The 29th International Scientific Conference of Young Scientists and Specialists (AYSS-2025)
Section: «Applied Innovation Activities»

Effect of drying on the polyaniline-coated Prussian White cathode material for sodium-ion batteries

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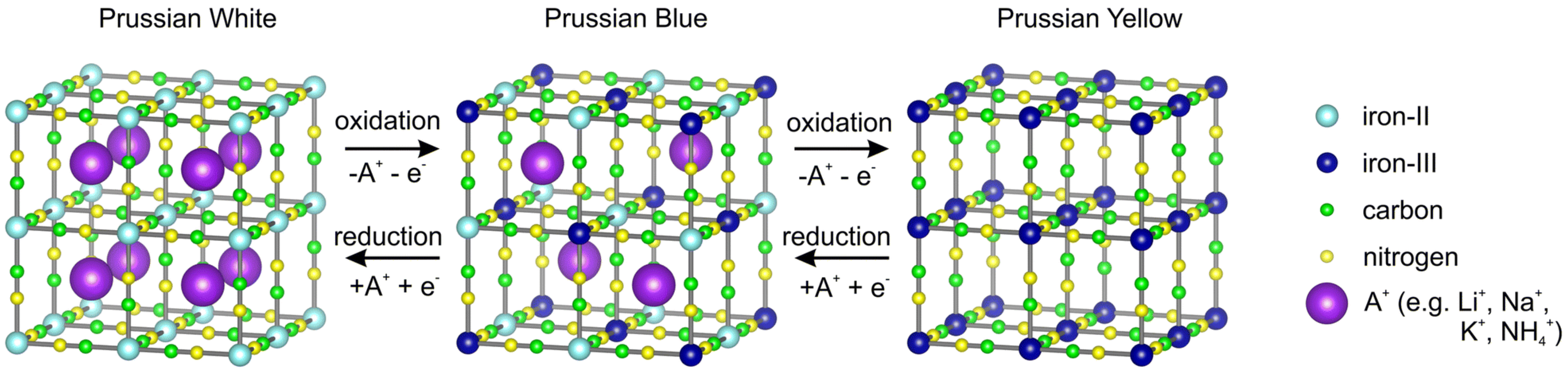
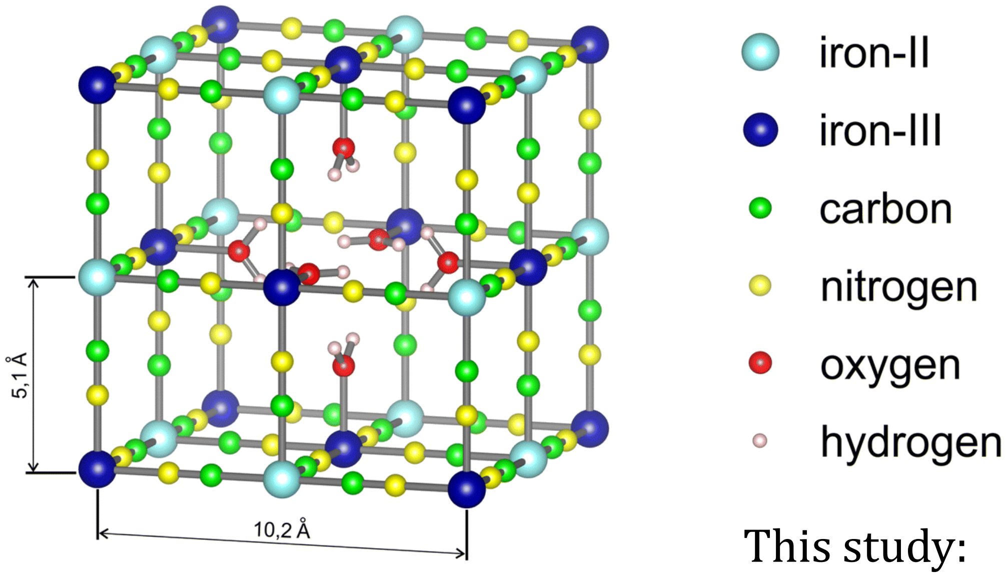
Dubna, Russia October 27-31, 2025 mdonets@jinr.ru

Perspective cathode materials: Prussian Blue and its analogues

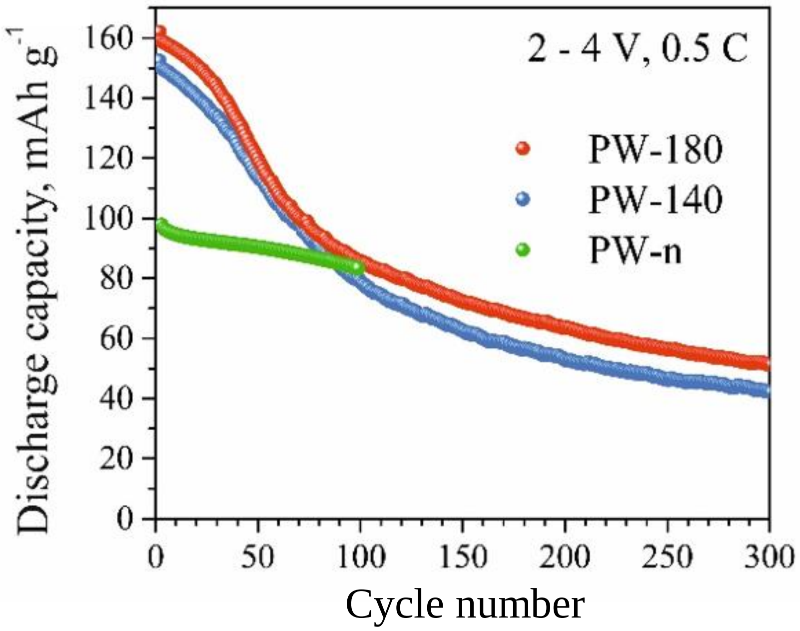


$Na_2Fe^{II}[Fe^{II}(CN)_6]$ $NaFe^{III}[Fe^{II}(CN)_6]$ $Fe^{III}[Fe^{III}(CN)_6]$



$Na_2Fe[Fe(CN)_6]_{1-y}\square_y \cdot mH_2O$

□ - $Fe(CN)_6$ vacancies,
y – the number of $Fe(CN)_6$ vacancies

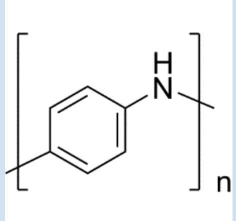


This study:

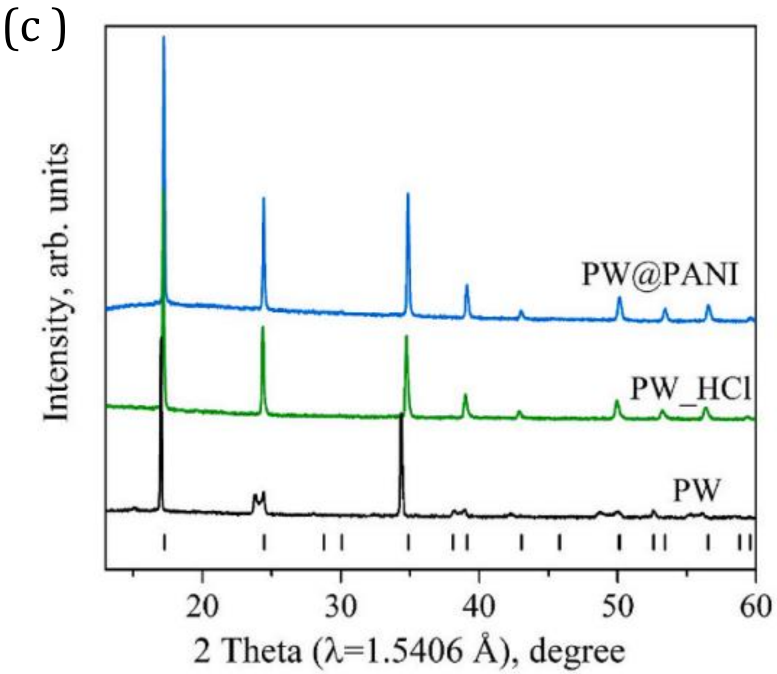
1) Polyaniline coating
2) Drying at 140 °C and 180 °C

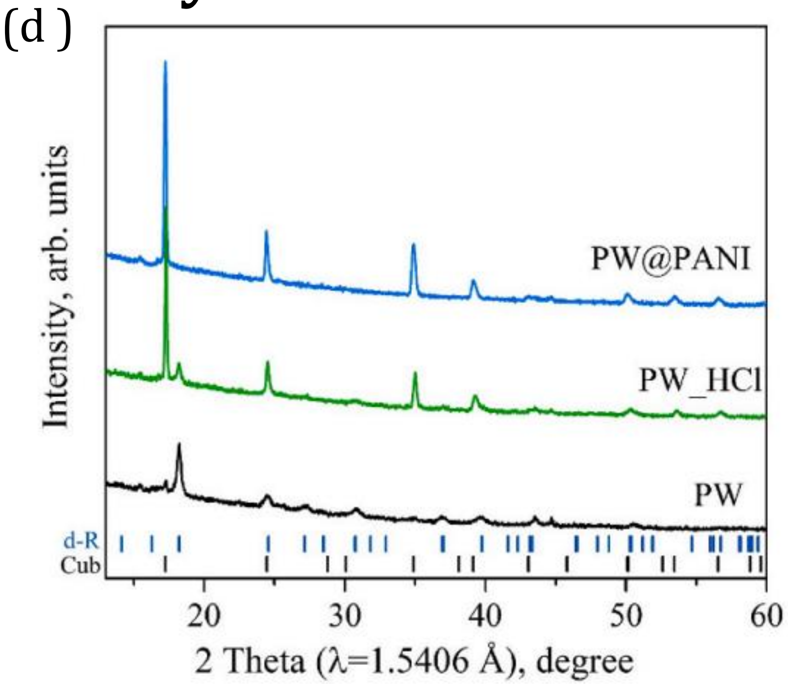
SEM

Polyaniline(PANI)

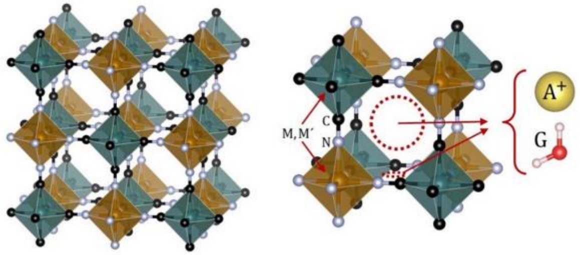


XRD data. Phase analysis.

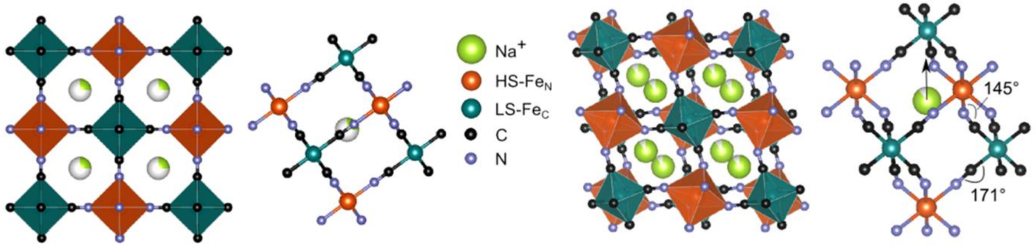




X-ray diffraction pattern of (c) the PW, PW_HCl and PW@PANI powders and (d) the PW-180, PW_HCl-180 and PW@PANI-180 electrodes measured at room temperature

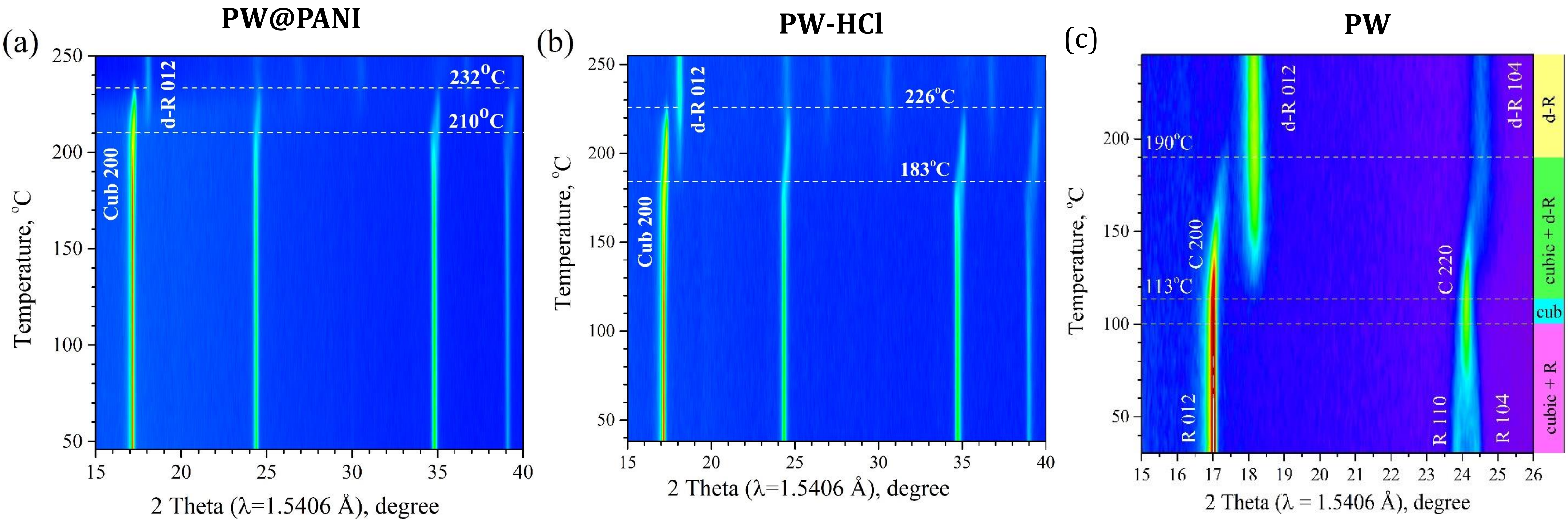


$Fm\overline{3}m$ $R\overline{3}$



Phase transitions under heating

Heating was performed in vacuum at 1°C/min rate up to 250°C.

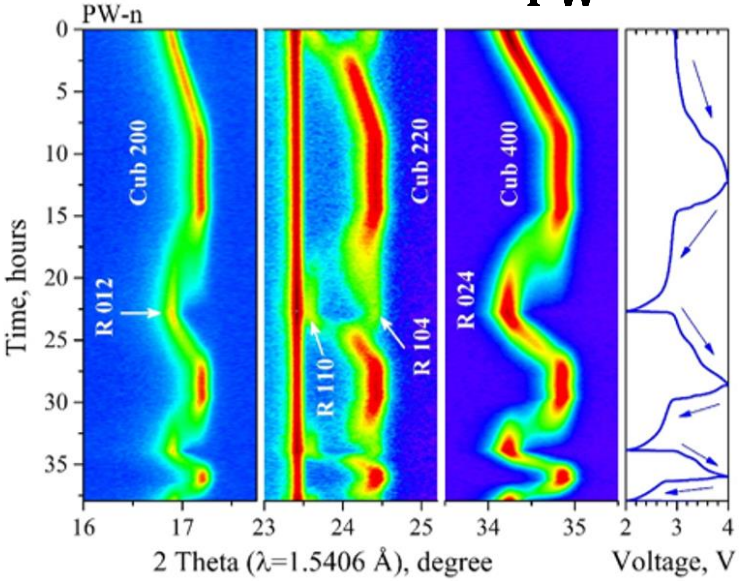


- Compared to pristine PW, the sodium deficiency in the structure of the PW_HCl sample shifts the phase transition from cubic phase to dehydrated d-R phase to significantly higher temperatures, and in PW@PANI the transition temperatures are even higher.

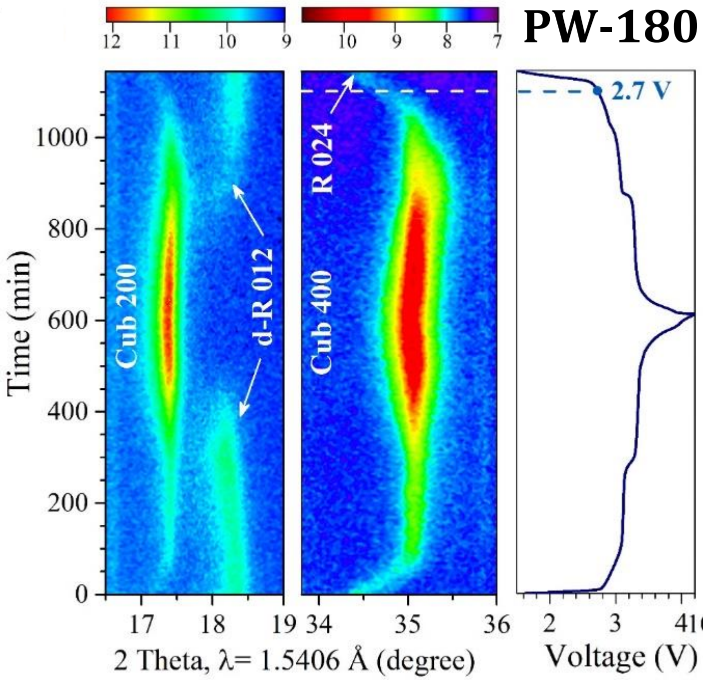
- These observations indicate that the PANI shell prevents the dehydration of the PW powder under heating!

Phase transitions during charge-discharge

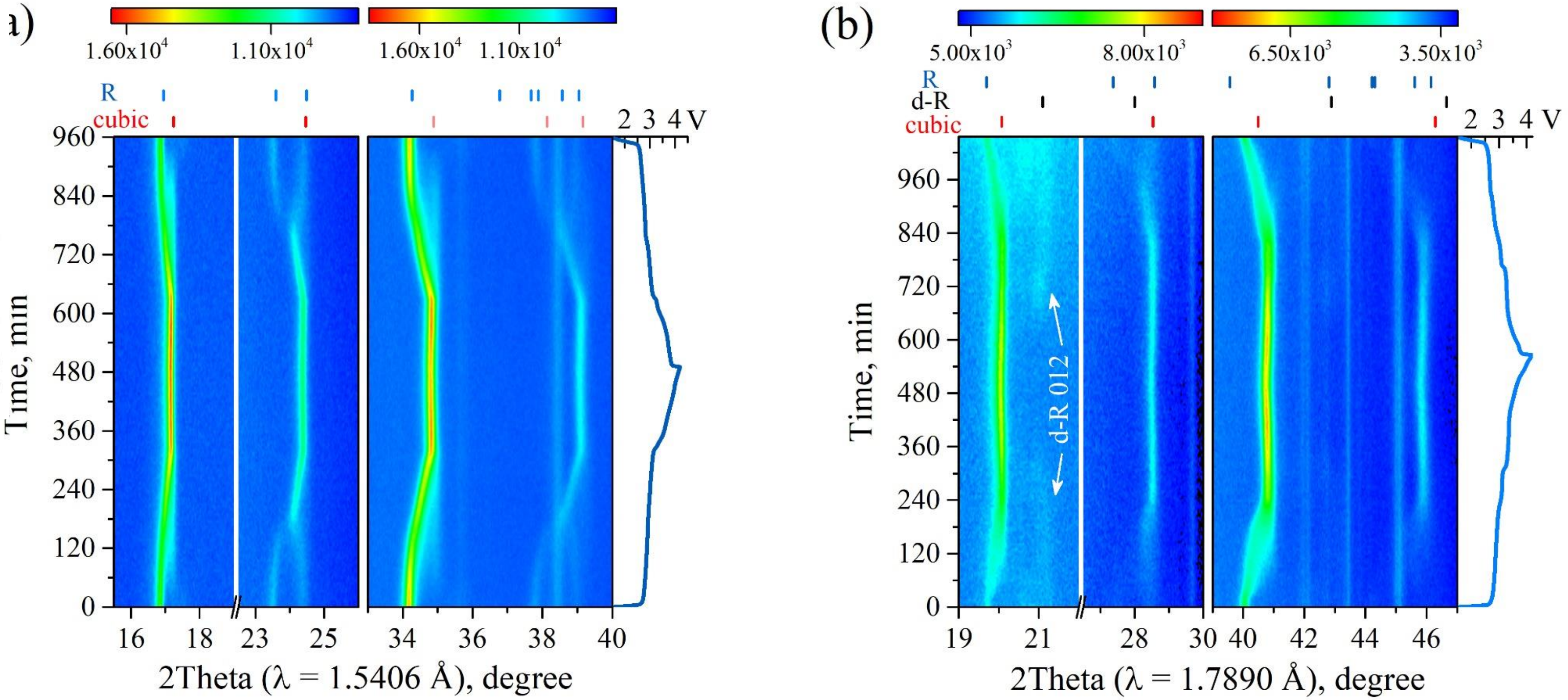
PW



PW-180

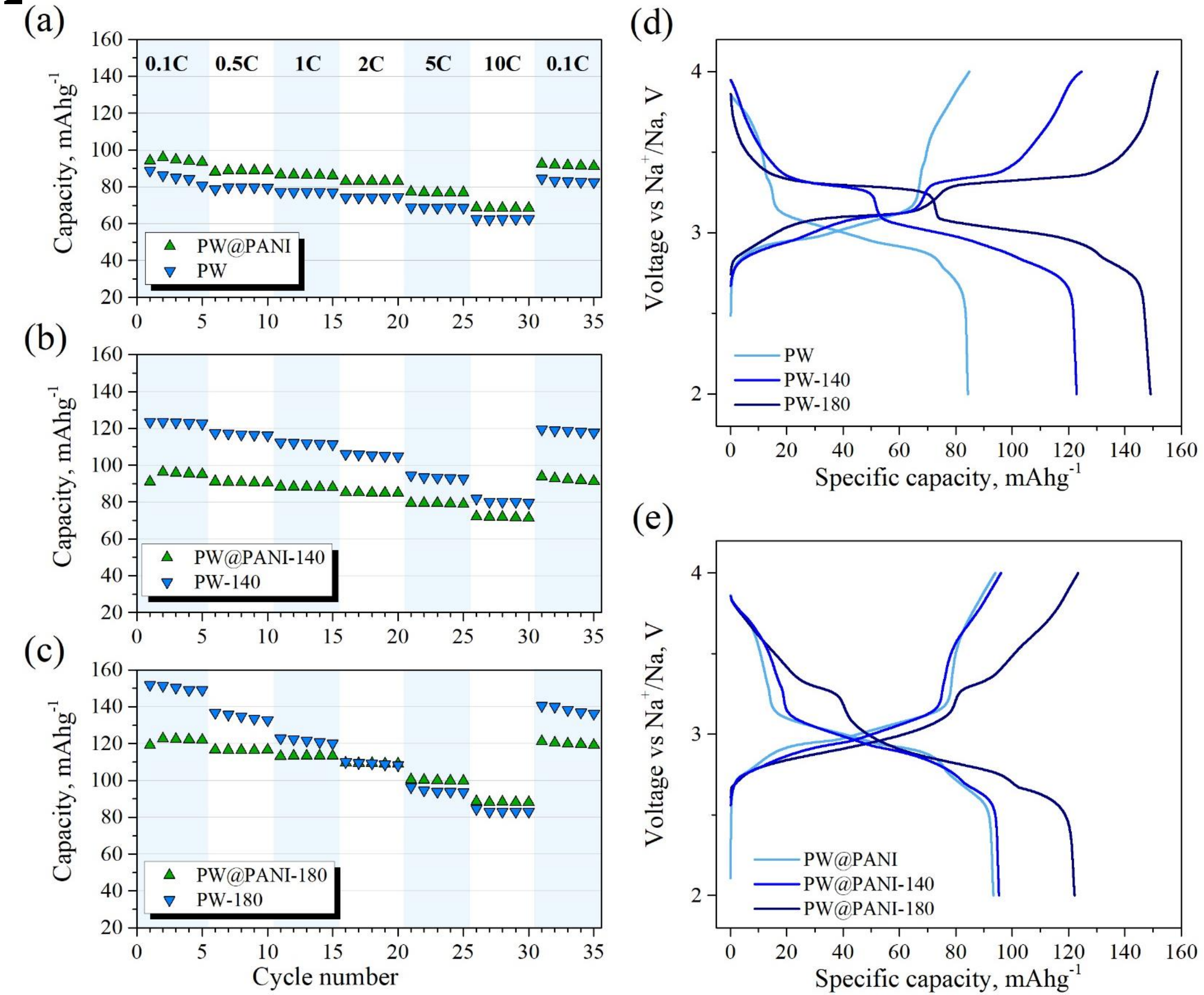


PW@PANI-180 **PW-HCl-180**



2D maps of the XRD patterns of (a) PW@PANI-180 and (b) PW_HCl-180 electrodes measured during charge and subsequent discharge in the second cycle at 0.1 C rate in a range between 1.5 and 4.2 V

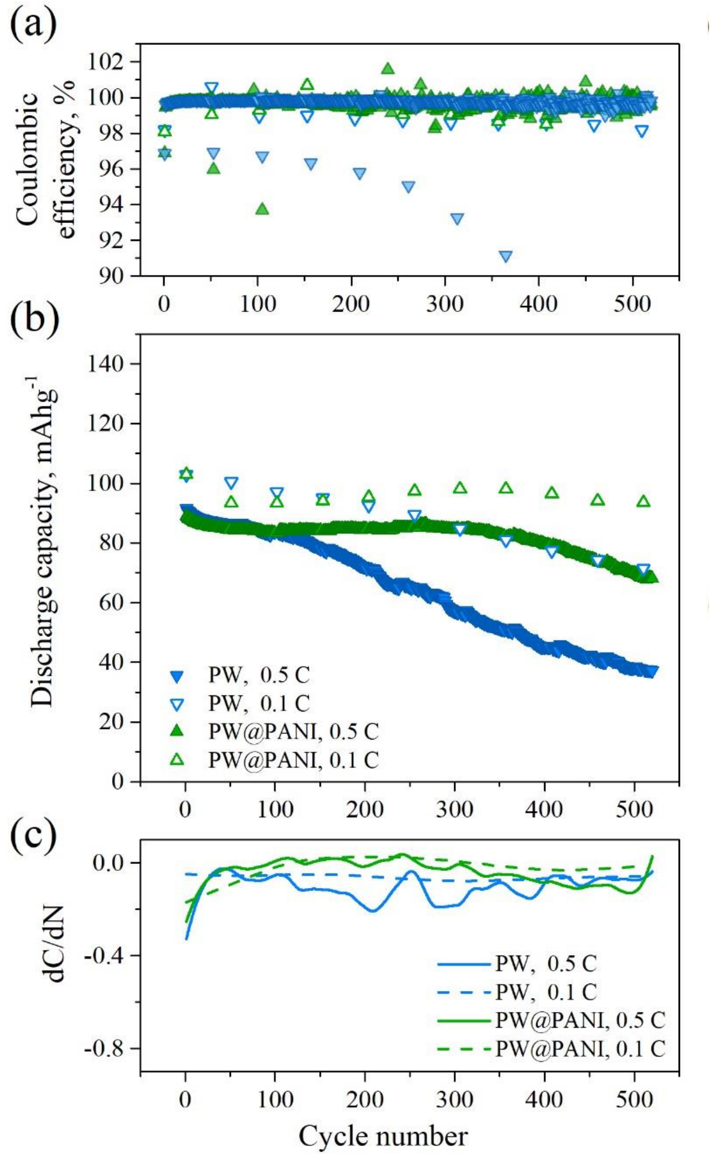
Rate performance of the PW and PW@PANI



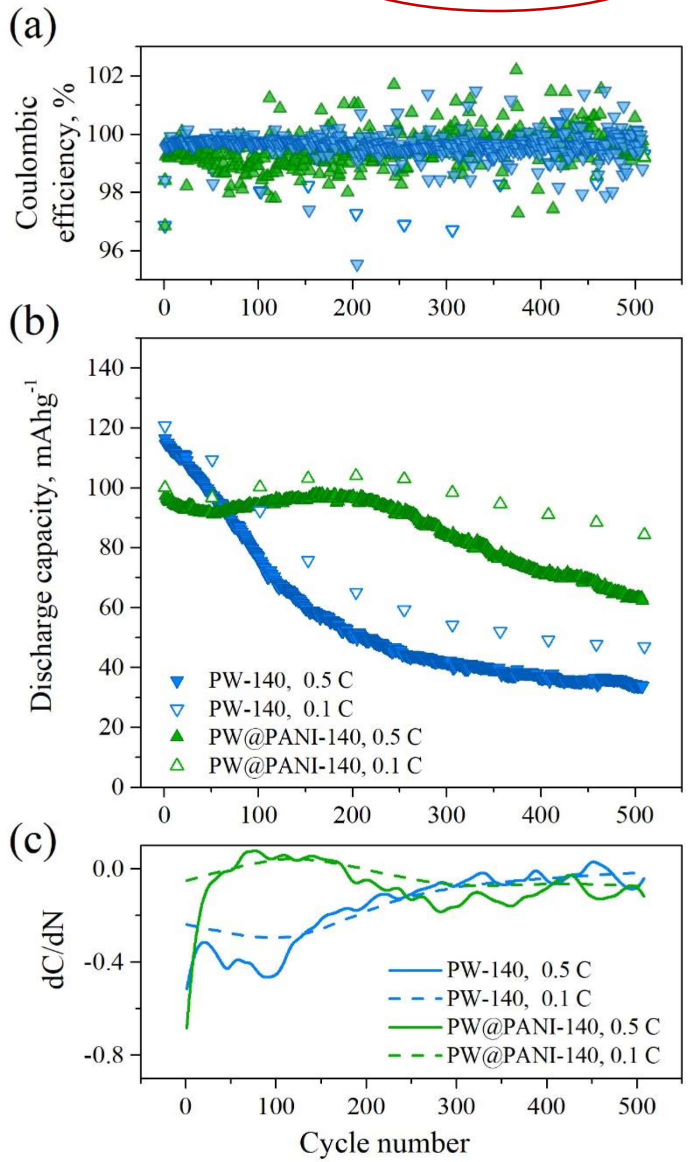
PW/KetjenBlack/PVDF: 80/10/10, 1C =170 mAh/g

Long-term electrochemical performance of the electrodes

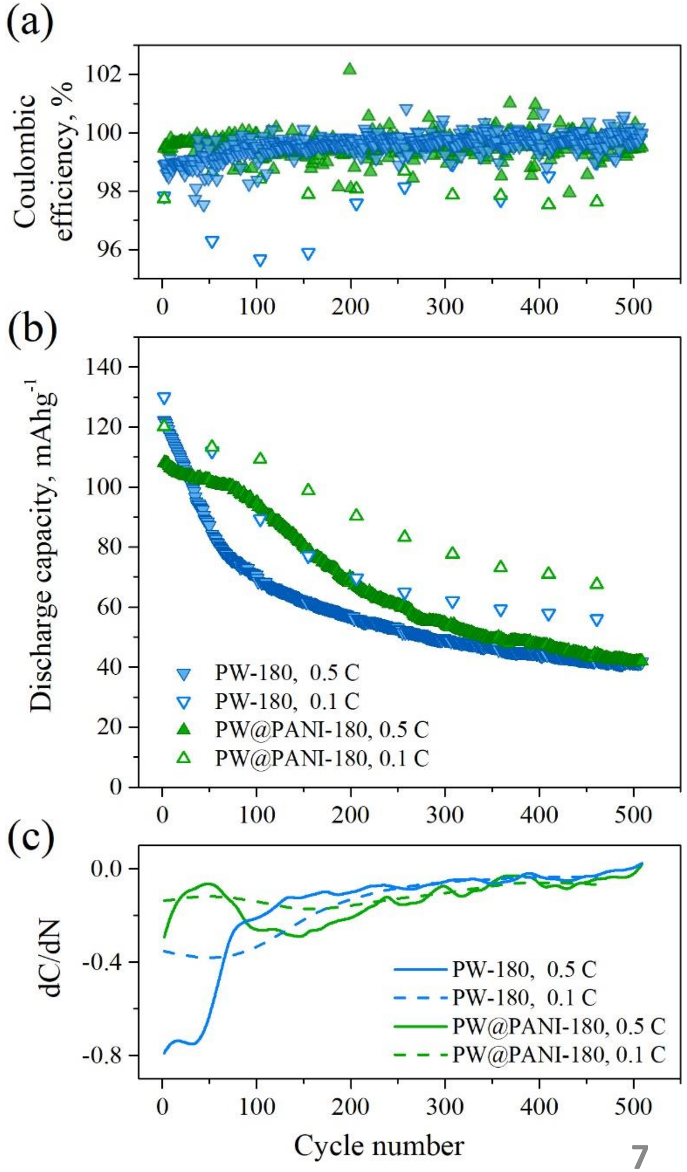
PW, PW@PANI



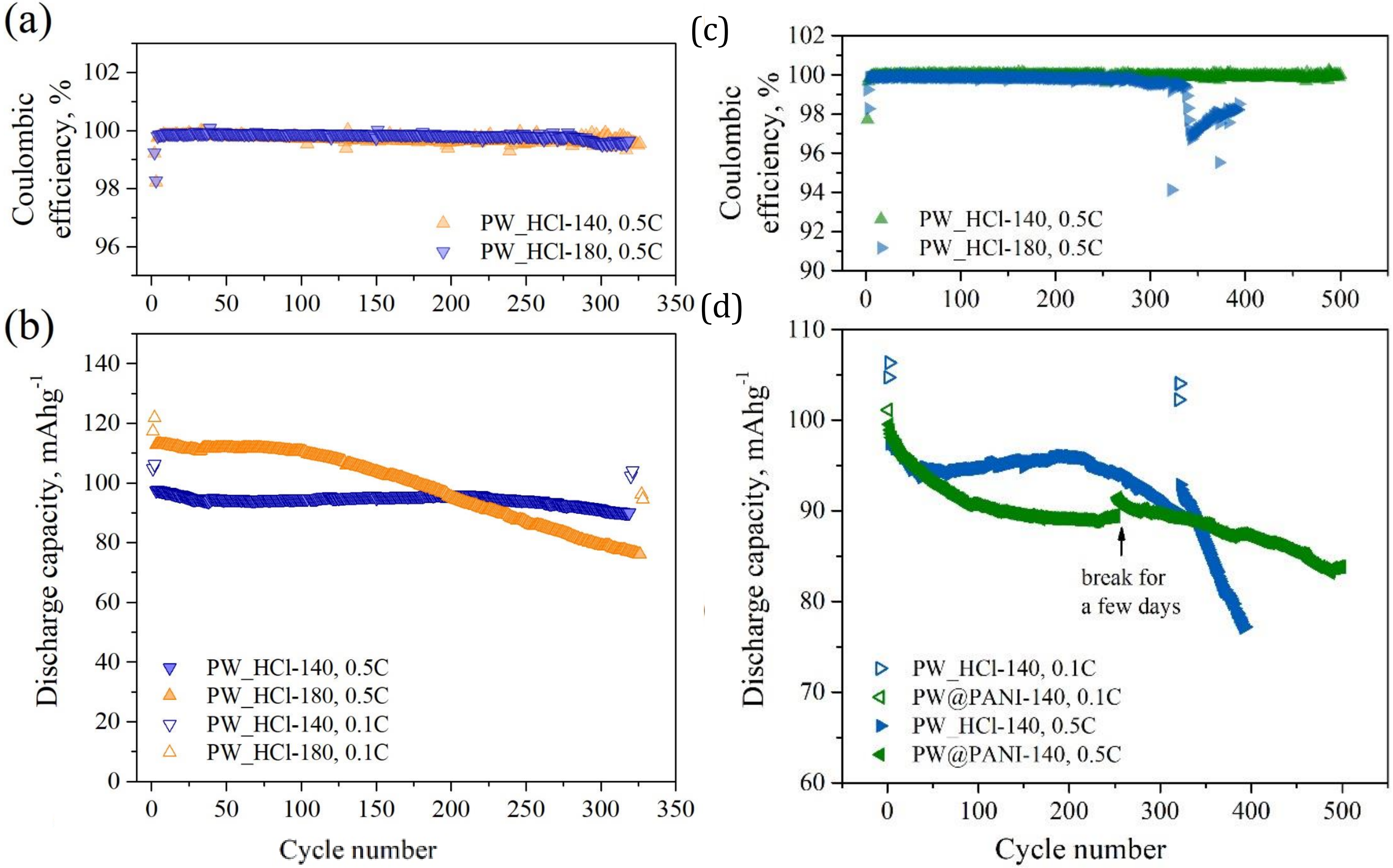
PW-140, PW@PANI-140



PW-180, PW@PANI-180



Electrochemical performance of the PW_HCl-140, PW_HCl-180 and PW@PANI-140 electrodes



Main results

- The procedure of deposition of polyaniline on the PW particle surface in an acidic medium leads to the formation of a sodium-deficient cubic structure of the PW@PANI material.

- PW@PANI compared to PW, PW_HCl: Cubic → d-R shifts towards higher temperatures during drying.

- PW_HCl, PW@PANI compared to PW: more stable electrochemical cycling.

- PW@PANI-180: R phase is stable in a wider range of voltages and there is no evidence of dehydrated rhombohedral d-R phase formation.

⇓

PANI layer prevents the release of water from the sodium hexacyanoferrate structure even when dried at high temperatures.

- PW@PANI-140 electrode demonstrates the best ratio of achieved capacity and cycling stability, having a capacity of up to ≈ 97 mAh/g during 200 cycles at 0.5C

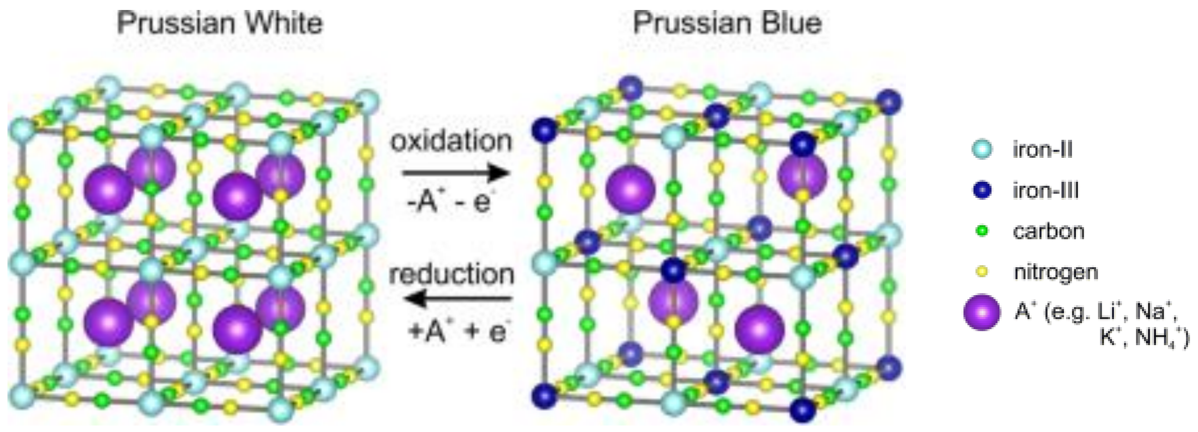
Thus, it is difficult to determine the effect of PANI coating itself on the electrochemical stability of cathode material.
At the same time, the structural phase transformations occurring in these materials during cycling are different.

Samoylova, N. Y., Vasin, R. N., Sumnikov, S. V., Ponomareva, O. Y., Donets, M. E., Korneeva, E. A., & Andreev, E. V. (2025). Effect of drying on the polyaniline-coated Prussian white cathode material for sodium-ion batteries. *Journal of Physics and Chemistry of Solids*, *204*, 112762.

Thank You for Your kind attention!

Prussian Blue and analogues

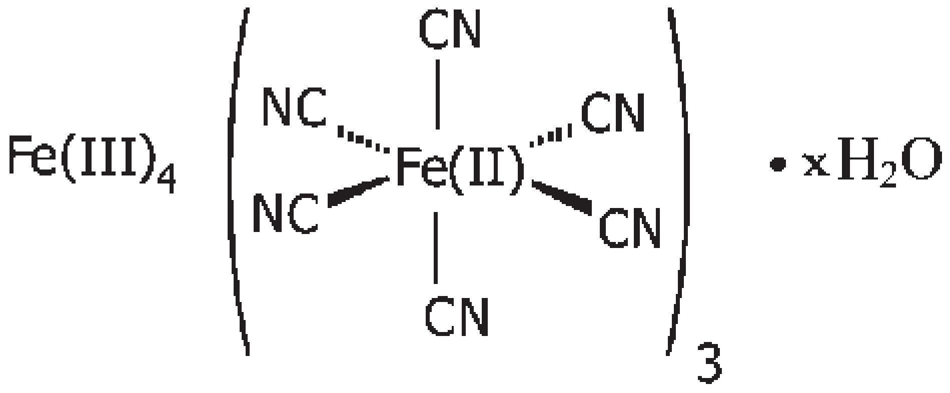
$Na_{2-x}Fe[Fe(CN)_6]_{1-y}\cdot\square\cdot y\cdot mH_2O$
$\square$ - $Fe(CN)_6$ vacancies
y – number of $Fe(CN)_6$ vacancies



PBAs are a class of transition metal cyanides, and their general chemical formula can be expressed as $A_xM[M'(CN)_6]_{y\square 1-y}\cdot mH_2O$ ($0 \leq x \leq 2$, $y < 1$), where A is an alkali metal element (Li, Na, and K); M is a transition metal element such as Fe, Mn, Co, Ni, and Cu; M′ is usually Fe, and $\square$ stands for $M'(CN)_6$ vacancy.[8,25]

$Fe_4[Fe(CN)_6]_3\cdot x\,H_2O$

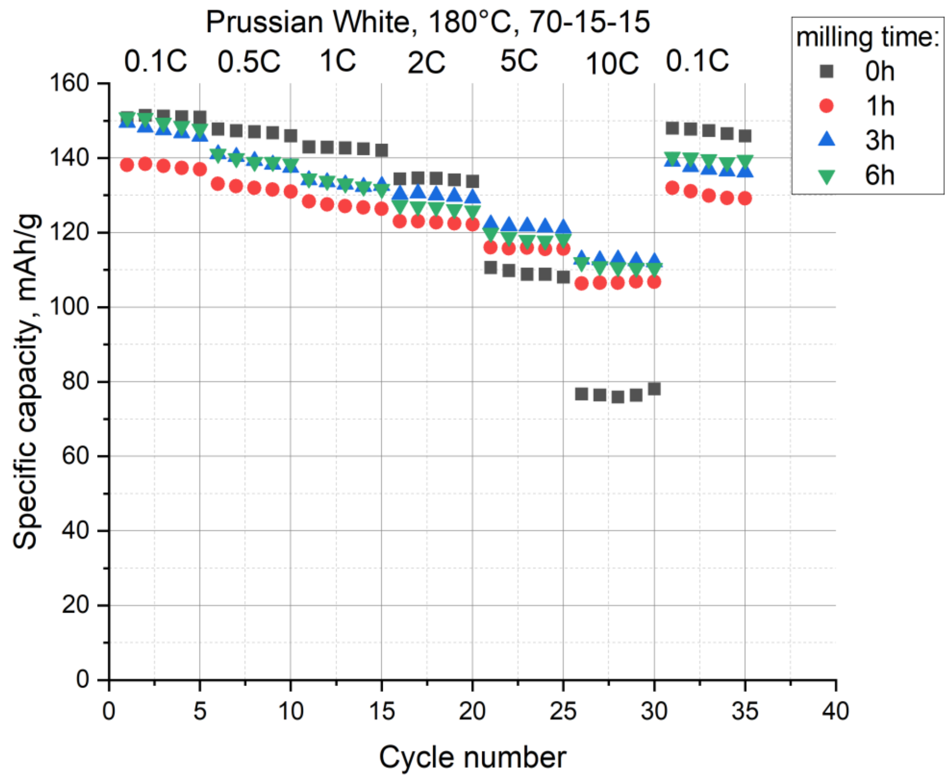
Prussian blue is an inorganic complex salt containing two differently charged iron ions Fe^{2+} and Fe^{3+} and the negatively charged hexacyanoferrate ions $[Fe(CN)_6]^{4-}$



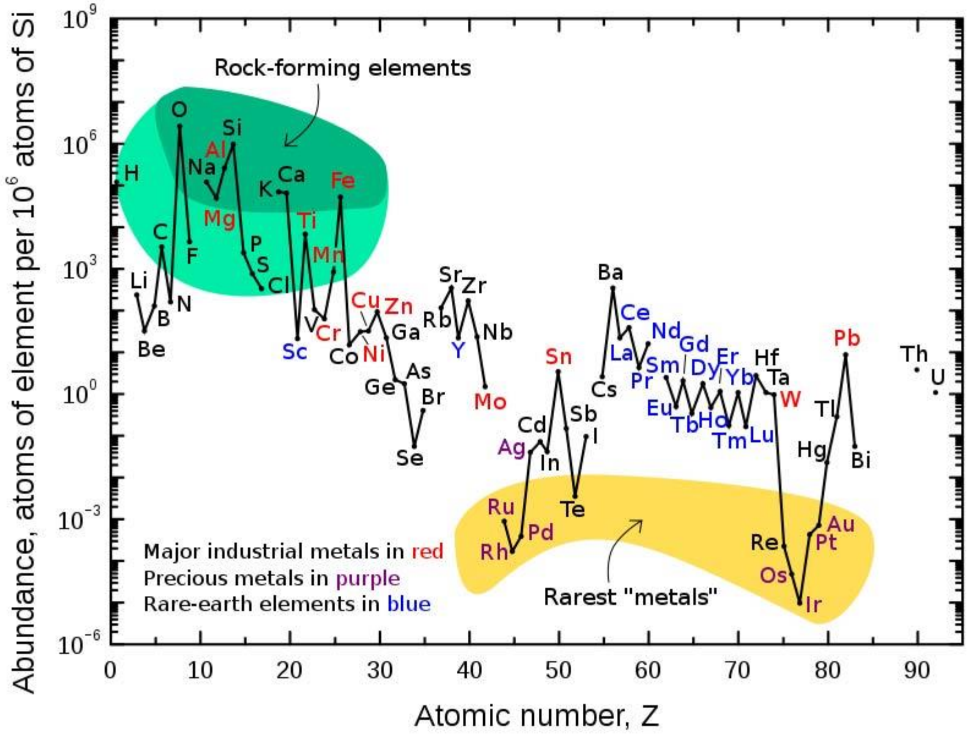
C-rate in electrochemical cycling

A C-rate is a measure of the rate at which a battery is discharged relative to its maximum capacity. **A 1C rate means that the discharge current will discharge the entire battery in 1 hour.**

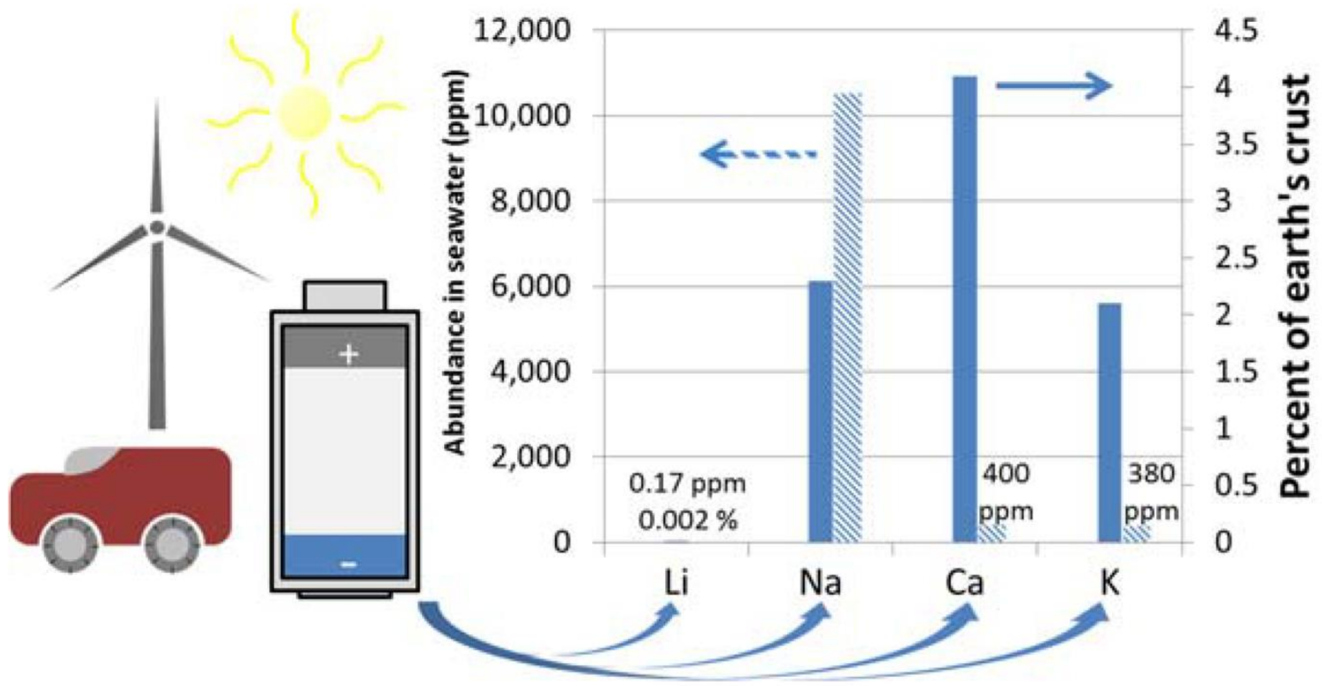
Example: For a battery with a capacity of 100 Ah, this equates to a discharge current of 100 A.



Terrestrial abundance of elements

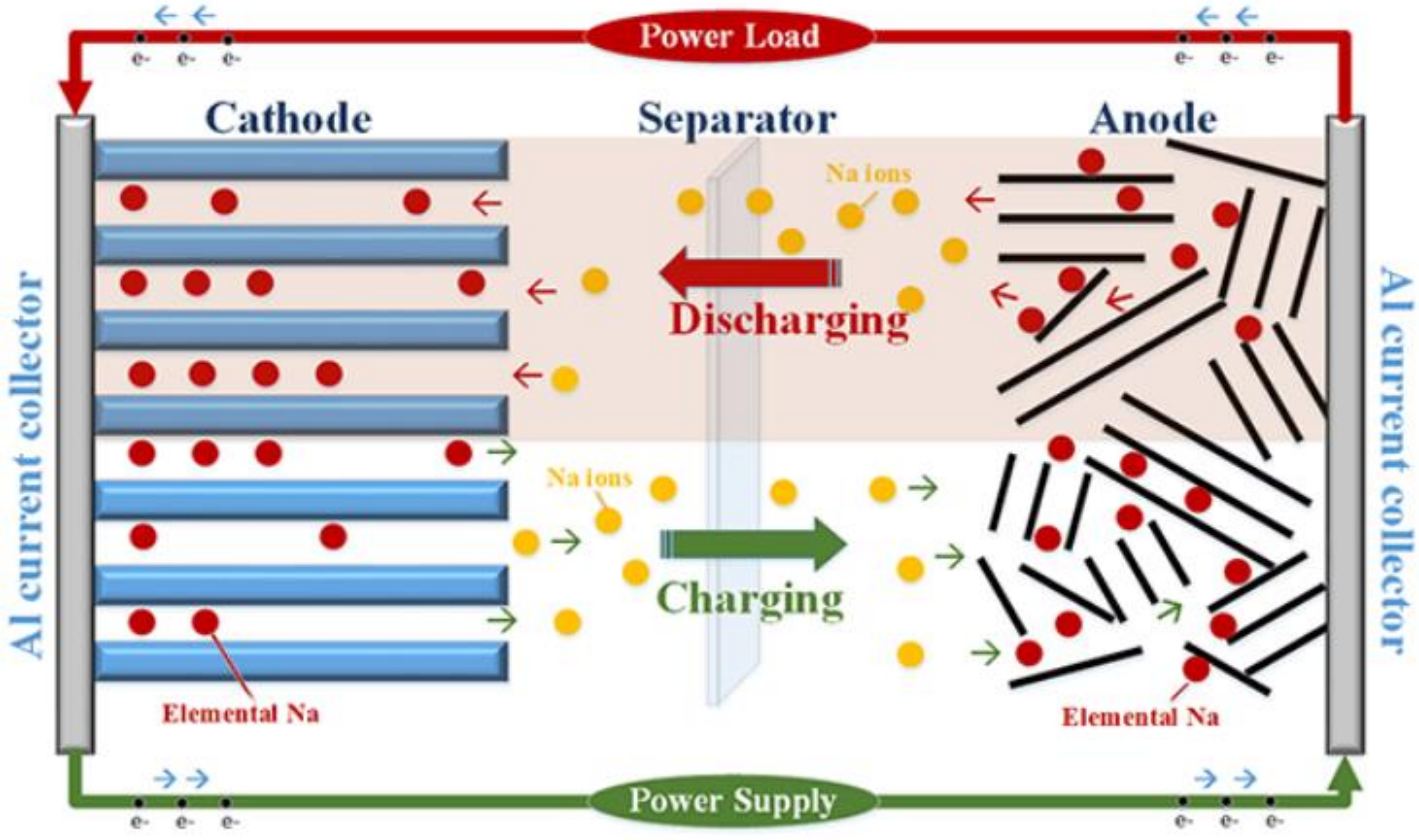


DOI: 10.1093/nsr/nwab050

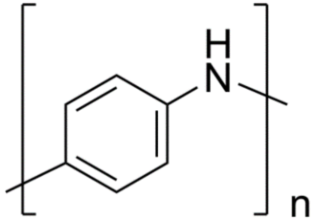


DOI: 10.3390/batteries6010011

Na-ion battery working principle



PW@PANI synthesis



First, the synthesis was carried out in an ice bath. Commercial PW powder (2.5 g) was dispersed in HCl solution (0.01 M, 250 mL) with continuous stirring for 30 min.

Then, aniline (C6H7N, 2.5 mmol) was added slowly into the above suspension and stirred for 30 min.

Ammonium persulfate ((NH4)2S2O8, 2.5 mmol) was dissolved in HCl solution (0.01 M, 250 mL) and added dropwise into the PW suspension with a rate of approximately 2 ml/min under stirring.

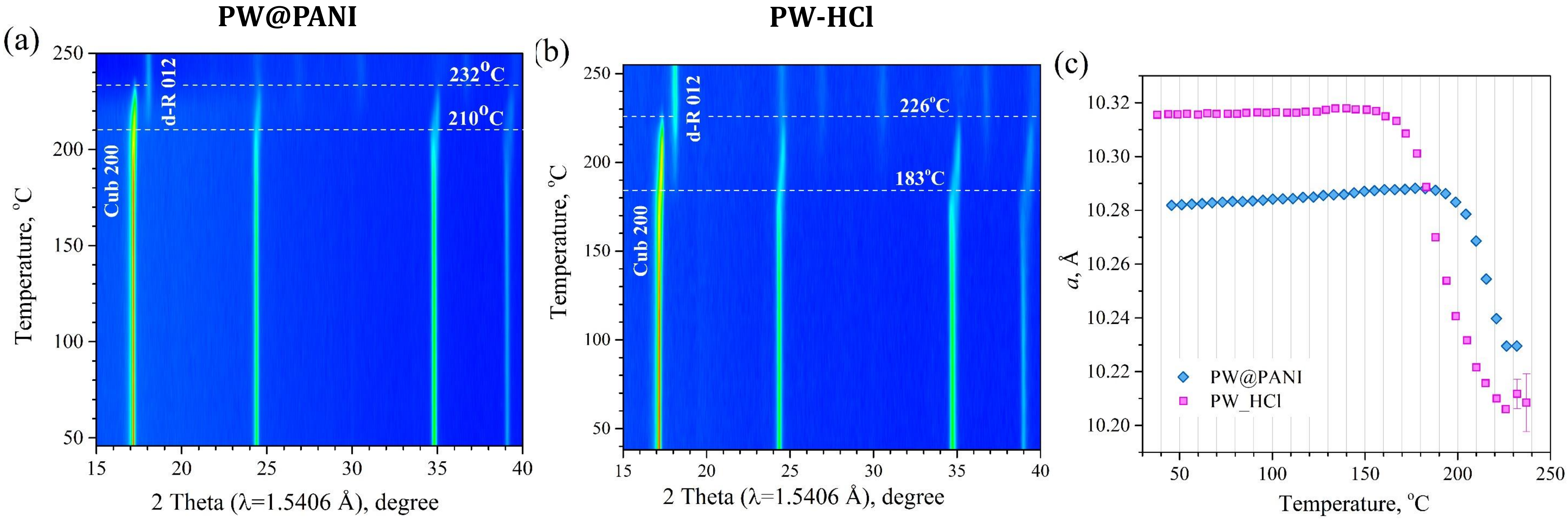
The mixed suspension was further stirred for 18 h, and the temperature was increased from 0 ∘C up to the room temperature.

Isolated polyaniline flakes floating on the surface of the solution were removed, and the obtained green powder was collected by vacuum filtration, washed with deionized water several times and dried in air at 90 ∘C for 3 h.

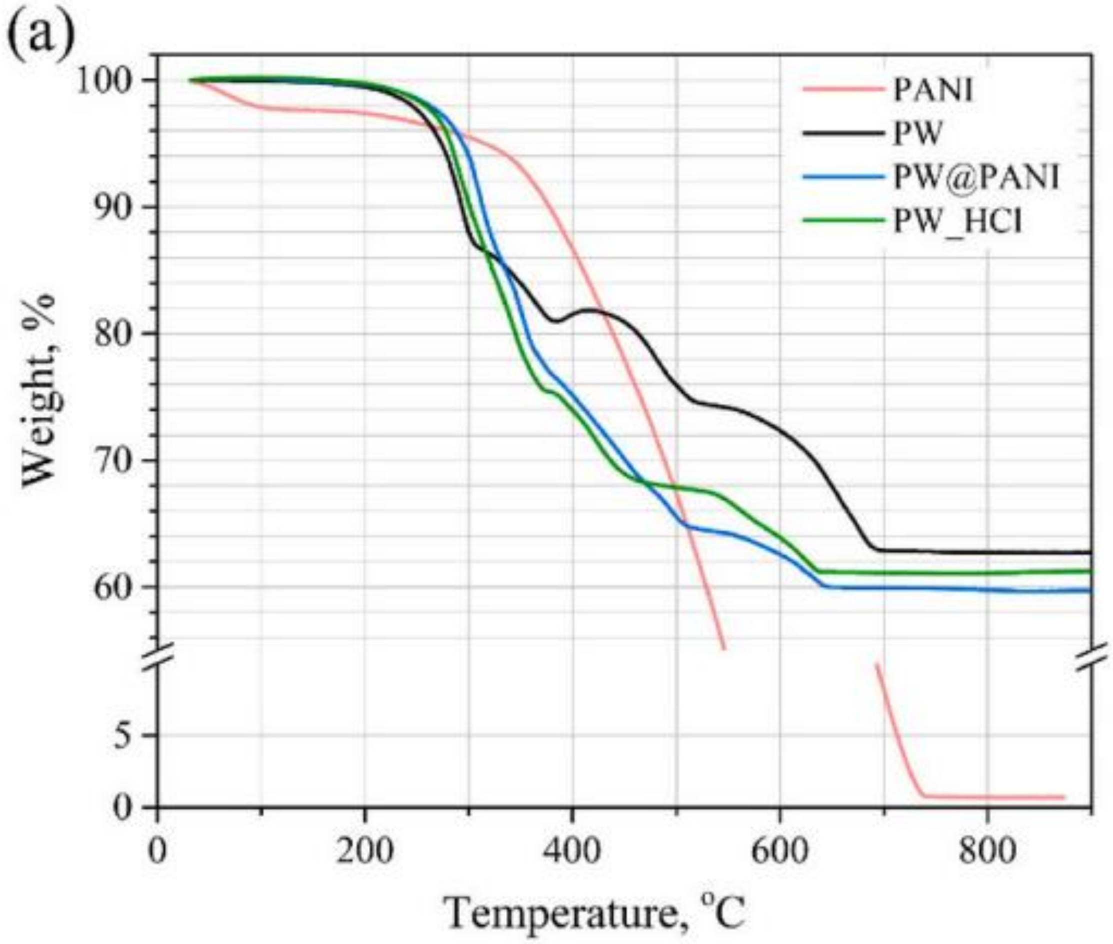
PW_HCl synthesis

The PW powder was soaked in 0.01 M HCl solution with (NH4)2S2O8 oxidizer (further denoted as “PW_HCl”) under conditions similar to those during the synthesis of PW@PANI

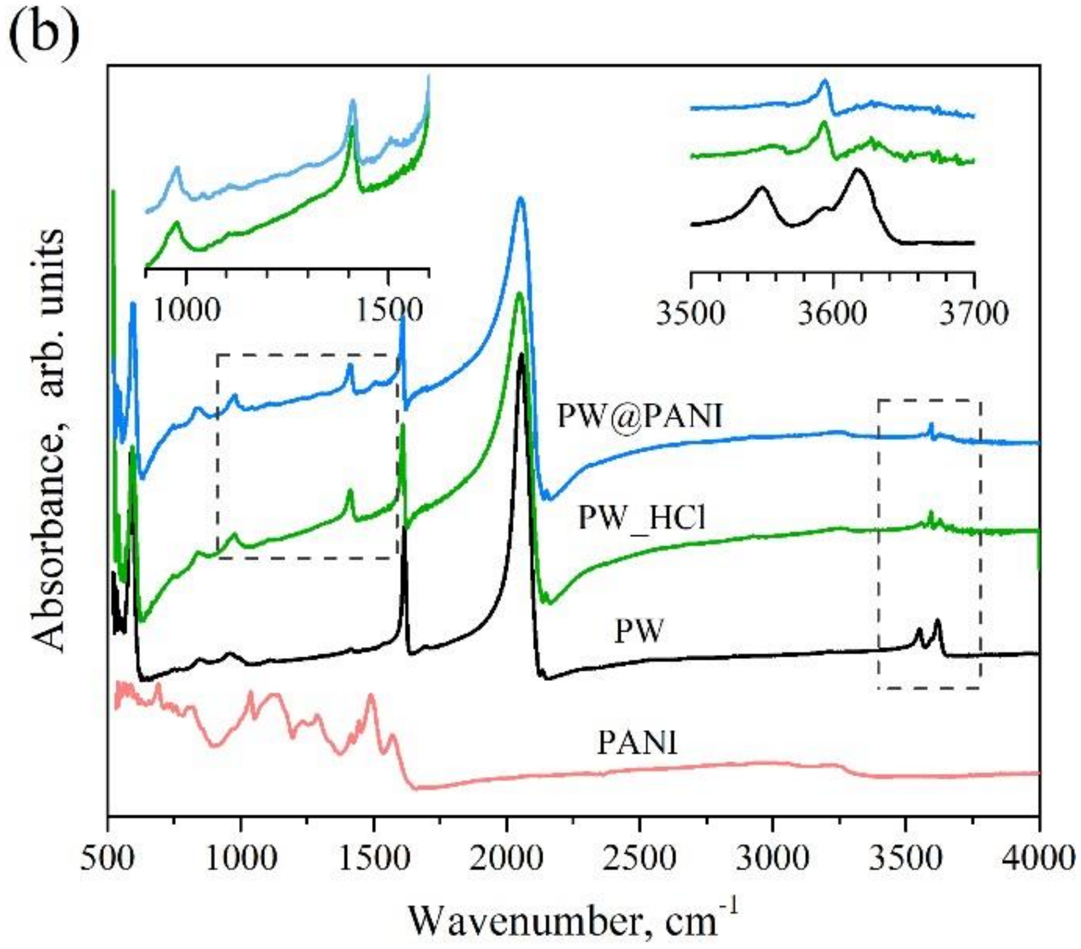
Phase transitions under heating



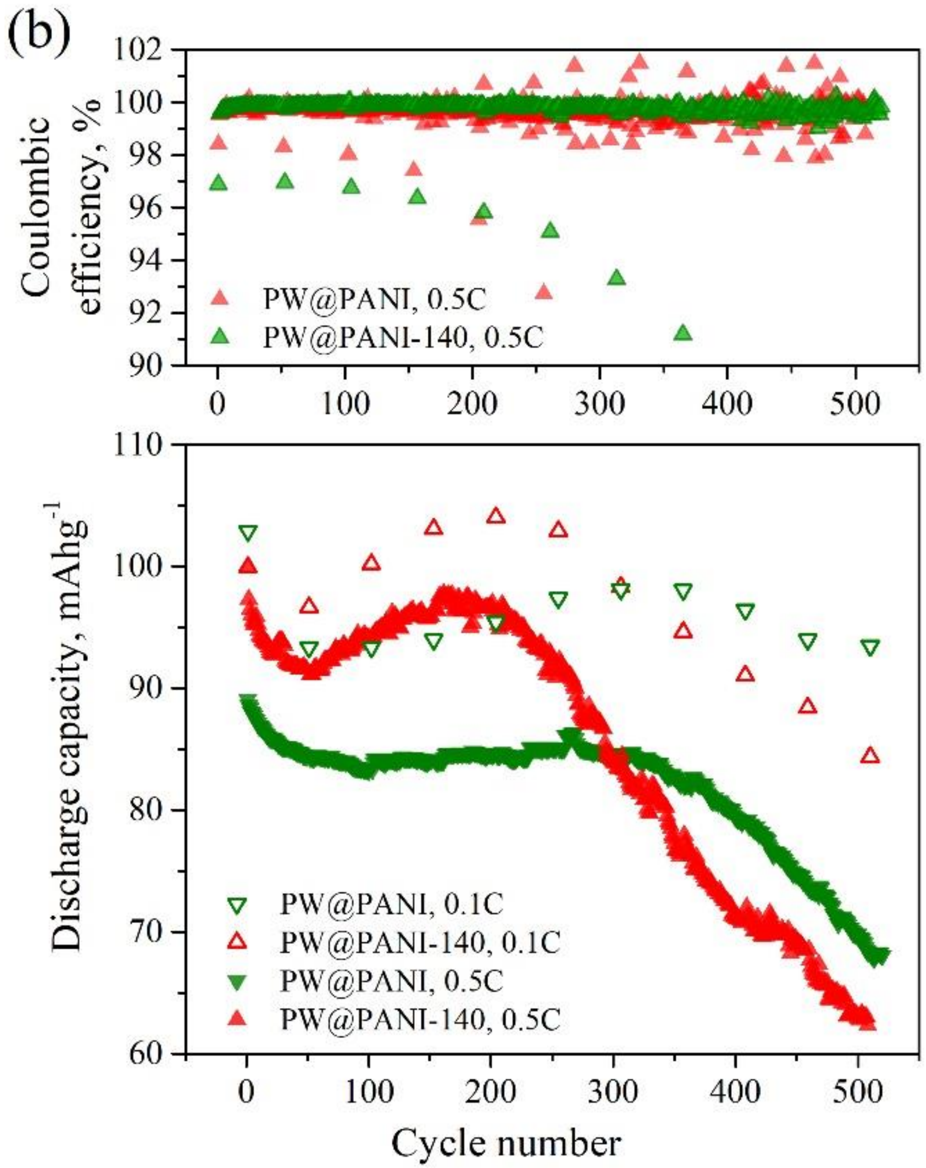
TGA measurement of PW, PW_HCl and PW@PANI powders and polyaniline in air at a heating rate of 10 ∘C/min



FT-IR spectra of PANI, PW, PW_HCl and PW@PANI powders



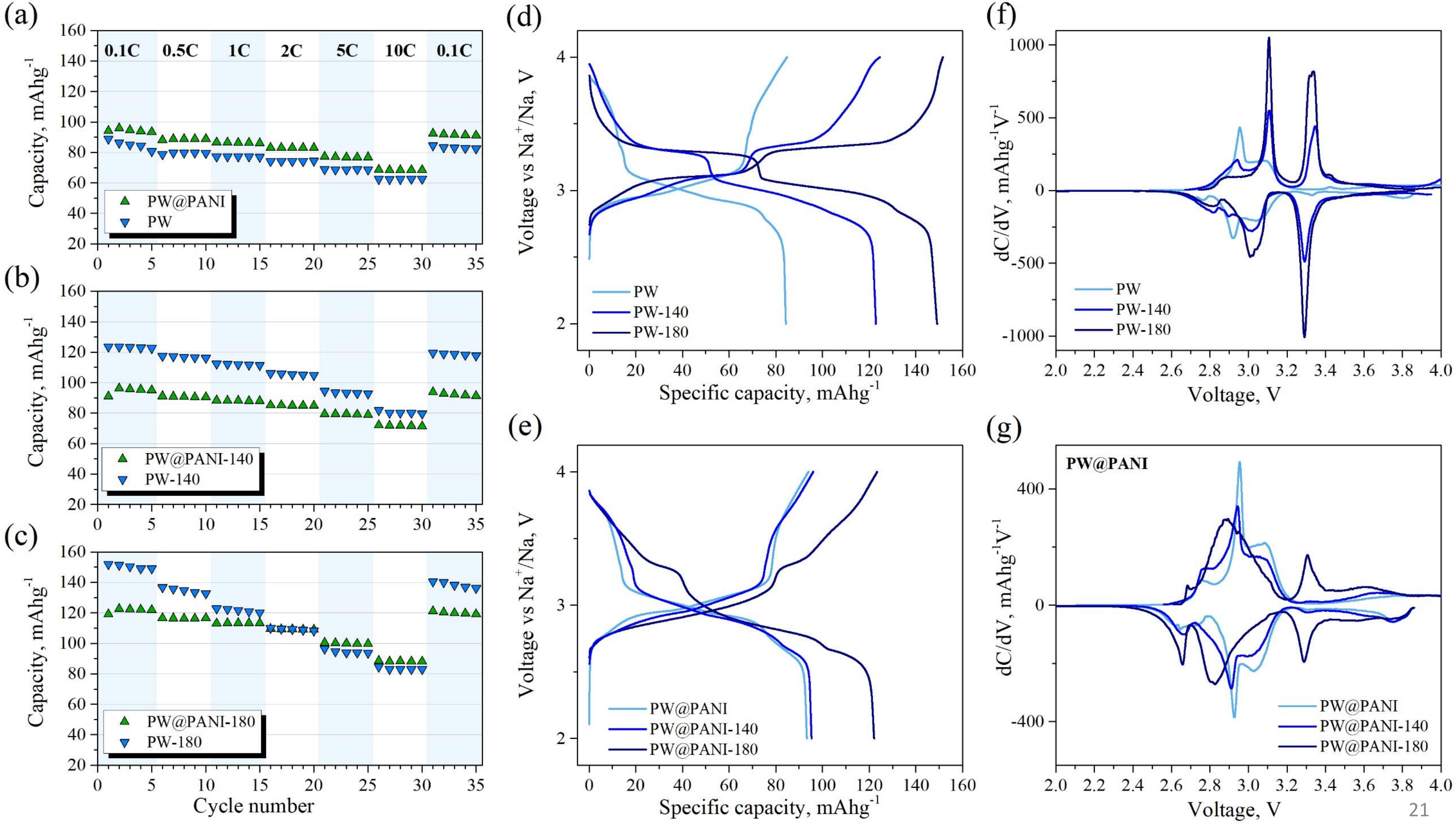
PW@PANI, PW@PANI-140



Capacity and corresponding capacity retention (CR) of the PW and PW@PANI electrodes after 500 cycles at 0.5 C rate and after 10 intermediate cycles at 0.1 C versus sodium.

	capacity (CR)			
	PW		PW@PANI	
	0.1 C	0.5 C	0.1 C	0.5 C
non-dried	71.4 mAh/g (69.4 %)	38.3 mAh/g (41.7 %)	93.5 mAh/g (90.8 %)	69.8 mAh/g (78.4 %)
dried at 140 °C	47.0 mAh/g (38.9 %)	34.2 mAh/g (29.4 %)	84.4 mAh/g (84.5 %)	62.9 mAh/g (62.9 %)
dried at 180 °C	56.0 mAh/g (43.1 %)	41.7 mAh/g (34.1 %)	67.5 mAh/g (56.1 %)	41.9 mAh/g (38.8 %)

Rate performance of the PW and PW@PANI



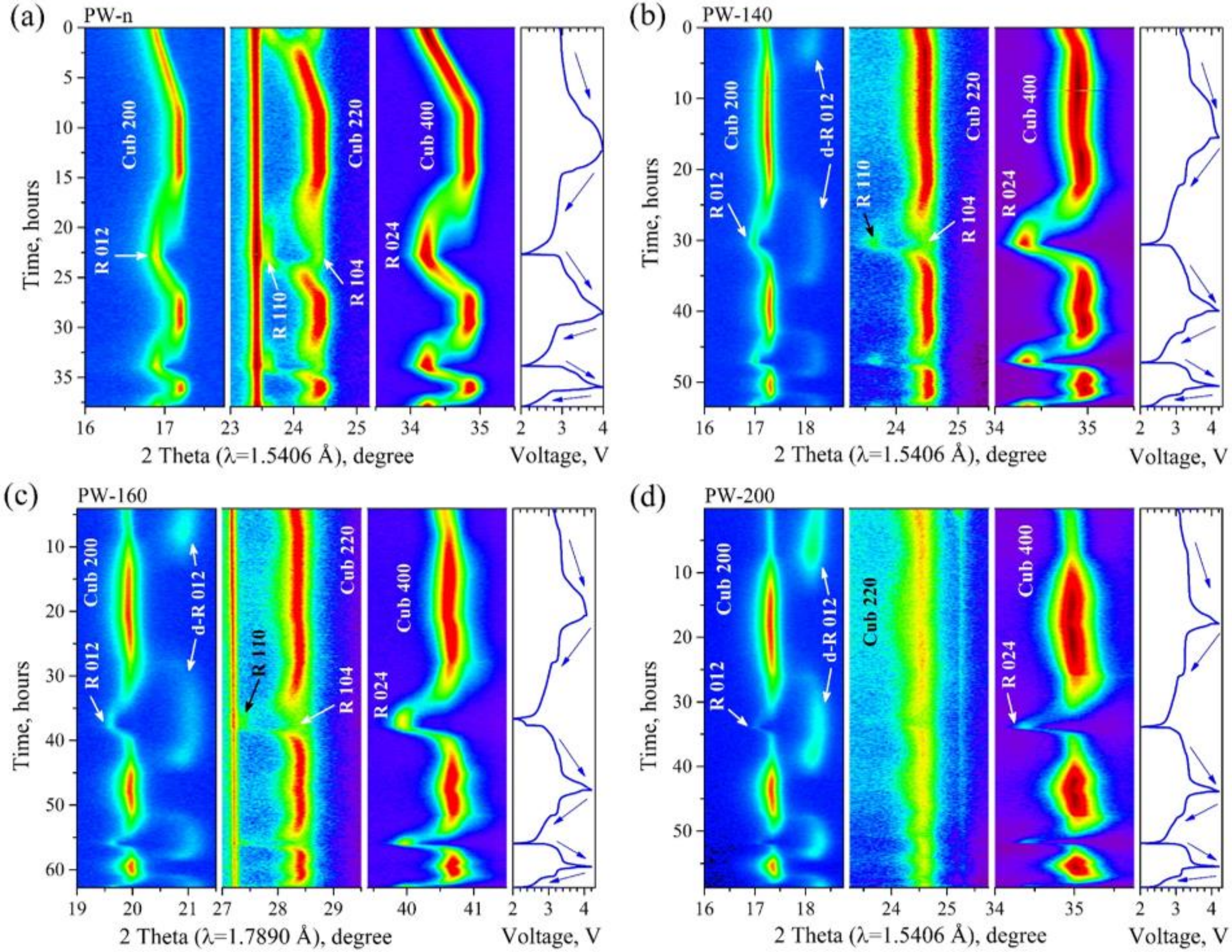
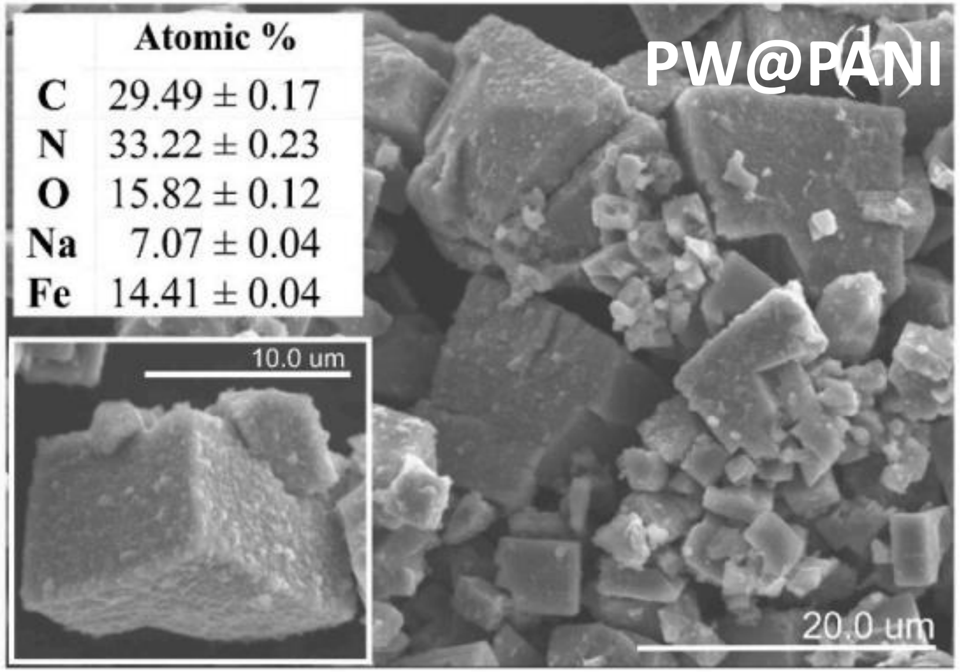
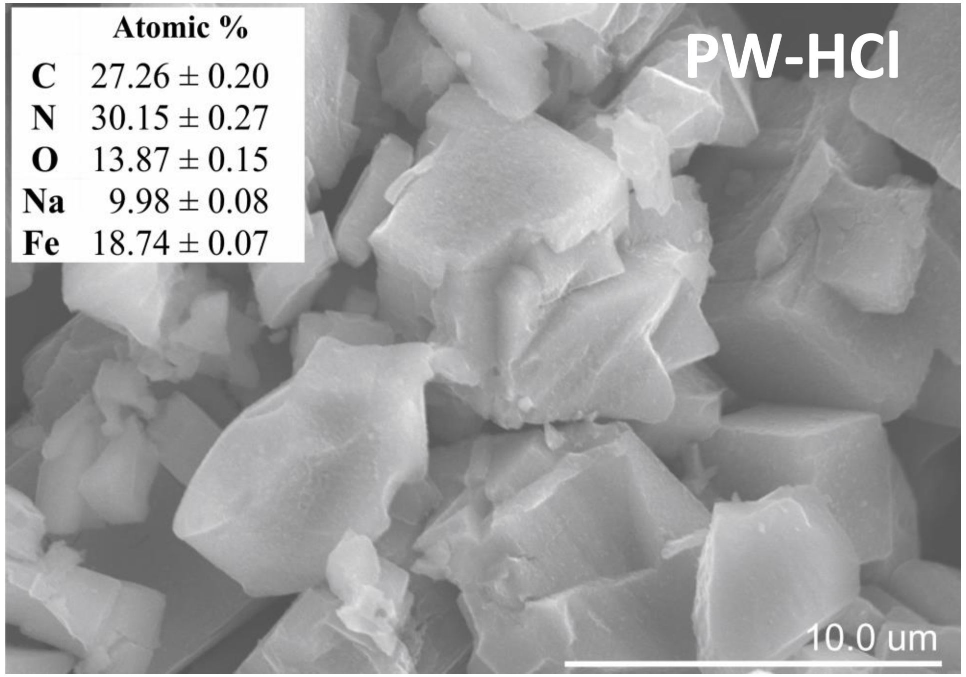


Fig. 6. Fragments of 2D maps of diffraction patterns of the XRD cell with (a) PW-n, (b) PW-140, (c) PW-160 and (d) PW-200 electrodes and corresponding voltage profiles during charge and subsequent discharge cycles with a current rate of 0.05 C, 0.1 C, 0.25 C versus sodium.

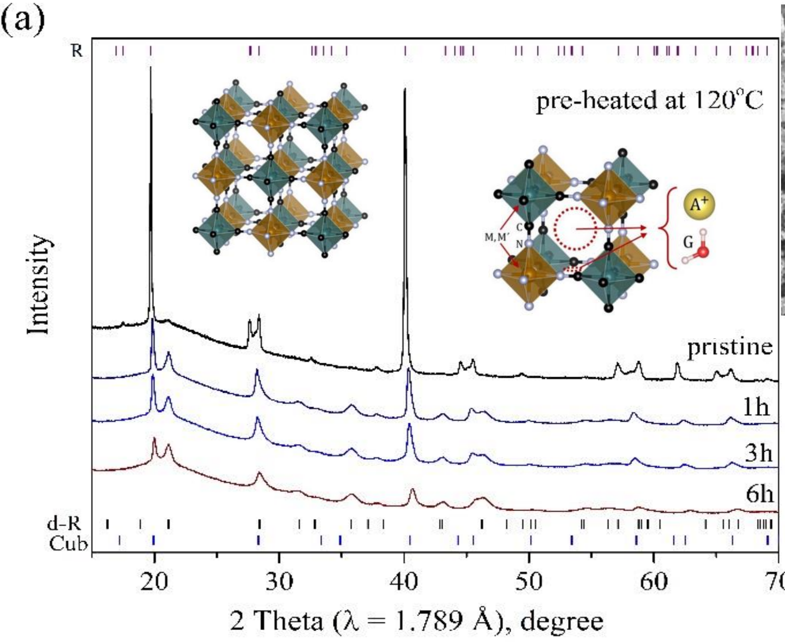
Table S1. Results of Rietveld analysis for the PW@PANI and PW_HCl powders.

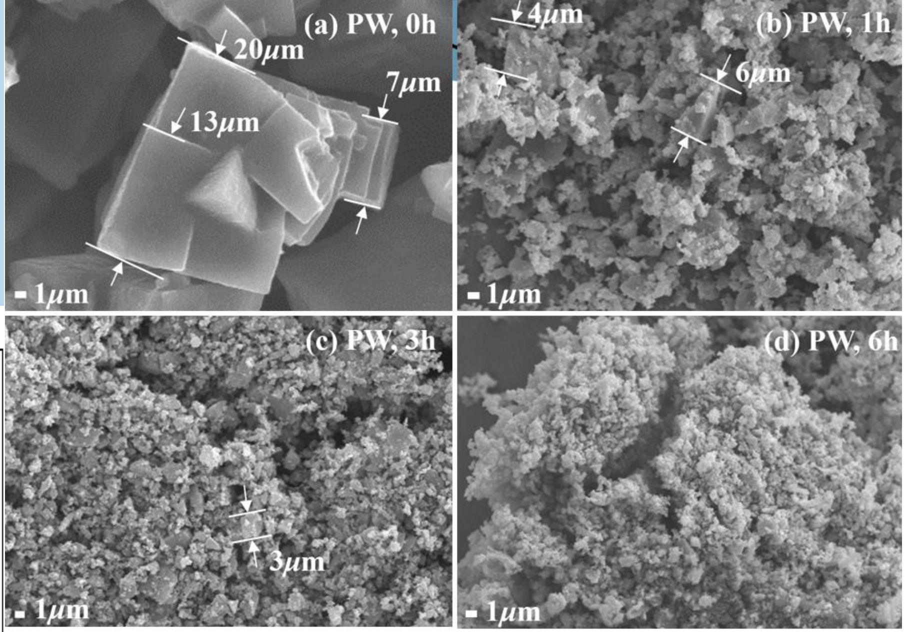
	PW@PANI	**PW_HCl**	
	cubic phase, sp. gr. *Fm*-3*m*	cubic phase 1, sp. gr. *Fm*-3*m*	cubic phase 2, sp. gr. *Fm*-3*m*
Volume content, %	100	77	23(6)
a, Å	10.2846(5)	10.3227(5)	10.279(6)
Na content	1.11(2)	0.95(16)	1.10(20)
Rwp, %	2.19	1.39	

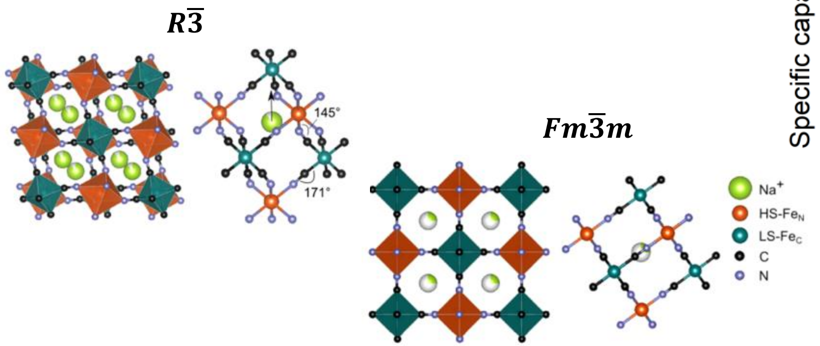


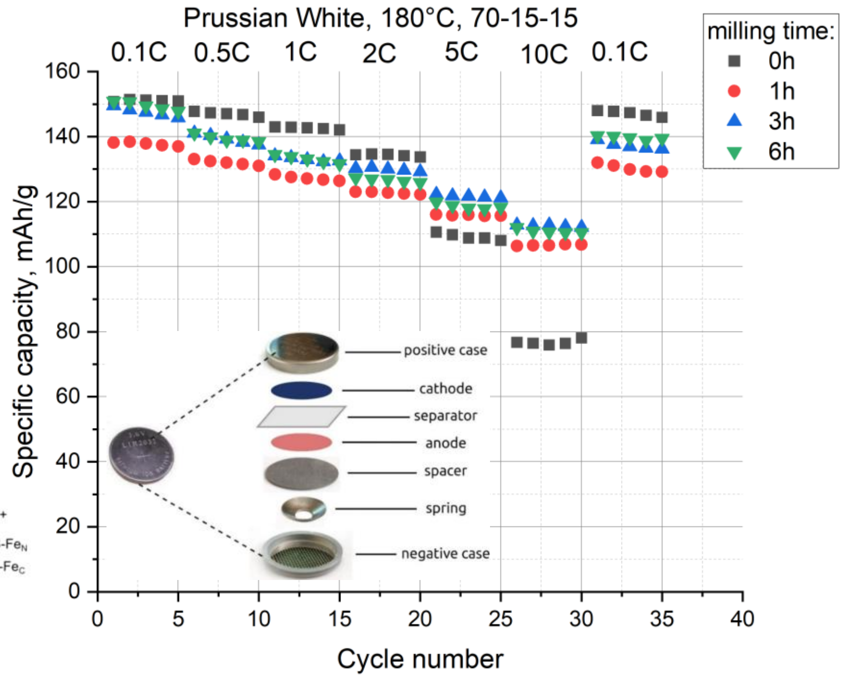


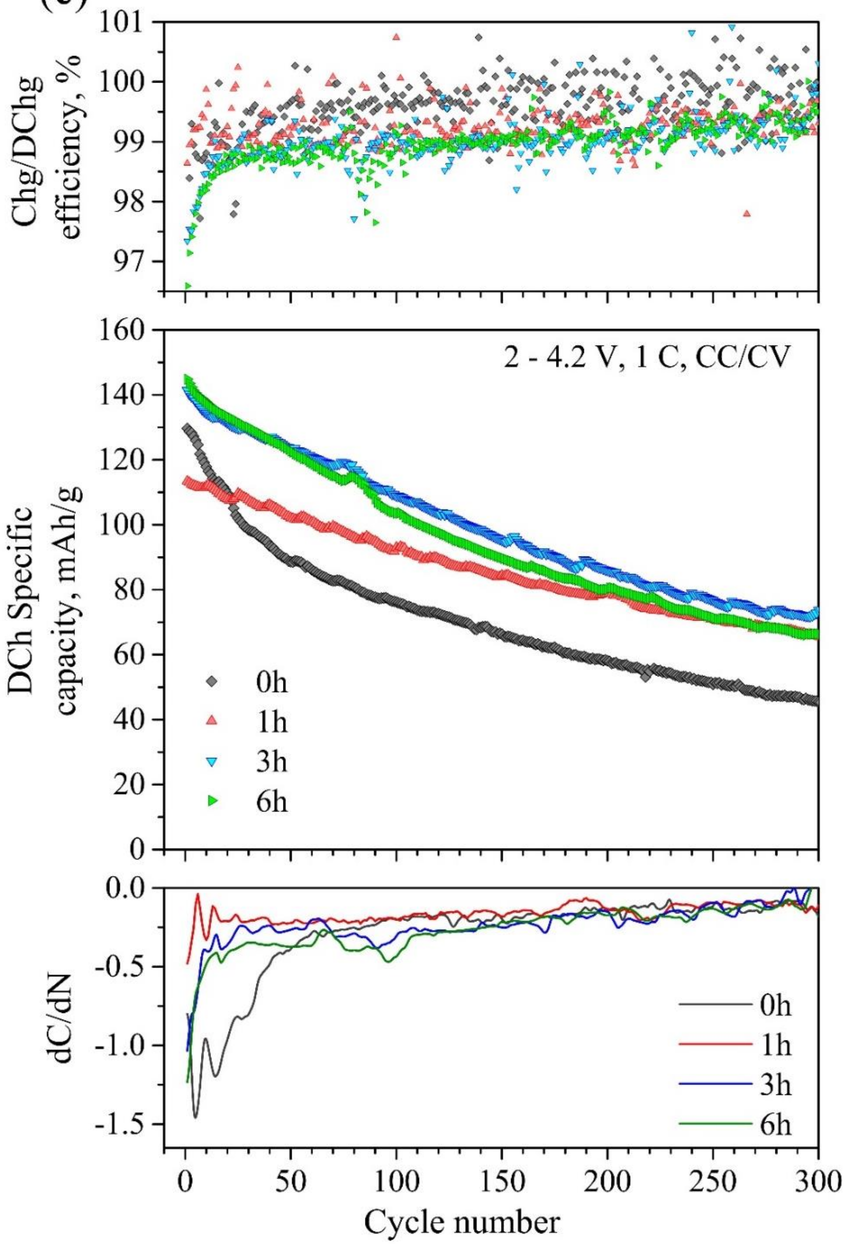
Microstructure modification of the Prussian White cathode material and its effect on the electrochemical performance of sodium-ion batteries











Samoylova, N. Y., Donets, M. E., Vasin, R. N., Sumnikov, S. V., Korneeva, E. A., Sohatsky, A. S., ... & Kolyshkin, N. A. (2025).
Correlation between structure, microstructure and electrochemical properties of Prussian white cathode material for sodium-ion batteries. Nano Research (Q1, IF=9.6).