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

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Aqueous sodium-ion batteries have attracted much attention, because it has 3 big advantages, the non-flammability, high ionic conductivity and low cost. In addition, water is ideal solvent that can dissolve various salts in large amount. However, there is a severe restriction as electrolyte in the selection of the cathode and anode active materials, because of the narrow electrochemical window of water.

3 years ago, the expansion of the working voltage in high concentrated aqueous Li-ion battery has been first reported by U.S. Army Research Laboratory [1], which effectively prevents the electrolysis of water. Recently, even in 17 mol/kg $NaClO_4$ high concentrated aqueous sodium-ion battery with Prussian blue-type $Na_2Mn[Fe(CN)_6]$ (Sodium Manganese Hexacyanoferrate; NMHCF) cathode and NASICON-type $NaTi_2(PO_4)_3$ (Sodium Titanium Phosphate; NTP) anode, we also successfully realized high voltage (~2 V) discharge [2]. However, the width of the electrochemical window of 17 mol/kg $NaClO_4$ aq. electrolyte is 3 V totally, and there is still a room to raise the discharge voltage by 1 V in maximum.

Especially Prussian blue-type $KMn[Cr(CN)_6]$ (Potassium Manganese Hexacyanochromate; KMHCC) is very suitable anode active material for the concentrated aq. Na-ion battery, because it has lower voltage plateau than NTP anode, and locates just above the lower limit of the expanded electrochemical window of 17 mol/kg $NaClO_4$ aq. electrolyte. Herein, as a first high voltage aq. Na-ion battery over 2 V, the concentrated aq. Na-ion battery with inexpensive Prussian blue-type open framework NMHCF cathode and KMHCC anode is introduced.

NMHCF cathode and KMHCC anode materials were obtained by co-precipitating method. By ICP-AES and TGA, the chemical compositions and theoretical capacities were determined roughly as $Na_{1.24}Mn[Fe(CN)_6]_{0.81}\cdot 1.28H_2O$ and 120 mAh/g, and $K_{0.01}Mn[Cr(CN)_6]_{0.72}\cdot 2.01H_2O$ and 80 mAh/g, respectively. Both NMHCF and KMHCC were mixed with acetylene black in a weight ratio of active material/AB = 70/25, respectively. The cathode and anode pellets were fabricated with 5 wt % of polytetrafluoroethylene binder and punched into disks, and then these pellets were sandwiched by titanium mesh. A two-electrode cell (full cell) with aqueous electrolyte was used for the galvanostatic charge/discharge test. The cathode/anode weight balance in the ion-type cell was 1:2, and the cathode/anode capacity balance is approximately 1:1.3 based on the theoretical capacities.

Figure 1 shows the charge/discharge profiles of NMHCF//KMHCC full cell in 17 mol/kg $NaClO_4$ aq. at the rate of 5 mA/cm^2. The full-cell showed the reversible behavior within 0.5 ~ 2.6 V operation range. To the best of our knowledge, it is the highest discharge voltage among the aqueous Na-ion battery.

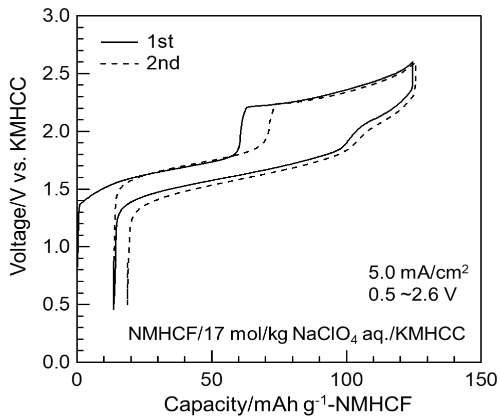

Fig. 1 Charge/discharge profiles of NMHCF//KMHCC full cell with 17 mol/kg $NaClO_4$ aq. electrolyte.

References

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