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$Na_2FeP_2O_7$ cathode material for aqueous sodium-ion batteries

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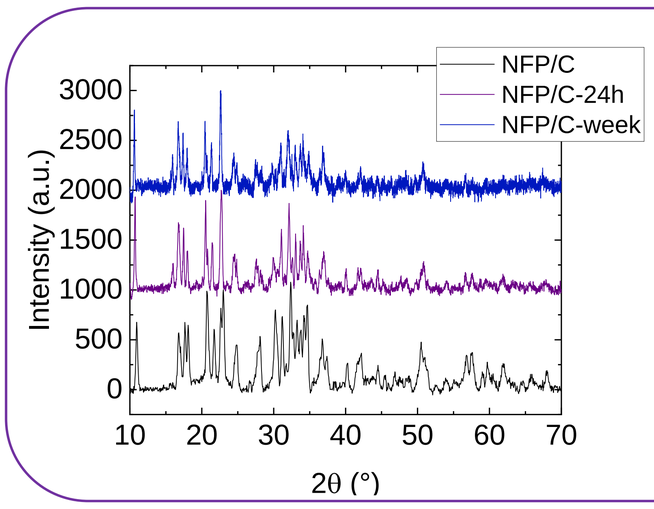
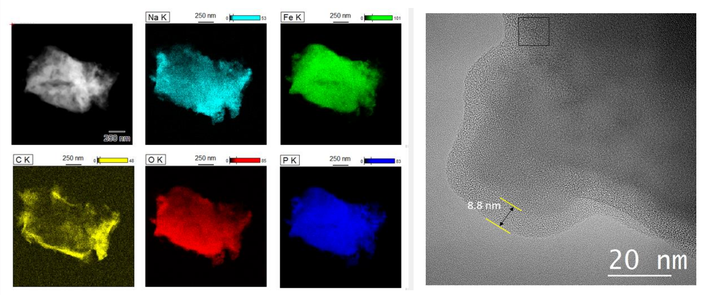
Introduction. Sodium-ion batteries have raised interest as a low cost alternative to lithium-ion batteries. In order to further reduce costs and introduce new technologies that would be safer and more environmentally friendly, batteries in which the electrolyte is water-based are being researched. Although the energy density of these batteries are not the highest, for many applications cost efficient and abundant batteries can be useful, especially for grid level energy storage. Many materials which are promising for organic sodium-ion batteries are not stable in water. $Na_2FeP_2O_7$ is one of the few sodium insertion materials, which shows very good stability in aqueous media.



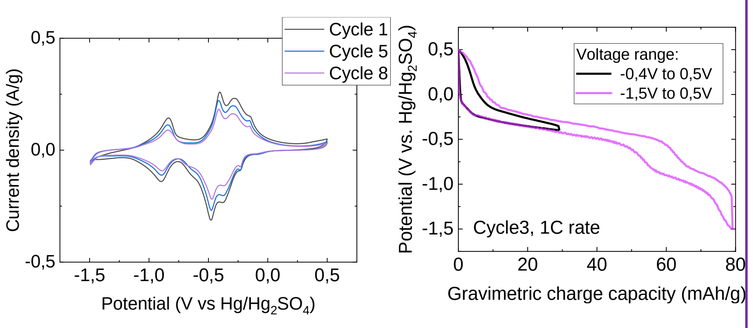
Stability of NFP/C in water was tested by immersion in water for 24h and 7 days. The XRD data of the subsequently dried samples is shown in the graph.

Results indicate that after 24 hours no significant changes in the peaks can be detected. After soaking the material in water for 24h and 7 days, most of the peaks have slightly lower intensity, but no phase impurities can be found.



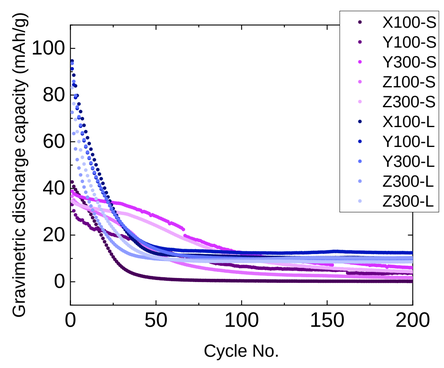
TEM analysis was done for raw $Na_2FeP_2O_7$ powder. Obtained images clearly show carbon coating with thickness fluctuating from 3 to 9 nm. Carbon coating is in part amorphous and in part graphitic.

Voltage range was determined by cyclic voltammetry (scan rate 1 mV/s). Peaks characteristic to NFP are observed – the shape of the curves is the same as in organic electrolyte [1]. Slow degradation can be observed over time. From the results it was decided to try two voltage ranges – from -1,5V to 0,5V and -0,4V to 0,5V. Charge – discharge curves for measurements in the larger voltage range show the same characteristic plateau as in organic electrolytes [2].

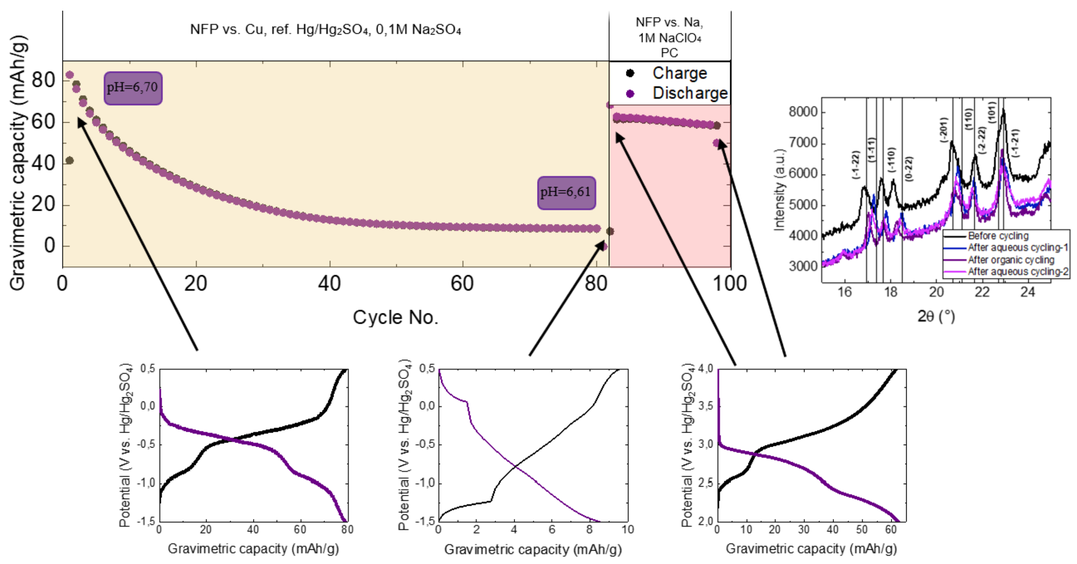


NFP was cycled at 1C in voltage range -0,4V to 0,5V and -1,5V to 0,5V. Capacity differs depending on the voltage range (close to 97 mAh/g in the wider voltage window).

Cycle life in both voltage ranges is low, albeit somewhat higher for the lower -0,4V to 0,5V range.

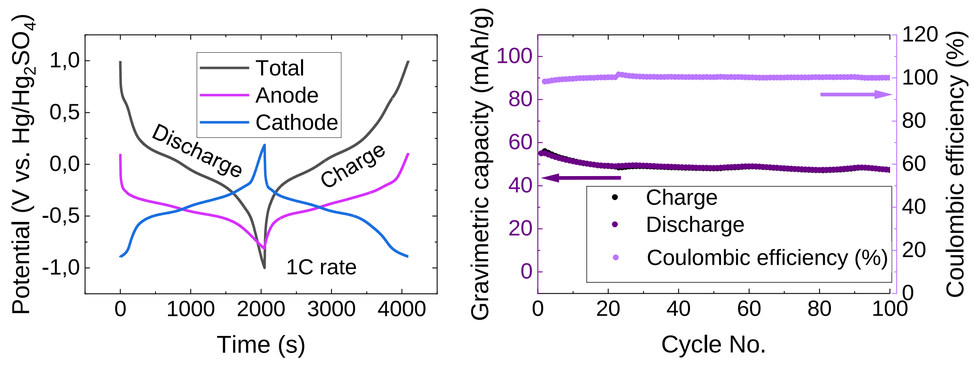


S (small) indicates voltage range from -0,4V to 0,5V and L (large) indicates voltage range from -1,5V to 0,5V, X - electrodes which were made by standard method, Y - electrodes prepared first with aluminum foil and treatment and Z - extra ball milled materials before preparation of slurry



The capacity loss for half-cells during cycling was concerning. To determine whether the rapid capacity fade is related to the measurement setup or active material, half-cells with organic electrolyte and the cycled $Na_2FeP_2O_7$ were assembled after the initial cycling. Ex-situ XRD of cycled electrodes was also performed. The higher capacity measured in the organic electrolyte setup and XRD data reveal that $Na_2FeP_2O_7$ experiences significant Na loss in the aqueous measurement setup.

Measurement setup: NFP | aq. 0,1 M Na_2SO_4 | NFP with Hg/Hg_2SO_4 reference



To better evaluate the cycle life, symmetrical $Na_2FeP_2O_7$ | $Na_2FeP_2O_7$ cell with 0,1M Na_2SO_4 electrolyte and Hg/Hg_2SO_4 reference electrode was assembled. Cycling shows initial capacity of 55 mAh/g. After 20 cycles it stabilizes and reaches approximately 50 mAh/g and stays relatively stable over 100 cycles. Charge and discharge capacity coincide with each other. From these results it can be concluded that making symmetrical cell gives much better results than using metallic copper as a counter electrode, eliminating at least some of the sodium loss observed in the $Na_2FeP_2O_7$ | Cu setup.

Conclusions. Electrochemical properties of $Na_2FeP_2O_7$/C in aqueous sodium-ion battery cells were determined and characterized. Best cyclability results are achieved in symmetrical cell rather than copper counter electrode. By experimenting with different counter electrodes and battery cell setup, it has been determined that $Na_2FeP_2O_7$ is a promising cathode material not only for organic battery systems, but also for aqueous Na-ion batteries.

References

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