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$NaFe_{0.5}Mn_{0.5}PO_4$–Ge electrochemical system for sodium-ion batteries

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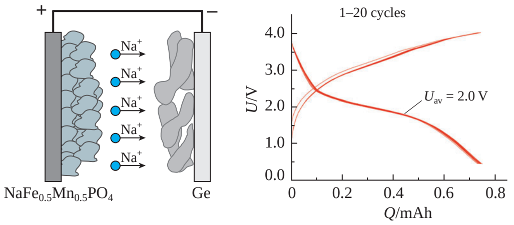
A new electrochemical system for sodium-ion batteries, sodium iron-manganese phosphate–germanium nanowires, has been developed and tested. The laboratory batteries possessed an average discharge voltage of ~2.0 V and an energy density based on the weight of active materials to 210 Wh kg^{-1}.



Keywords: sodium-ion battery, germanium, sodium iron-manganese phosphate, nanowire, charge–discharge curves, energy density.

Sodium-ion batteries are the main chemical power sources of the so-called ‘post-lithium era’.[1–3] The advantages of sodium-ion batteries are the wide occurrence and relatively low price of sodium raw materials as well as higher stability and safety. Hard carbon is the best material for anodes in these batteries, while the choice of the best material for cathodes is still debatable.[4] Layered oxides and certain compounds with polyanions were mentioned among the cathodic materials.[5–18]

Germanium-based nanostructured materials can compete with hard carbon in negative electrodes of sodium-ion batteries.[19,20] Germanium nanowire electrodes demonstrated specific capacity for sodium reversible insertion about 590 mAh g^{-1}, which is twice the capacity of hard carbon.

In this work, we manufactured negative electrodes in accordance with a published procedure[19,21] *via* the electrolysis of an aqueous solution of a Ge^{IV} complex using a titanium substrate with indium seeds.[†] The active material of positive electrodes, maricite-type $NaFe_{0.5}Mn_{0.5}PO_4$/C, was synthesized according to Kapaev *et al.*[23] using a Pechini approach and a solid-state method.[‡] Three-electrode laboratory cells were manufactured according to a procedure described previously[24] with changing sodium reference and auxiliary electrodes for lithium ones.[§]

According to the results of X-ray diffraction (XRD) analysis, the $NaFe_{0.5}Mn_{0.5}PO_4$/C sample was a single crystalline phase with a structure of maricite, space group *Pnma* [Figure 1(*a*)]. The size of coherent scattering regions was ~40 nm. According to electron microscopy data, the $NaFe_{0.5}Mn_{0.5}PO_4$ materials were agglomerated particles 100 nm in size with a uniform distribution of Na, Fe, Mn, and P [Figure 1(*b*)]. The carbon content of the resulting composites was 14–16 wt%, and the carbon was X-ray amorphous.

Figure 2 shows charge–discharge curves for electrodes made of $NaFe_{0.5}Mn_{0.5}PO_4$/C [Figure 2(*a*)] and germanium nanowires [Figure 2(*b*)] taken in the above three-electrode cells. The shape of a curve during the first anodic polarization (sodium extraction) differed significantly from those in the subsequent cycles [see

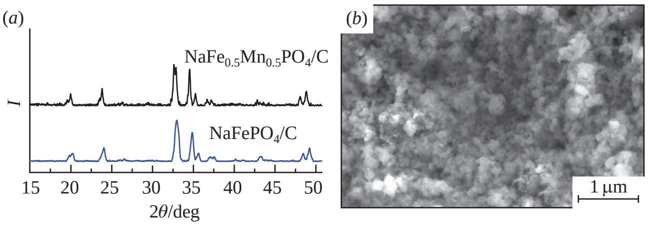


Figure 1 (*a*) XRD pattern and (*b*) SEM image of $NaFe_{0.5}Mn_{0.5}PO_4$/C.

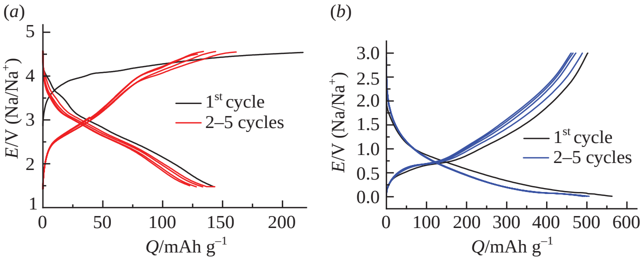


Figure 2 Charge–discharge curves (*a*) for the electrodes made of $NaFe_{0.5}Mn_{0.5}PO_4$/C with a current density of 15 mA g^{-1} and (*b*) for the electrodes of germanium nanowires with a current density of 50 mA g^{-1}.

[†] After the application of In, the substrates were annealed in vacuum. The plating solution contained GeO_2 (0.05 M), K_2SO_4 (0.5 M) as a supporting electrolyte, and succinic acid (0.5 M) as a buffering and complexing additive. The deposition was performed at 90 °C at a potential of –1.3 V (SCE) in accordance with a published plating procedure.[22]

[‡] $Fe(NO_3)_3 \cdot 9H_2O$, $Mn(OAc)_2$, $NaH_2PO_4 \cdot 2H_2O$, and citric acid were dissolved in ethylene glycol in a molar ratio of 1 : 1 : 1 : 2. Then, the solution was heated to form a polymer matrix. The final stages were annealing in air (300 °C) and argon (600 °C).

[§] A laboratory cell with a nominal capacity of about 0.85 mAh contained separated positive and negative electrodes. The surface area of each electrode was 6 cm^2. The loadings of active materials per 1 cm^2 were 0.23 and 1.0 mg for negative and positive electrodes, respectively, according to specific capacities of the materials.

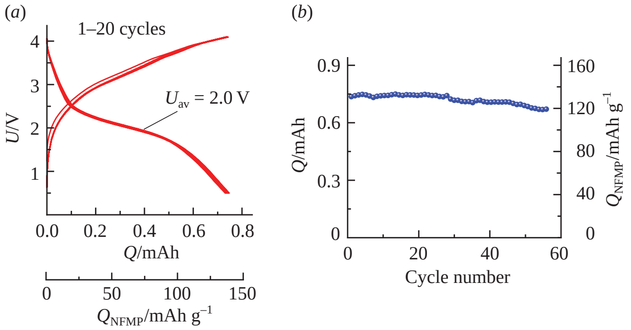


Figure 3 (*a*) Charge–discharge curves and (*b*) changes of discharge capacity upon cycling the laboratory sodium-ion battery (cycling current, 0.07 mA).

Figure 2(*a*)]. A similar picture was observed for sodium iron phosphate.[25] The discharge capacity of the $NaFe_{0.5}Mn_{0.5}PO_4/C$ electrode in the first cycle was 142 mAh g^{-1}, and it did almost not decrease in the course of cycling. The discharge (anode) capacity of germanium was about 500 mAh g^{-1}. The average discharge potentials for $NaFe_{0.5}Mn_{0.5}PO_4/C$ and germanium nanowires were about 2.6 and 0.55 V, respectively.

Figure 3 shows the results of cycling a laboratory sodium-ion battery. The average discharge voltage of the sodium-ion battery was about 2 V, and the discharge curve had a well-defined plateau. The discharge capacity of the battery was about 0.83 mAh (83% of the nominal capacity). Cycling degradation was about 0.15% per cycle.

The theoretical energy density of a sodium-ion battery of the $NaFe_{0.5}Mn_{0.5}PO_4/C$–Ge system, based on the weight of active materials, was about 310 Wh kg^{-1}. Actually, a laboratory battery with the $Na_{2/3}Ni_{1/3}Mn_{2/3}O_2$–Sb electrochemical system[26] demonstrated an energy density of ~100 Wh kg^{-1}. Oh *et al.*[27] described a laboratory battery with the $Na[Ni_{0.25}Fe_{0.5}Mn_{0.25}]O_2$−$Fe_3O_4$ system with an energy density of ~120 Wh kg^{-1}. It was reported that CNRS and RS2E have launched the first commercial cylindrical 18650 sodium-ion batteries with an energy density of 90 Wh kg^{-1}.[1] The practical energy density of a laboratory sodium-ion battery in this study was 210 Wh kg^{-1}.

Thus, the proposed new electrochemical system can be considered as a promising basis for the significant improvement of sodium-ion batteries.

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