

The weird, but wonderful, maricite $\text{NaMn}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3}\text{PO}_4$

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Over a decade, energy storage has become a growing global concern as a result of increasingly steep oil prices combined with depletion of fossil fuels, and the environmental consequences of their use. This has created increasing activity around environmentally benign alternative sources of both energy generation and storage. Renewable energy, such as wind- and solar-generated electricity, has begun to penetrate the market, but these sources provide only intermittent energy. Storage systems are required to store the energy generated until it is needed by the electricity grid.

Water-based sodium batteries may have potential application as large-scale, stationary storage devices for electrical grid stabilization and load levelling. Sodium is abundant in nature, inexpensive and environmentally benign, with obvious advantages over, for example, its lithium counterpart, in terms of cost and safety. However, the ionic volume of sodium is 2.5 times larger than that of lithium, so host compounds need to have larger sites to accommodate Na^+ in the matrix. The success of MnO_2 as a cathode material for aqueous sodium battery [1] inspired the present investigation on the phosphate compound. In this work, the new mixed transition metal sodium phosphate, $\text{NaMn}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3}\text{PO}_4$ as host compound was synthesized by sol-gel and combustion approaches.

The olivine LiFePO_4 have been considered as an attractive cathode material in lithium ion batteries. Similar to olivine, substitution for lithium by sodium produces the analogue, NaFePO_4 , maricite [2]. The maricite structure is similar to the olivine structure, except that the alkali (Na) occupies the M(2) site, and the transition metal occupies the M(1) sites. To date, it has been claimed that NaFePO_4 is not viable as a cathode material for battery applications in non-aqueous media [3].

In this paper, we will present the potential applicability of this maricite cathode for plausible non-portable electrical or renewable energy storage applications using aqueous NaOH electrolyte. The maricite with mixed transition metal sodium phosphate, $\text{NaMn}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3}\text{PO}_4$ compound was obtained in pure form via sol-gel and combustion processes with the resulting products showing a smaller particle size and narrower size range yielded by the combustion method. Physical and electrochemical characterization indicates that the maricite host material electrochemically intercalates and de-intercalates sodium ions over multiple cycles in a water based NaOH electrolyte, with preservation of the maricite structure. The efficiency of this process was greater for the combustion-synthesised product, an effect that is attributed to the smaller particle size and lower diffusion barrier. To the best of our knowledge, this is the first time the reversible intercalation of sodium ions in a maricite host synthesized by non-ceramic methods has been reported. These are unexpected, but very promising results for the scientific battery community.

Figure 1 shows the galvanostatic charge – discharge characteristics of host maricite $\text{NaMn}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3}\text{PO}_4$ at a constant current density of 5 mA/cm^2 . The reported values are with respect to Hg/HgO electrode. The galvanostatic charge-discharge characteristics of a full cell ($\text{NaMn}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3}\text{PO}_4$ as cathode versus activated carbon (AC) as anode) are shown in Fig. 2, exhibiting a discharge capacity of 60 mAh/g . The cathode material is fully reversible and holds good for multiple cycles. The proposed maricite in water based sodium battery develops an important new family of energy storage devices based on an affordable, globally available element: sodium. The innovative science in this study involves reversible aqueous sodium electrochemistry at low temperature (against the available relatively high temperature at which Na is molten). The sodium energy storage technology will offer immediate advantages over existing primary battery technologies in terms of high energy density, cost, safety and environmental considerations.

References

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- [3] B. L. Ellis, W.R.M. Makahnouk, Y. Makimura, K. Toghill and L.F. Nazar, *Nat. Mater.* **6** (2007) 749.

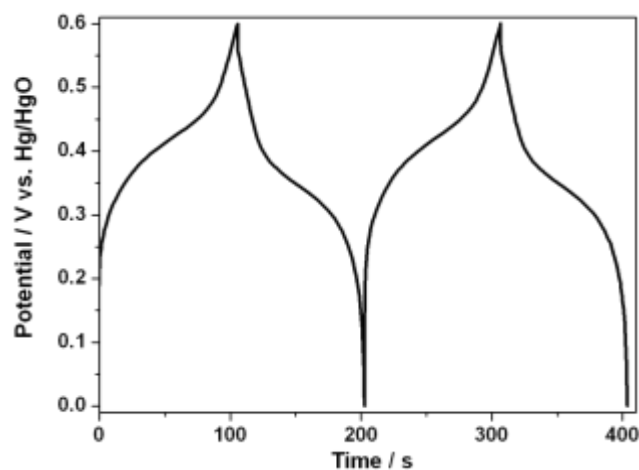


Figure 1 Galvanostatic charge-discharge cycle for $\text{NaMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{PO}_4$ at a current density of 5 mA/cm^2

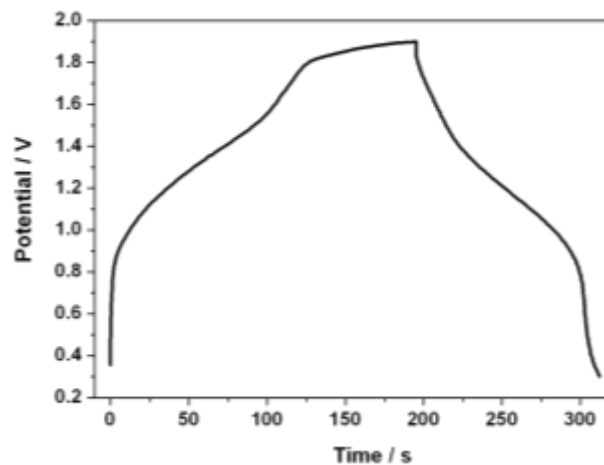


Figure 2 Galvanostatic charge-discharge cycle for AC || $\text{NaMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{PO}_4$ at a current density of 5 mA/cm^2