(CN)6] NaTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> 17 mol/kg NaClO<sub>4</sub> aq 1.4 2.0 2.0 KMn[Cr(CN)<sub>6</sub>] Na<sub>3</sub>(VOPO<sub>4</sub>)<sub>2</sub>F NaTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> 35 mol/kg NaFSA aq. ND 1.5 1.5 Na<sub>2</sub>[Mn<sub>2</sub>Ti]O<sub>6</sub> NaTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> 9 mol/kg NaOTf aq. 31 (electrodes) 1.0 4 2 10 12 6 8 14 Fig. 1. Stability window of water and candidates of materials for aqueous alkali metal ion batteries 17 mol/kg NaClO<sub>4</sub> aq. > 2 Na<sub>2</sub>Mn[Fe(CN)<sub>6</sub>] KMn[Cr(CN)6] 111 (cathode) Aqueous sodium-ion battery with Na2Mn[Fe(CN)6] (sodium manganese hexacyanoferrate; NMHCF) cathode, KMn[Cr(CN)6] (potassium manganese hexacyanochromate; KMHCC) anode, and highly concentrated NaClO4 aqueous electrolyte may realize high voltage operation and high cost effectiveness. [1] W. Li, et al., Science, 264 (1994) 1115. [2] J.Y. Luo, et al., Adv. Funct. Mater. 17 (2007) 3877. [5] L. Suo, et al., Science, 360 (2015) 383. [6] L. Suo, et al., Angew. Chemie., 55 (2016) 7136. [9] J. Whitacre et al., J. Power Sources, 273 (2012) 2255. [10] P. Winar, et al., Mater. Chem. A, 32 (2015) 2271. [13] X. Wu, et al., Electrochem. Commun., 31 (2013) 145. [14] X. Wu, et al., ChemSusChem. 7 (2014) 407. [17] X. Nakamoto, et al., Electrochemstry, 58 (2017) 179. [16] K. Khinel, et al., ACS Energy Lett. 2 (2017) 2005. H. Qin, et al., J. Power Sources, 249 (2014) 367. C. Yang, et al., PNAS, 114 (2017) 6197. Y. Nakamoto, et al., J. Power Sources, 327 (2016) 327. K. N. Wu, et al., ChemNanoMat., 1 (2015) 188. J. Luo, et al., Nat. Chem., 2 (2010) 76 Y. Yamada, et al., Nat. Energy, 1 (2016) 16129. W. Wu, et al., J. Electrochem. Soc., 162 (2015) A803. M. Pasta, et al., Nat. Commun., 5 (2014) 3007. L. Suo, et al., Adv. Energy Mater., 7 (2017) 1701189. Experimental K<sub>3</sub>Cr(CN)<sub>6</sub> aq. NaCl aq Ag/AgCl in sat. KCl aq. Strong stir @ RT (III) MnCl<sub>2</sub> aq Ti mesh Cathode Anode KMn[Cr(CN)6] Na<sub>2</sub>Mn[Fe(CN)<sub>6</sub>] 17 mol/kg NaClO<sub>4</sub> 17 mol/kg NaClO<sub>4</sub> ag. SEM and crysta Fig. 3. Configuration of 3/2 electrodes beaker-type cell with/without Aa/AaCl reference electrole •CV of Ti current collector Voltage/V vs. Na/Na\* •FT-IR (ATR) Half cell Cvclability Capacity/mAh g<sup>-1</sup>-cathode 2.5 3.0 2.0 3.5 40 4.5 1.5 bility window of 17 m NaClO<sub>4</sub> aq. 0.2 ca. 2.8 V Ag/AgCI 0.1 ja 0.9 Ti mesh Intage// vs Curren 0.0 17 m NaClO, ad NaCIO, Ti mesh ₹0.8 60 mA cm -0. 30 mA cm<sup>-2</sup> 20 mA cm<sup>-2</sup> 🗕 1 m 0 0.7 10 n 10 mA cm : -0.2 - 14 m 0.6 5 mA cm <sup>1</sup>A cm<sup>-2</sup> 0.5 ~ 2.6 V NMHCF/17 m NaClO₄ aq./KMHCC - 10 • 17 m 0.5 mV s -0.3 27 30 17 52 (D) 0.5 3600 3400 3200 3000 2800 47 77 52 a 10 20 30 Cvcle number Wave number/cm hAh α<sup>−1</sup> -anode Full cell Rate capability Ionic conductivity CV of active materials 120 11 NMHCF/17 m NaClO4 aq./KMHCC 12 1 0.5 ~ 2.6 V \_ 100 1.0 CN)。 KMHCC NaClO<sub>4</sub> ad > 2 ' 80 ctive 0.5 ٧S. capac densitv/A a<sup>-1</sup> 60 /oltage/V 0.0 > 1.23 V theoretical limi Discharge 40 13 -0.5 Current 0.5 ~ 2.6 \ 20 5.0 mA cm<sup>-2</sup> NMHCF/17 m NaClO<sub>4</sub> aq./KMHCC -1. KMn[Cr(CN)] 150 µr 0.5 m 0 1 20 30 40 10 -1.5 Capacity/mAh g<sup>-1</sup>-NMHCF 15.0 5 10 Molality/mol kg<sup>-1</sup> 15 20 -1.5 -1.0 -0.5 0.0 0.5 1.0 1.5 Current density/mA cm-2 Voltage/V vs. Ag/AgCl Fig. 6. Cyclicvoltammogram of (upper) Ti mesh curren collector, (lower) NMHCF cathode, and KMHCC anode 5. (upper) FT-IR/ATR spectra and (lower) ionic uctivities of NaCIO4 aq. dependence on Fig. 6. (upper) Cyclabilities and (lower) rate capabil of NMHCF/17 mol kg $^{1}$ NaClO $_{4}$ aq./KMHCC full cell Fig 7 Charge/discharge KMHCC anode e curves of (upper) NMHCF half cells, and (lower) its full er) its full cell. Highly concentrated NaClO4 aqueous electrolyte differs from diluted in terms of NMHCF/17 m NaClO<sub>4</sub> aq./KMHCC aqueous sodium-ion battery operated interaction between Na<sup>+</sup> and H<sub>2</sub>O, ionic conductivity, and electrochemical stability at high voltate over 2 V with remarkable high rate performance. Conclusion A combination of Prussian blue-type Na2Mn[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.

Na<sub>4</sub>Fe(CN)<sub>6</sub> aq. Strong stir @ RT MnCl<sub>2</sub> aq. Filter & Wash H<sub>2</sub>O and EtOH Filter & Wash H<sub>2</sub>O and acetone Vacuum dry 120 °C over night Vacuum dry 120 °C over night Na2Mn[Fe(CN)6] (NMHCF) KMn[Cr(CN)<sub>e</sub>] (KMHCC) Fig. 2. Synthesis route, photo, SEM and structure images of Na<sub>2</sub>Mn[Fe(CN)<sub>6</sub>] cathode ma Fig. 4. Synthesis route, photo, SEM and crystal structure images of KMn[Cr(CN)<sub>6</sub>] anode material Result & Discussion