Promising cathode material for sodium-ion batteries: Prussian White modified with polyaniline

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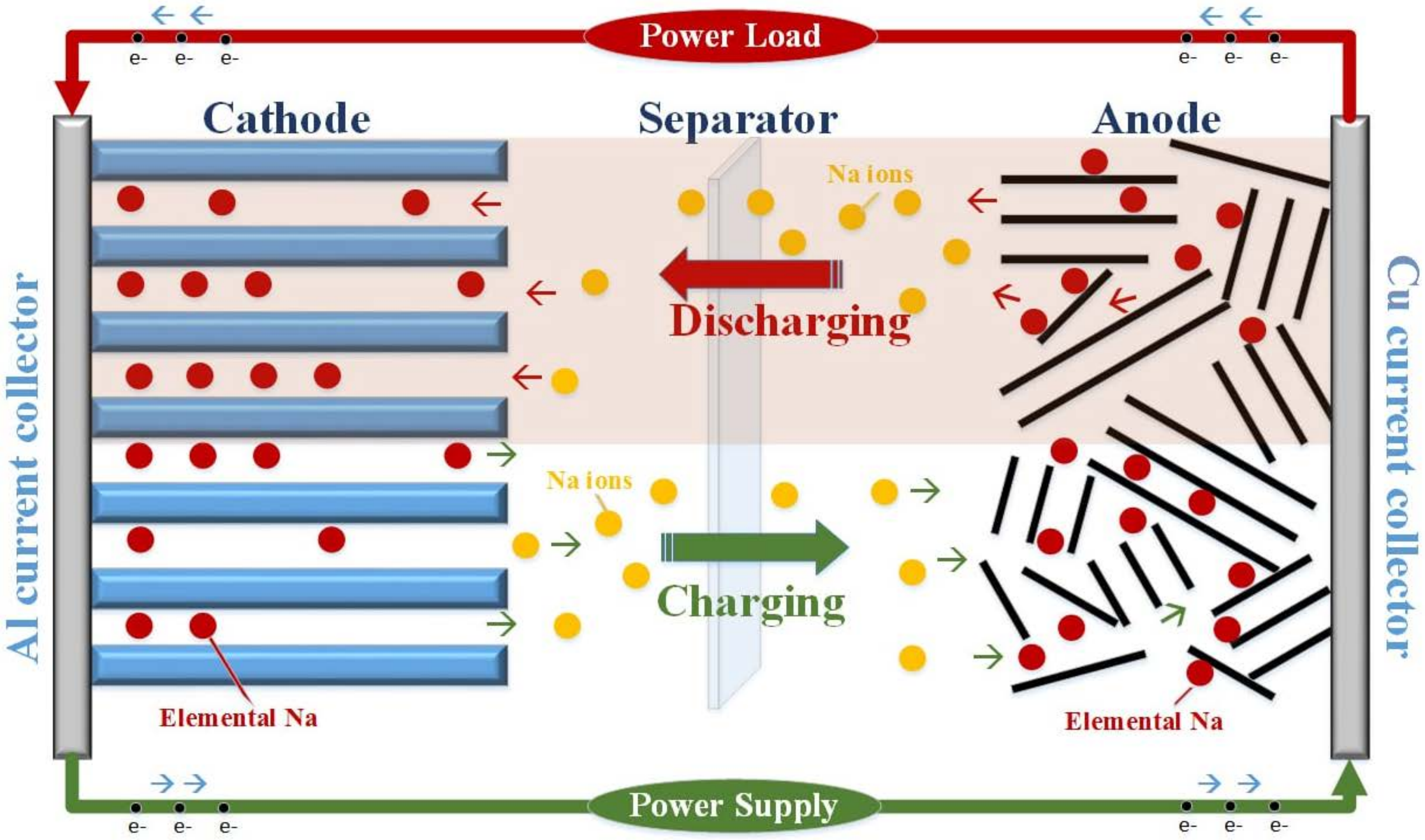
SIB operation diagram

As sodium is abundant and inexpensive compared to lithium, sodium-ion batteries (SIB) has recently regained interest within the scientific community as a promising alternative to lithium-ion battery for large-scale energy storage applications.

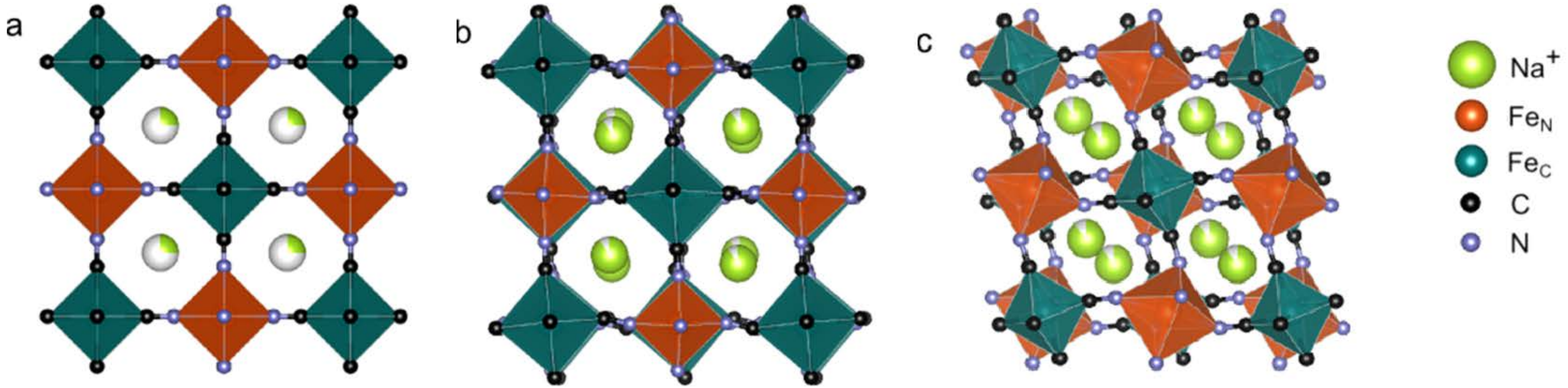


Developing efficient cathode materials is very important task for the wide distribution of the electrochemical devices, in particular SIB.

Sodium iron (II) hexacyanoferrate (II) materials

One of the perspective cathode materials for SIB is an iron (II) hexacyanoferrate (II) (Prussian White, PW) currently being produced by Altris AB, Sweden [W. Brant et al. // US Patent No: 2019/0270649 A1].

It is one of Prussian Blue Analogues $A_xM'[M(CN)_6]_{1-y}\cdot zH_2O$ (where A is an alkaline metal and M and M' are transition metal cations), the promising cathode materials for SIB due to their open framework structure and low-temperature synthesis.



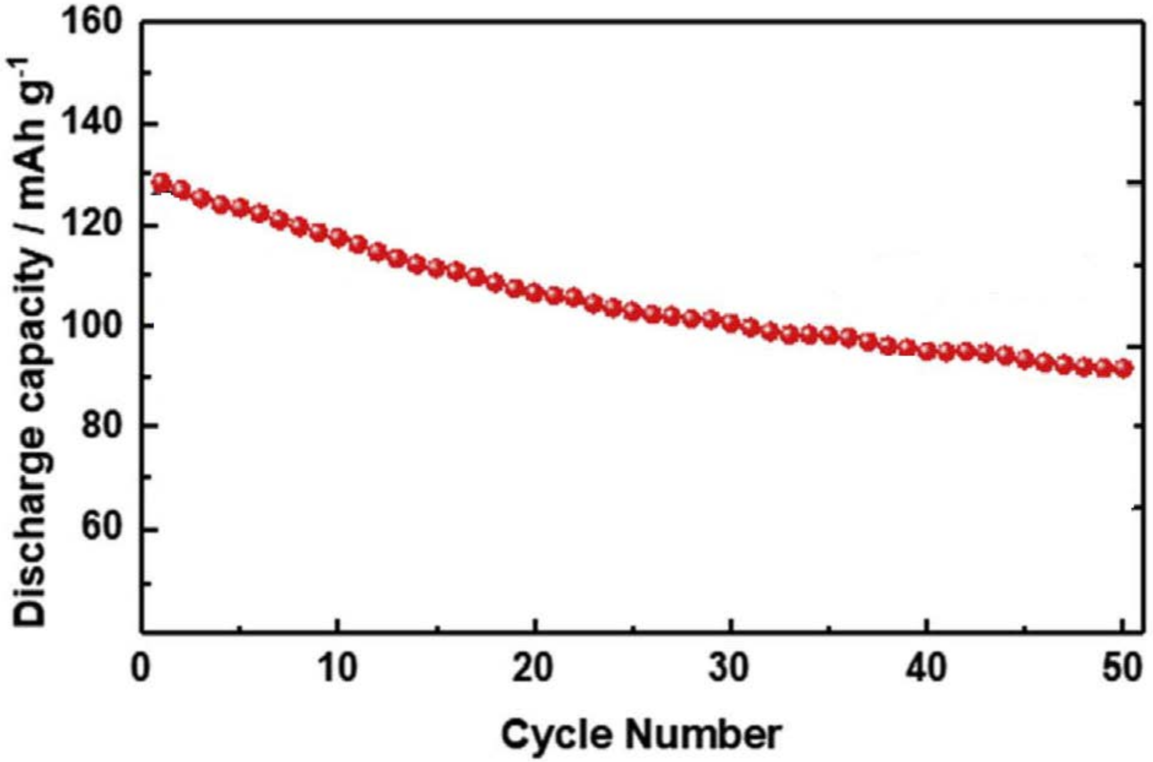
Local structures of cubic $Fm\bar{3}m$ (a), monoclinic $P2_1/n$ (b), and rhombohedral $R\bar{3}$ (c) Prussian blue analogues.

It is believed that the electrochemical capacity of the rhombohedral phase is maximal.

[W. Brant et al. // Chem. Mater. 2019, 31, 7203−7211]

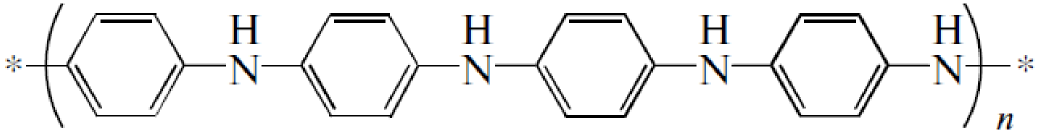
PW problem and possible solution path

One of the main problems of PW-based cathodes in SIB is the degradation processes on the surface of the active material.

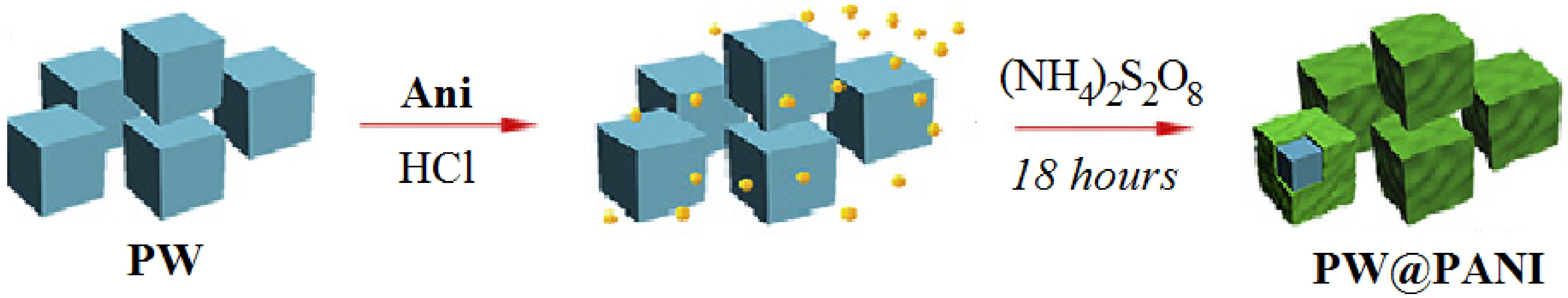


[X. Bie et al. // Journal of Power Sources 378 (2018) 322–330]

There is a hypothesis that the organic coating on the active material would lead to an improving of the rate capability and capacity retention. Our aim was to evaluate the effect of polyaniline (PANI) coating on the electrochemical properties of PW.



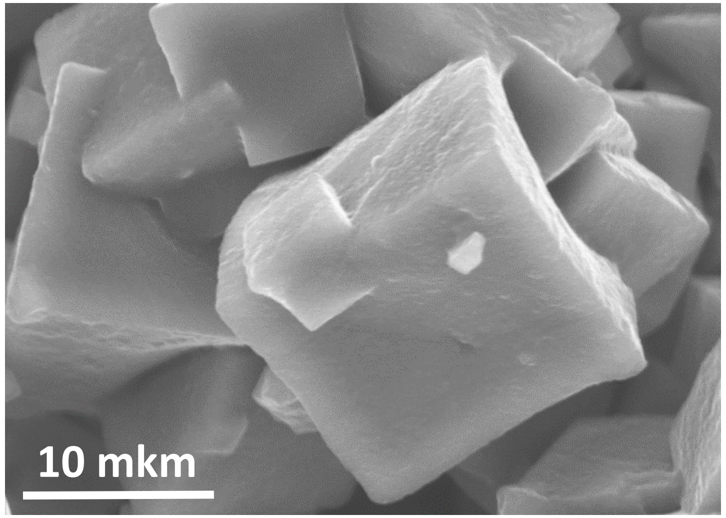
Synthesis scheme



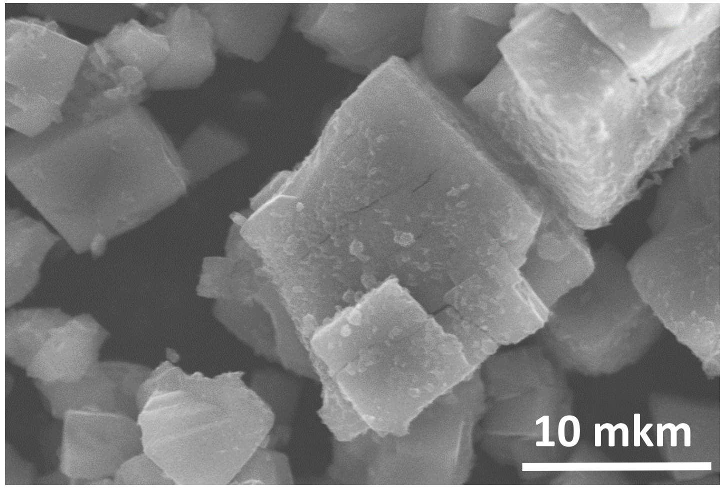
The commercial sodium iron (II) hexacyanoferrate (II) (PW) was coated with PANI via chemical oxidative polymerization according to *Zhang* methodology. It is important to note that the synthesis of polyaniline occurred in the presence of PW. Thus, the material was not a simple mixture of PW and PANI.

[L. Zhang et al. // RSC Advances (2017) V. 7, PP. 50812–50821]

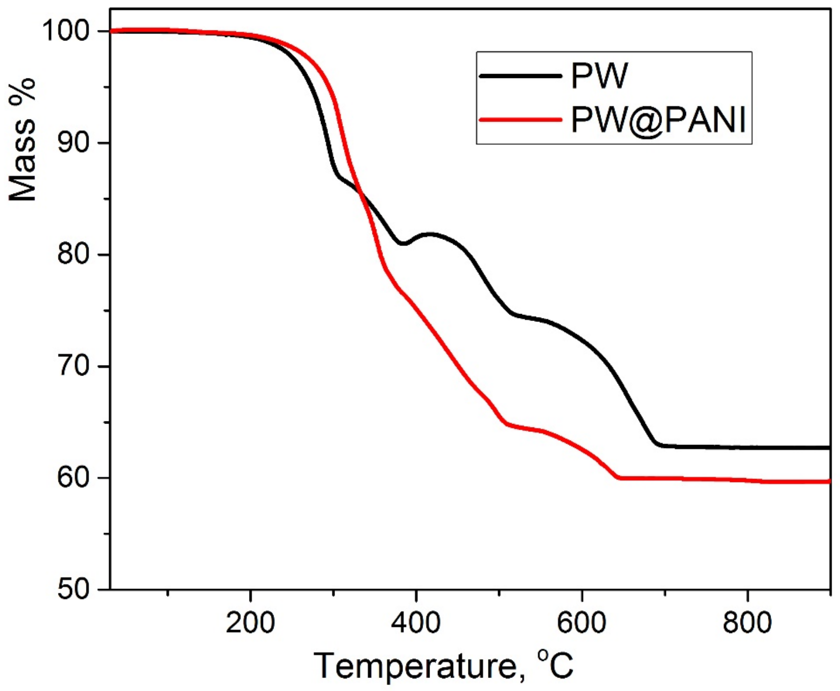
Synthesis results:



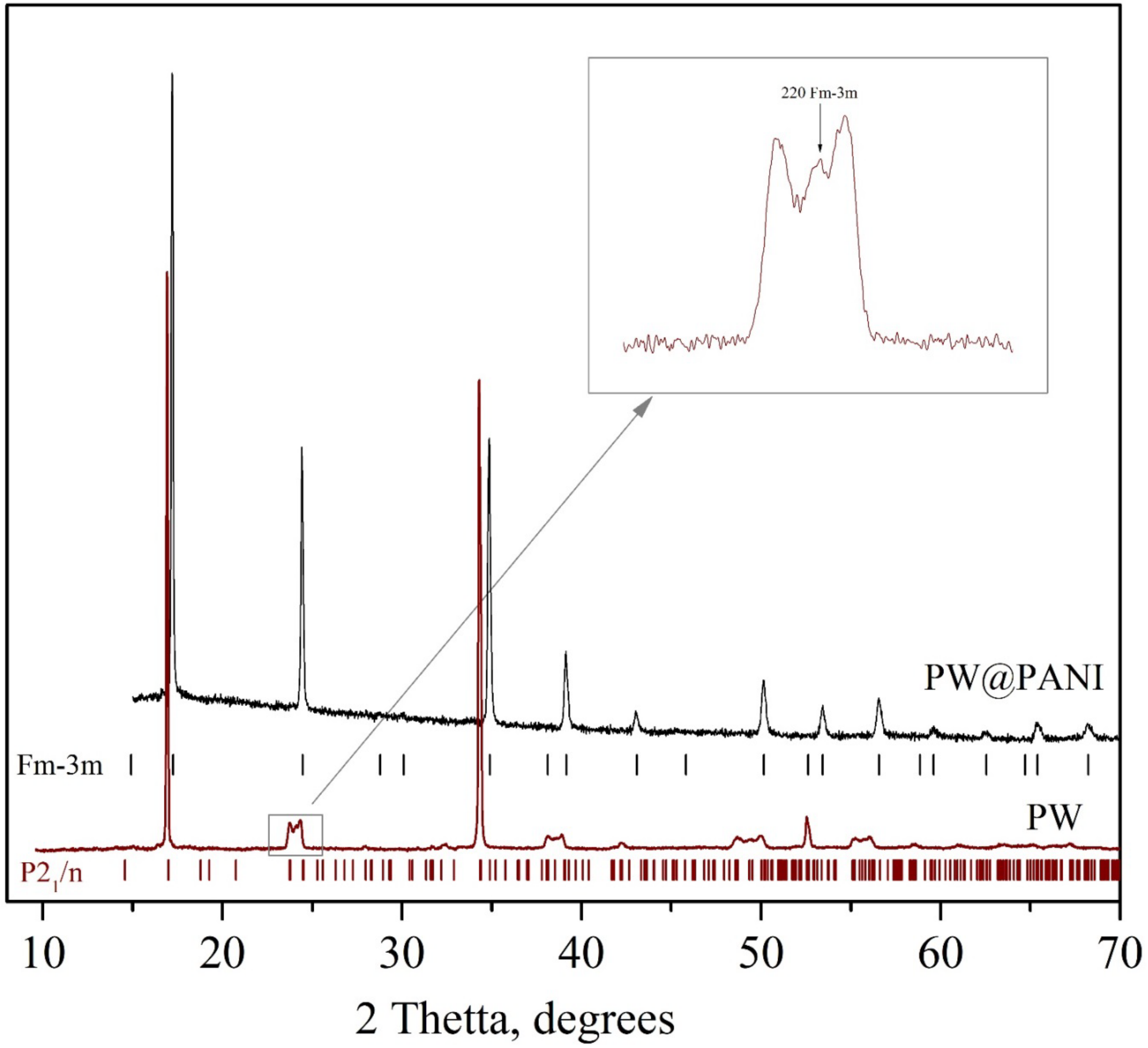
Scanning electron microscopy showed that PANI was uniformly coated on the surface of PW nanocubes.



Synthesis results



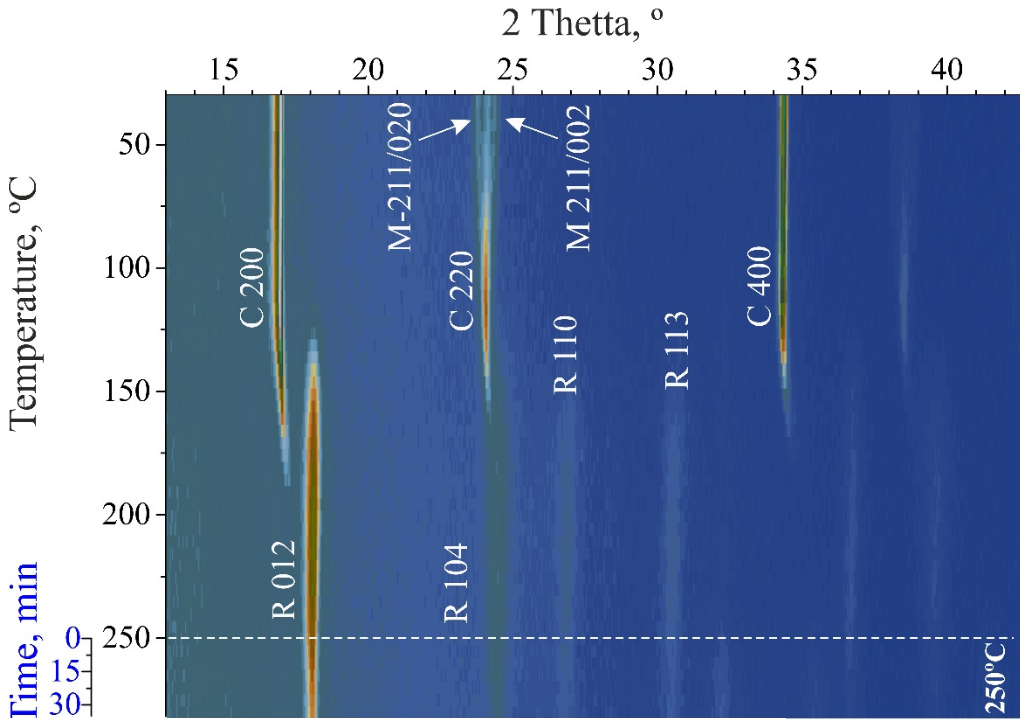
Thermogravimetric analysis showed that PANI mass fraction in PW@PANI samples is ~ 5%.

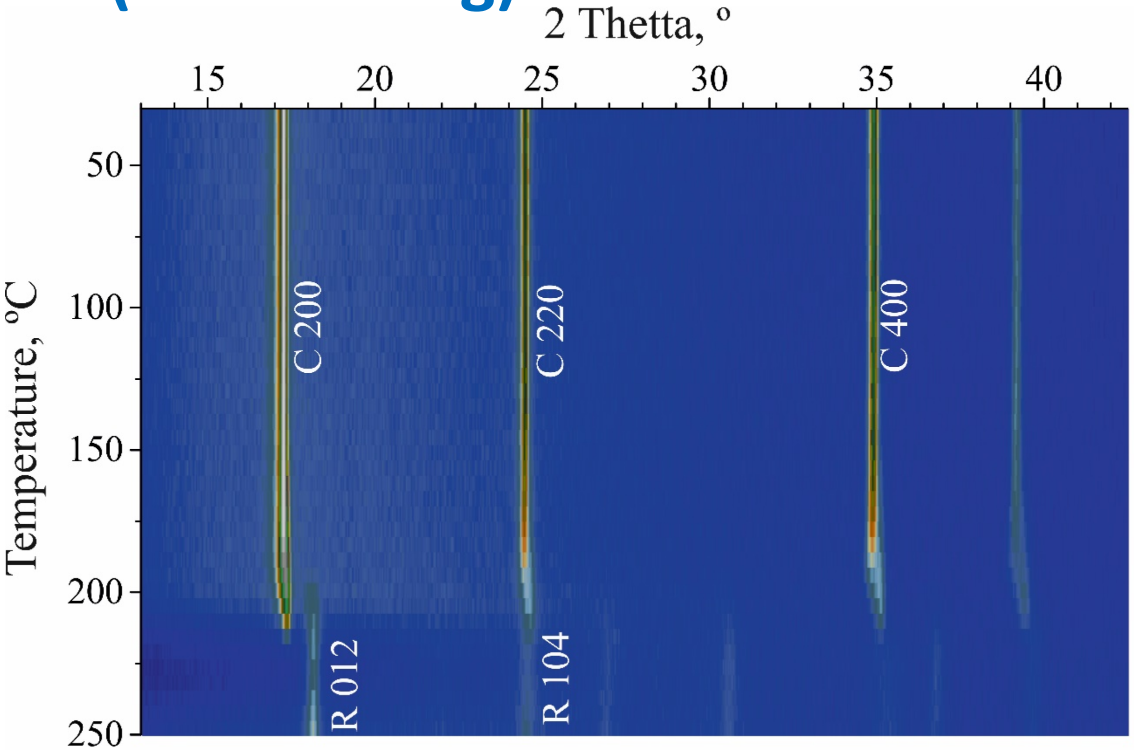


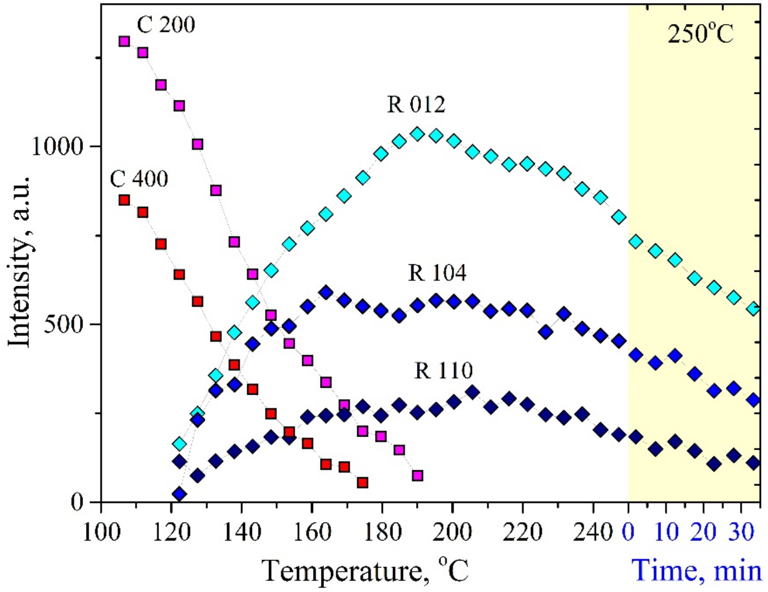
Using X-ray diffraction, it was revealed, that PANI promotes the formation of the cubic phase.

The structure of pure commercial PW material is a mixture of monoclinic and cubic phases.

In situ X-ray diffraction (PW Heating)

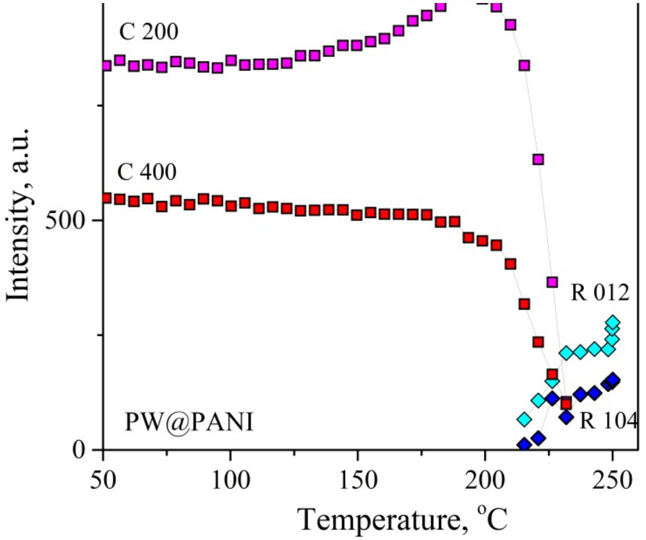






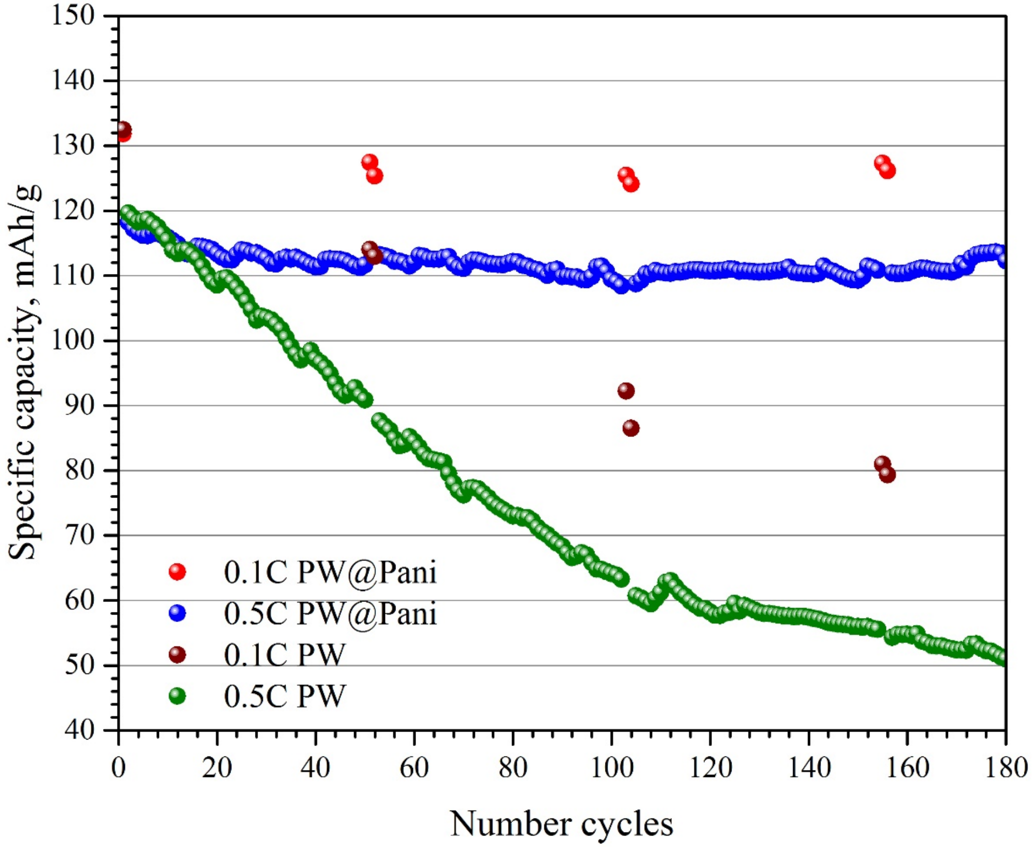
The rhombohedral phase appears at temperatures above 120 ℃

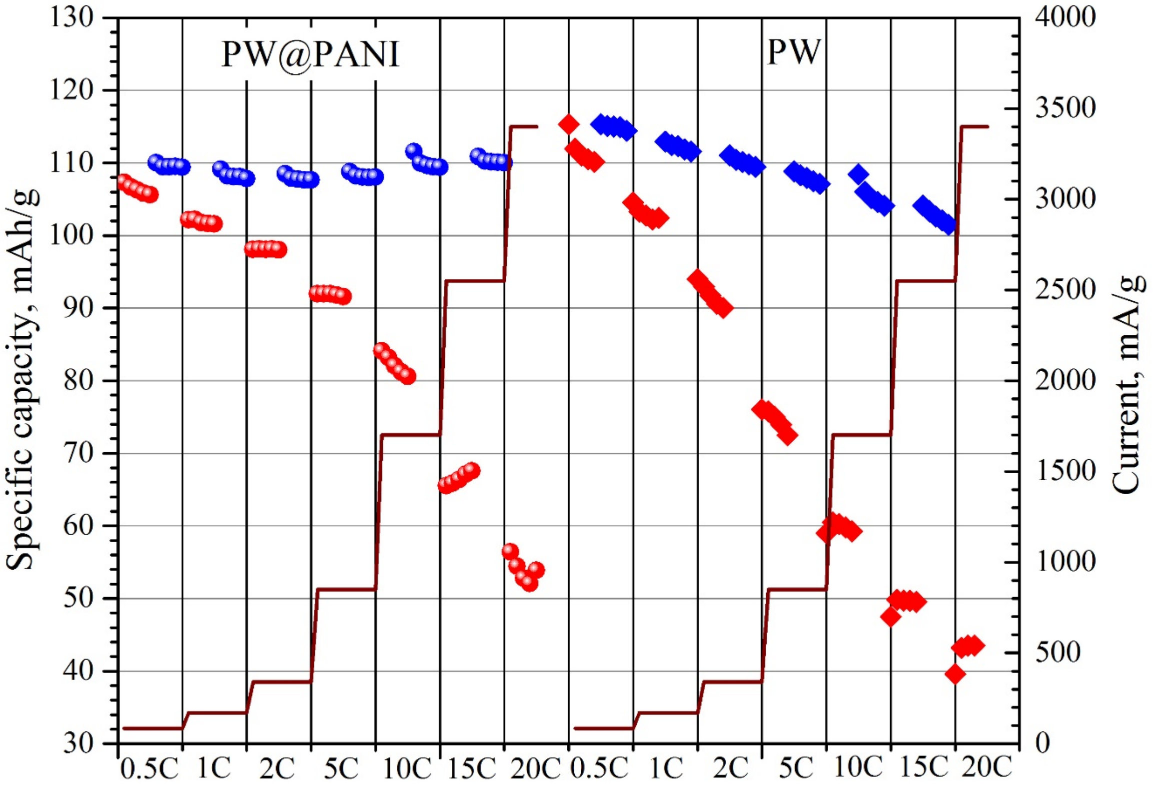
PANI shifts the temperature of transition from cubic to rhombohedral phase to higher temperature.



Electrochemical research

The PW material was dried at a temperature 140 ℃.





The electrochemical cell assembled with PW@PANI as an active cathode material demonstrates the less capacity fall during long performance compared with the cell with the pure PW.

Larger capacities at high cycling rates.

Conclusions

- An improvement in the performance of the commercial sodium iron (II) hexacyanoferrate (II) cathode material after its coating with polyaniline has been demonstrated.

- An indirect explanation of this fact is proposed using X-ray diffraction.

This work was supported the Russian Science Foundation, project No. 21-12-00261

Thank you very much for your attention!