LXXV International Conference
«NUCLEUS – 2025. Nuclear physics and elementary particle physics. Nuclear physics technologies» 1/07/25 → 6/07/25

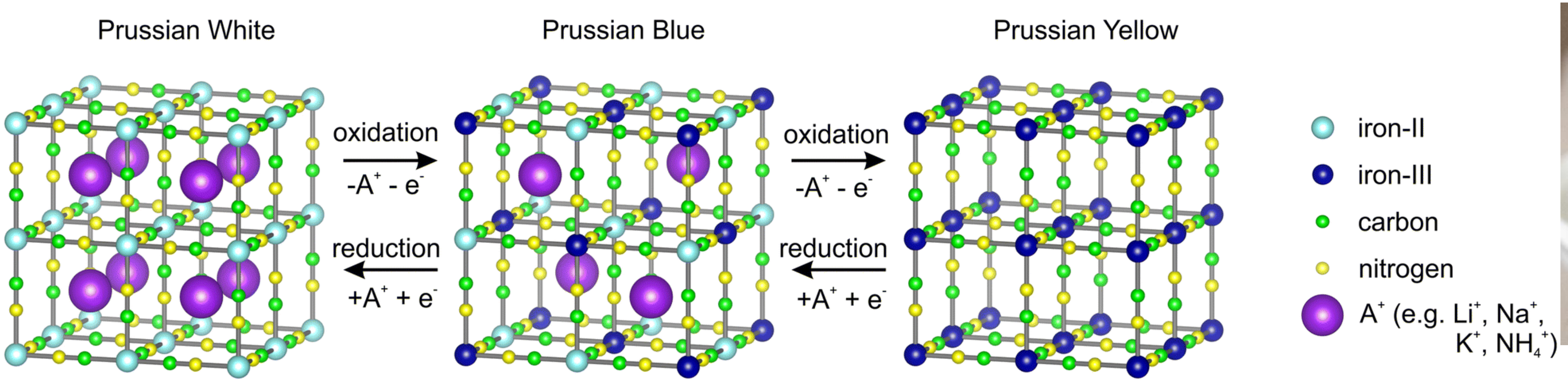
Session 6: Neutron and synchrotron research and infrastructure for its realization

MICROSTRUCTURE MODIFICATION OF THE PRUSSIAN WHITE CATHODE MATERIAL AND ITS EFFECT ON THE ELECTROCHEMICAL PERFORMANCE OF SODIUM-ION BATTERIES

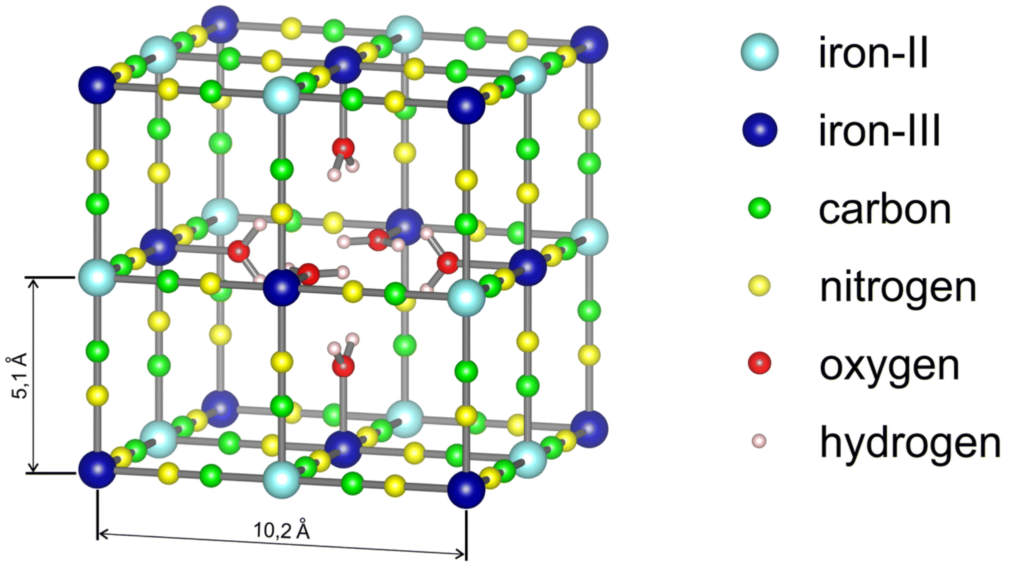
M. E. Donets, R. N. Vasin, S. V. Sumnikov,
E. A. Korneeva, N. Yu. Samoylova

Joint Institute for Nuclear Research, Dubna, Russia

Perspective cathode materials: Prussian Blue and its analogues

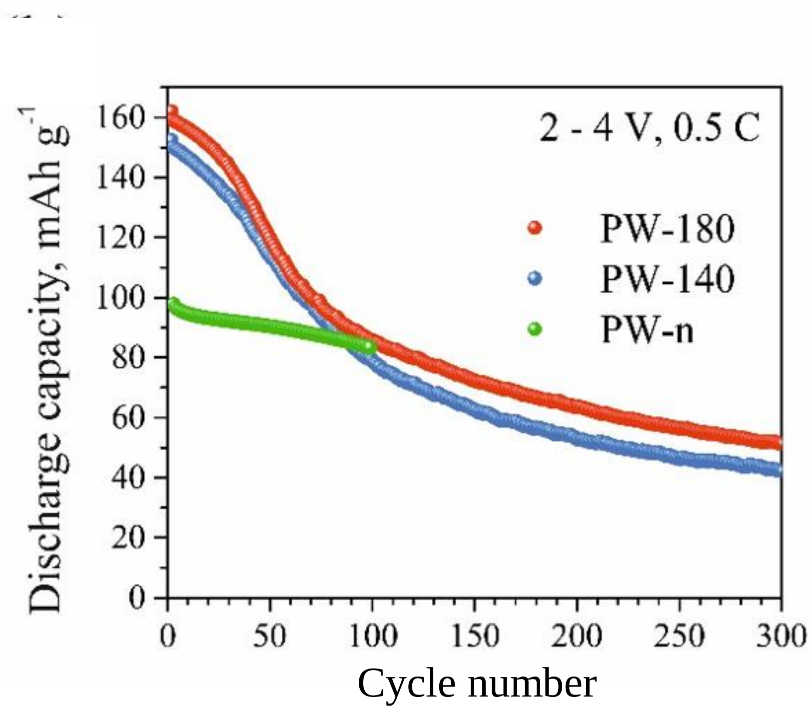


$Na_2Fe^{II}[Fe^{II}(CN)_6]$ $NaFe^{III}[Fe^{II}(CN)_6]$ $Fe^{III}[Fe^{III}(CN)_6]$

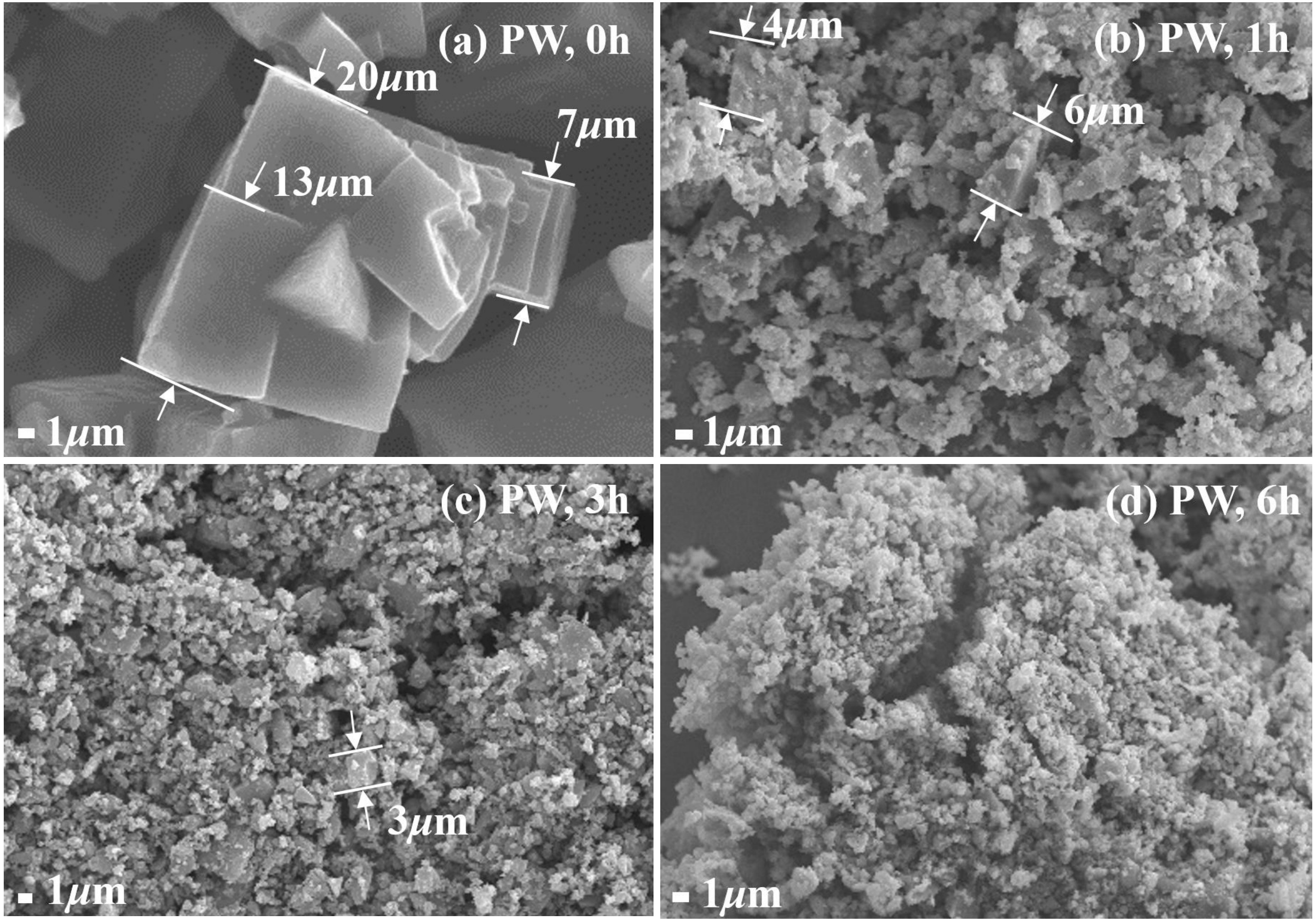


$Na_2Fe[Fe(CN)_6]_{1-y}\square_y \cdot mH_2O$

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



SEM-images of pristine and milled Prussian White samples



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

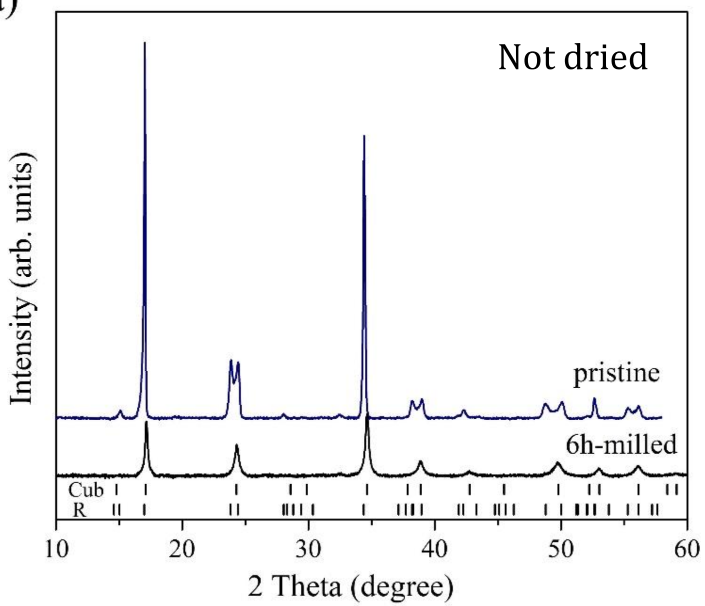
$\square$ - $Fe(CN)_6$ vacancies

y – number of $Fe(CN)_6$ vacancies

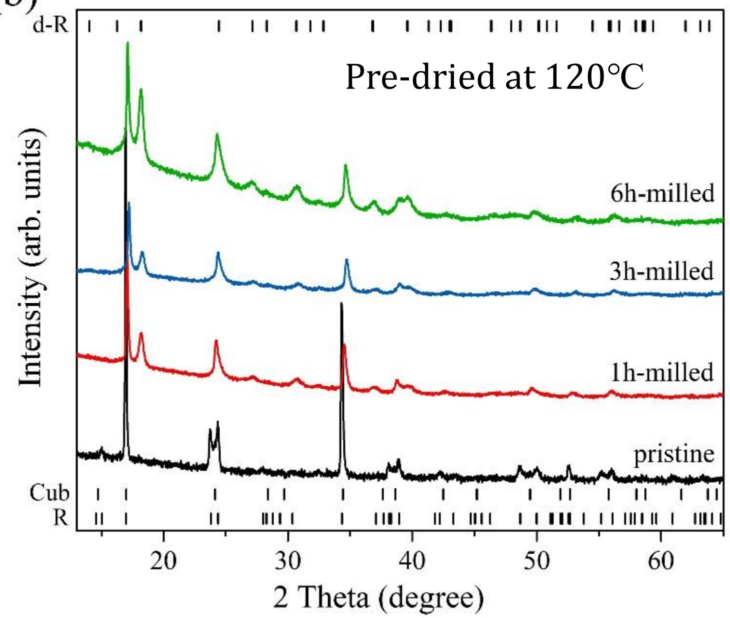
- Pristine PW material has cubic morphology.
- Milling program in planetary mill:
  1h, 3h and 6h, ω=600rpm.
- Milling was carried out with acetone to obtain a more homogenized sample.
- The destruction of cube-shaped particles occurs as milling time increases.

Structural study. XRD spectra of pristine and milled PW samples. Phase analysis.

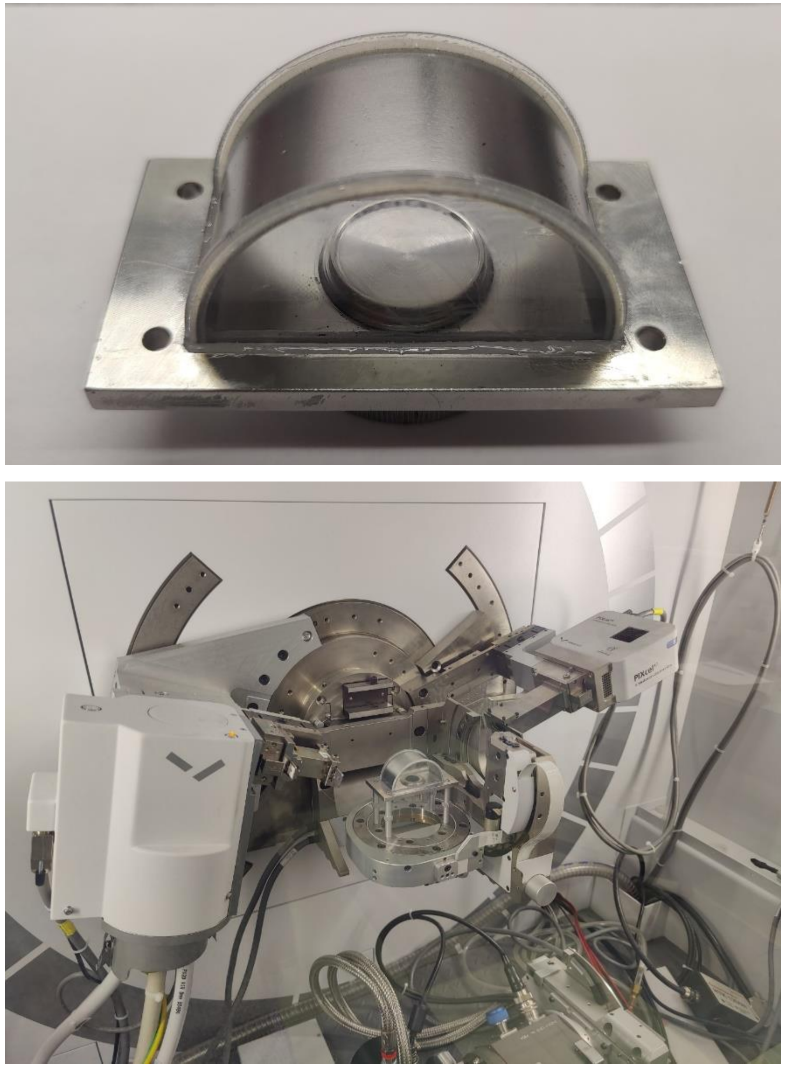
(a)



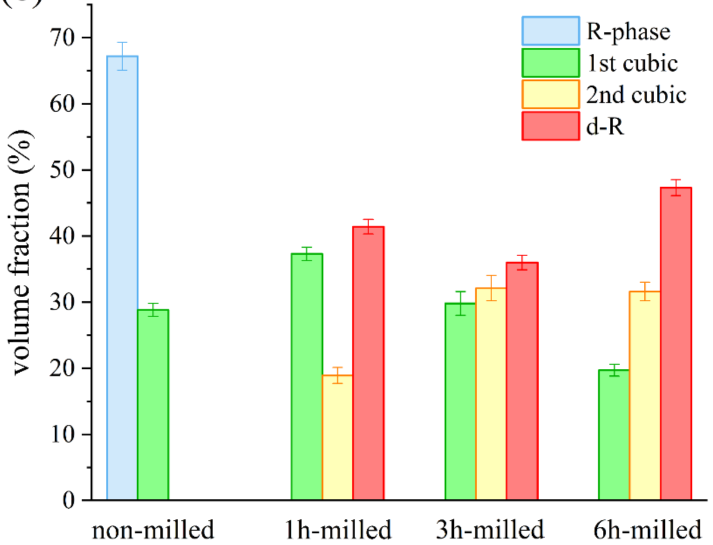
(b)



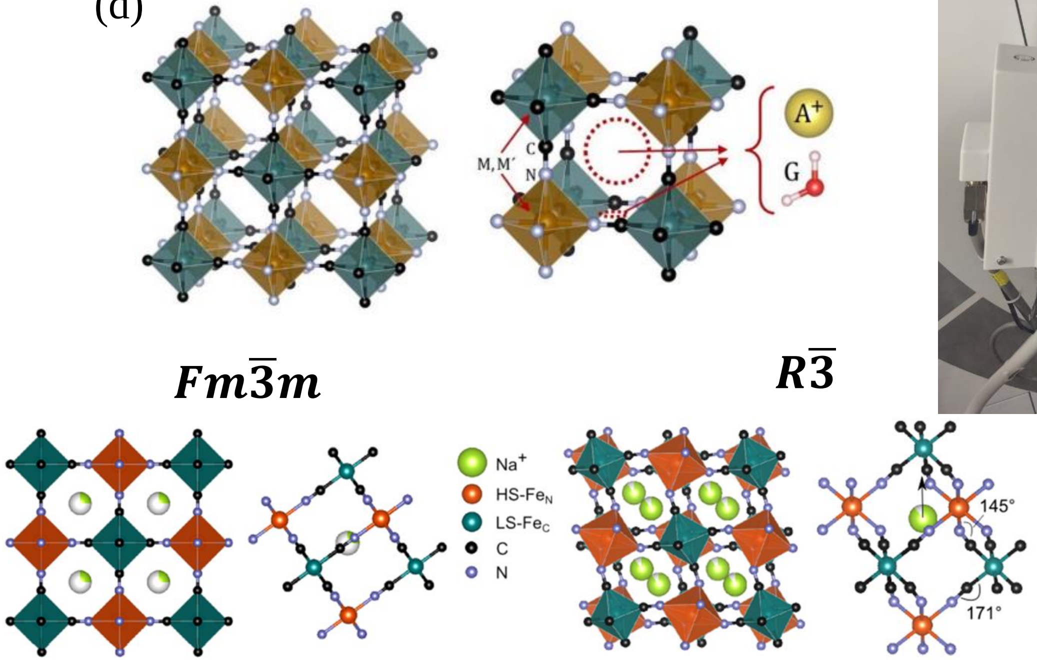
(e)



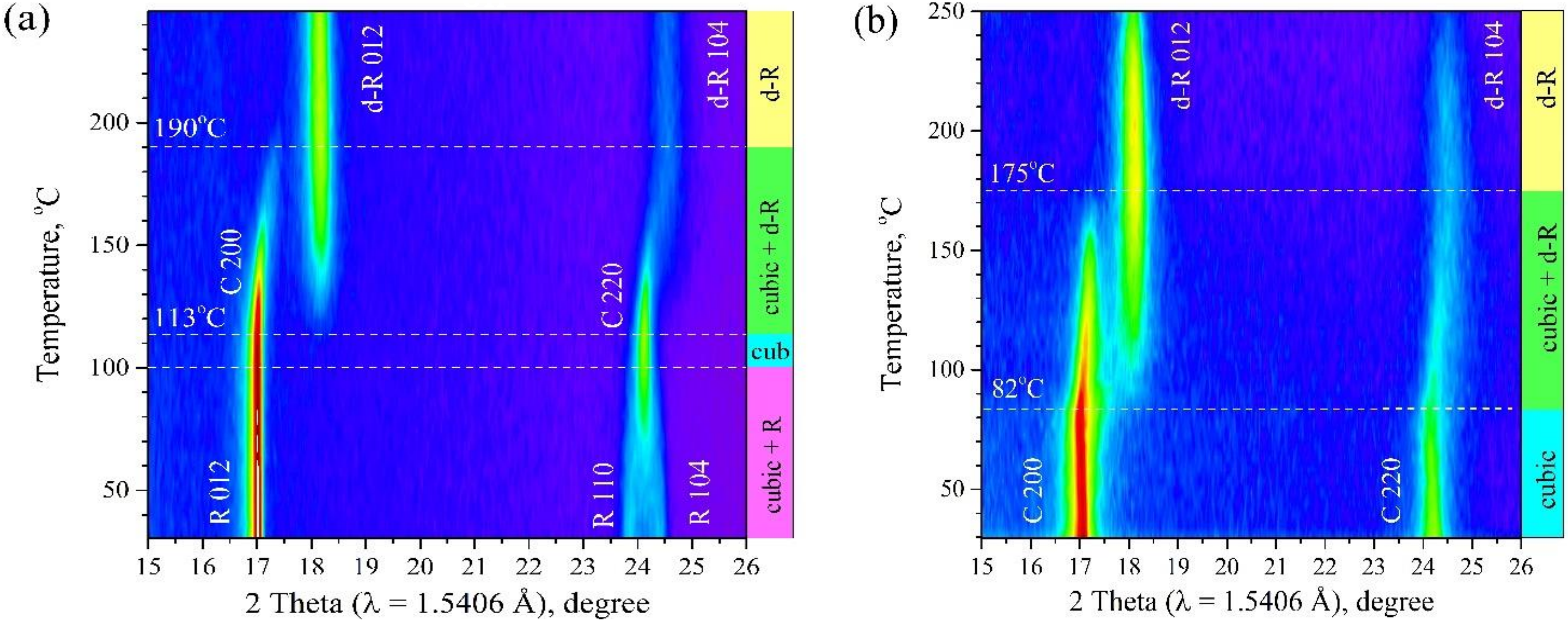
(c)

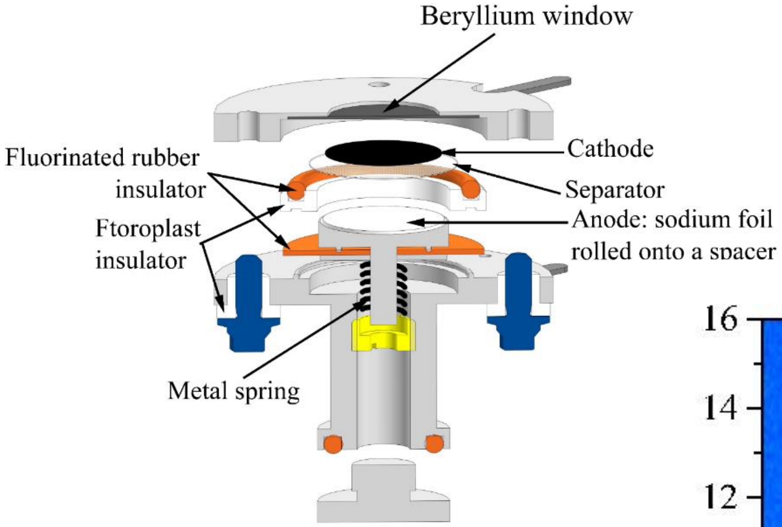


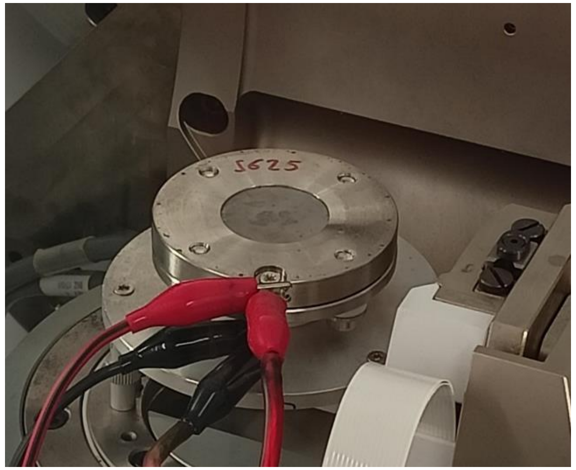
(d)

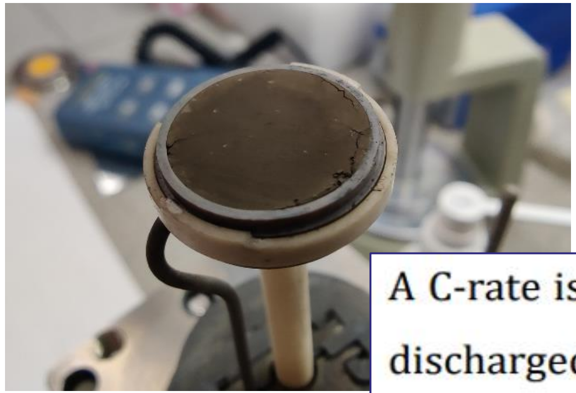


2D evolution of XRD patterns from the pristine PW and 6h-milled PW powders during heating up to 250ºC in vacuum

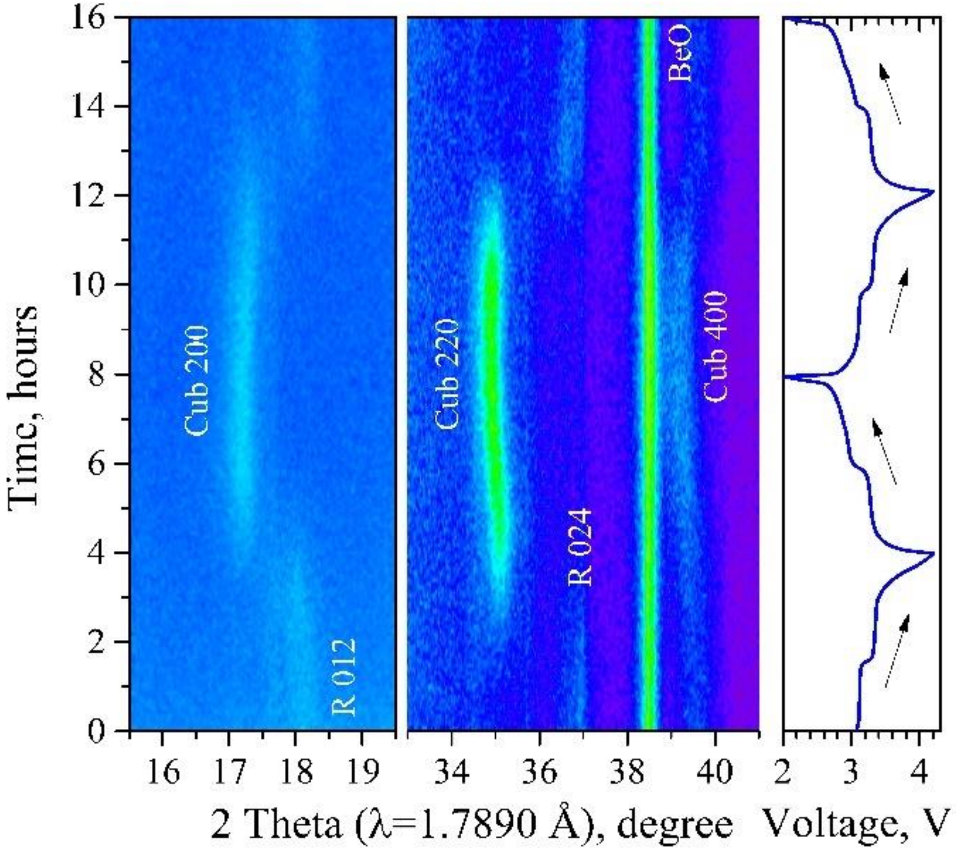






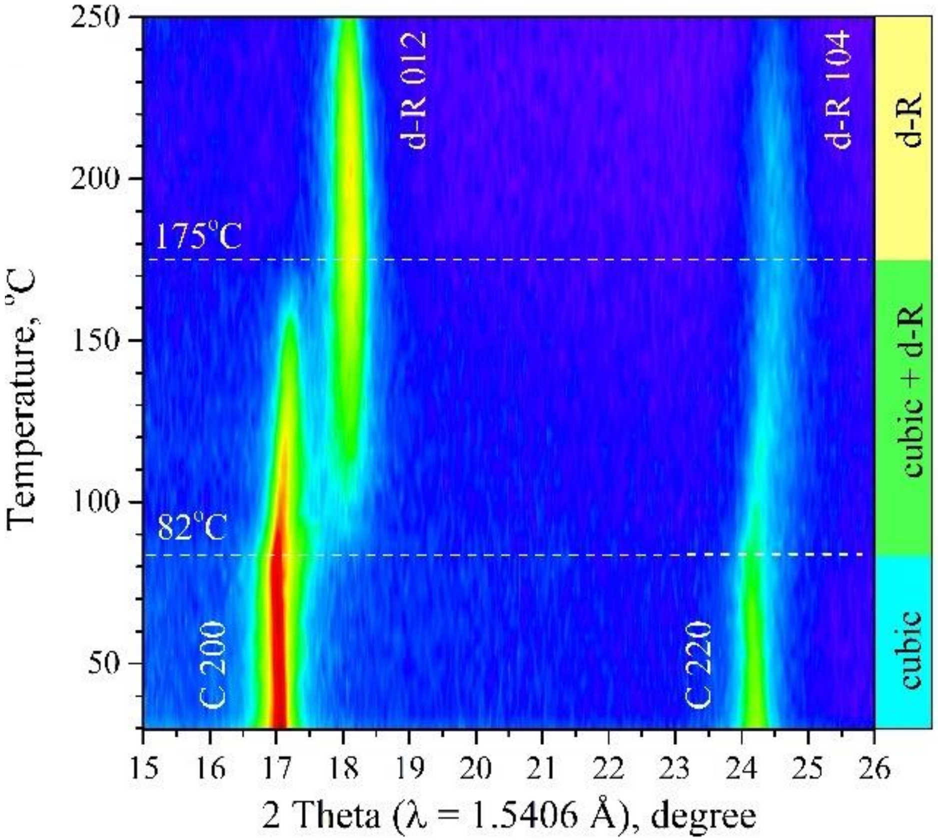


2D map plot of X-ray diffraction patterns of the 6h-milled PW electrode during electrochemical cycling versus sodium at 1C rate



PW/KetjenBlack/PVDF: 70/15/15

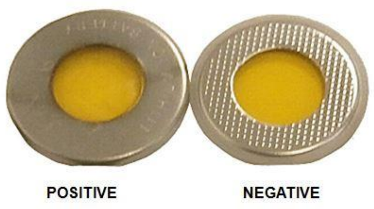
2D evolution of XRD patterns from the 6h-milled PW powders during heating up to 250ºC in vacuum

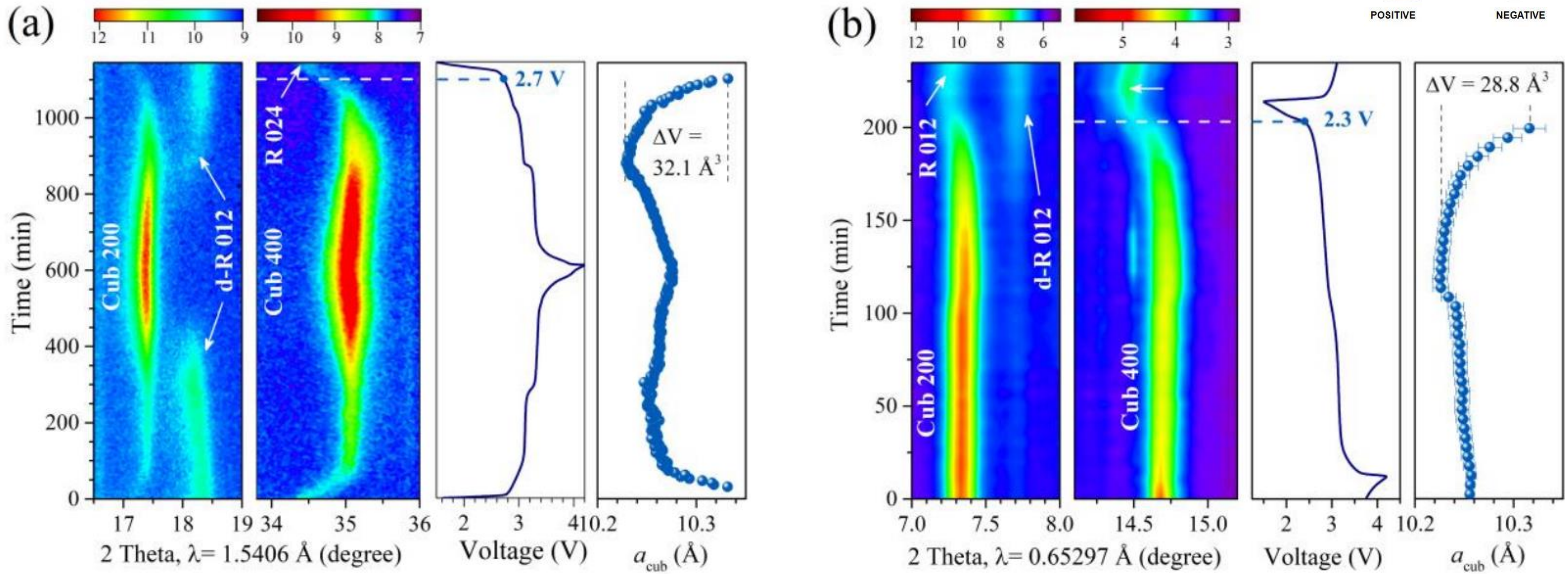


A C-rate is a measure of the rate at which a battery is discharged relative to its maximum capacity.

A 1C rate means that the discharge current will discharge the entire battery in 1 hour.

Fragment of 2D map plot of X-ray diffraction patterns of the electrodes





(a) with non-milled PW material measured during charge/discharge at 0.1C rate

(b) with 3h-milled PW material measured during discharge at 0.25C rate

STM station of the Kurchatov Synchrotron Radiation Source (NRC Kurchatov Institute, Moscow, Russia)

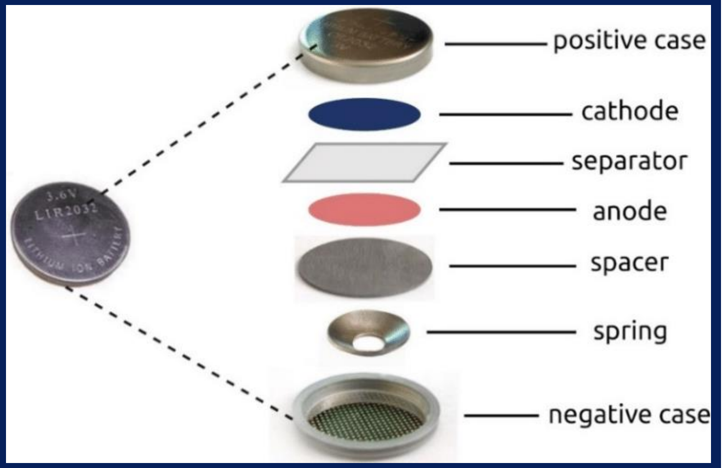
Electrochemical study

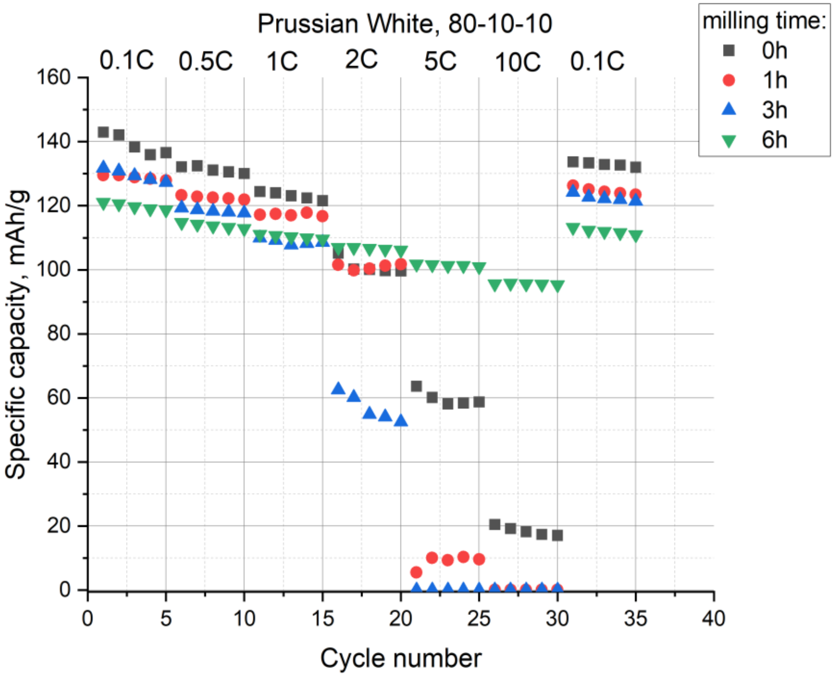
PW/KetjenBlack/PVDF:

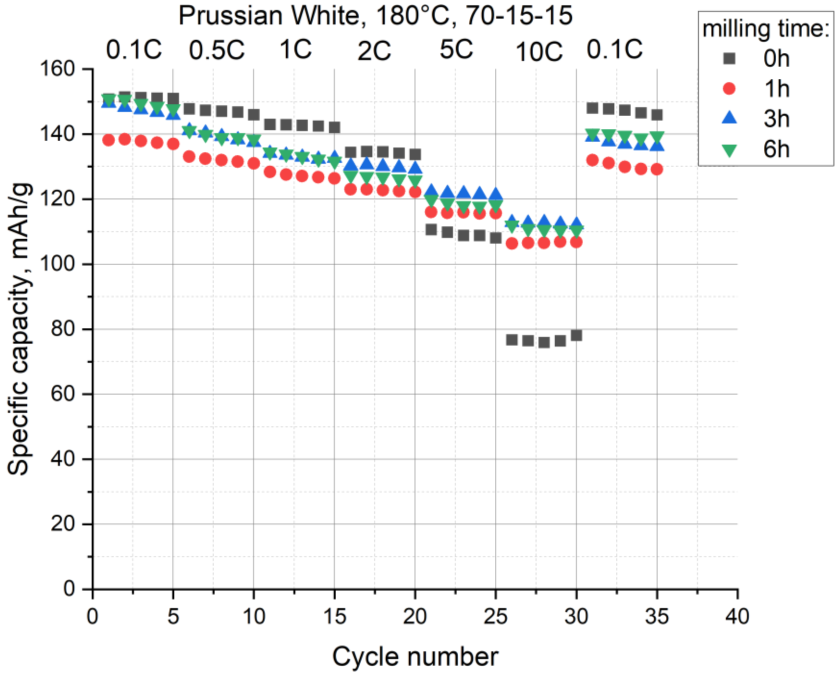
(a)– 70/15/15

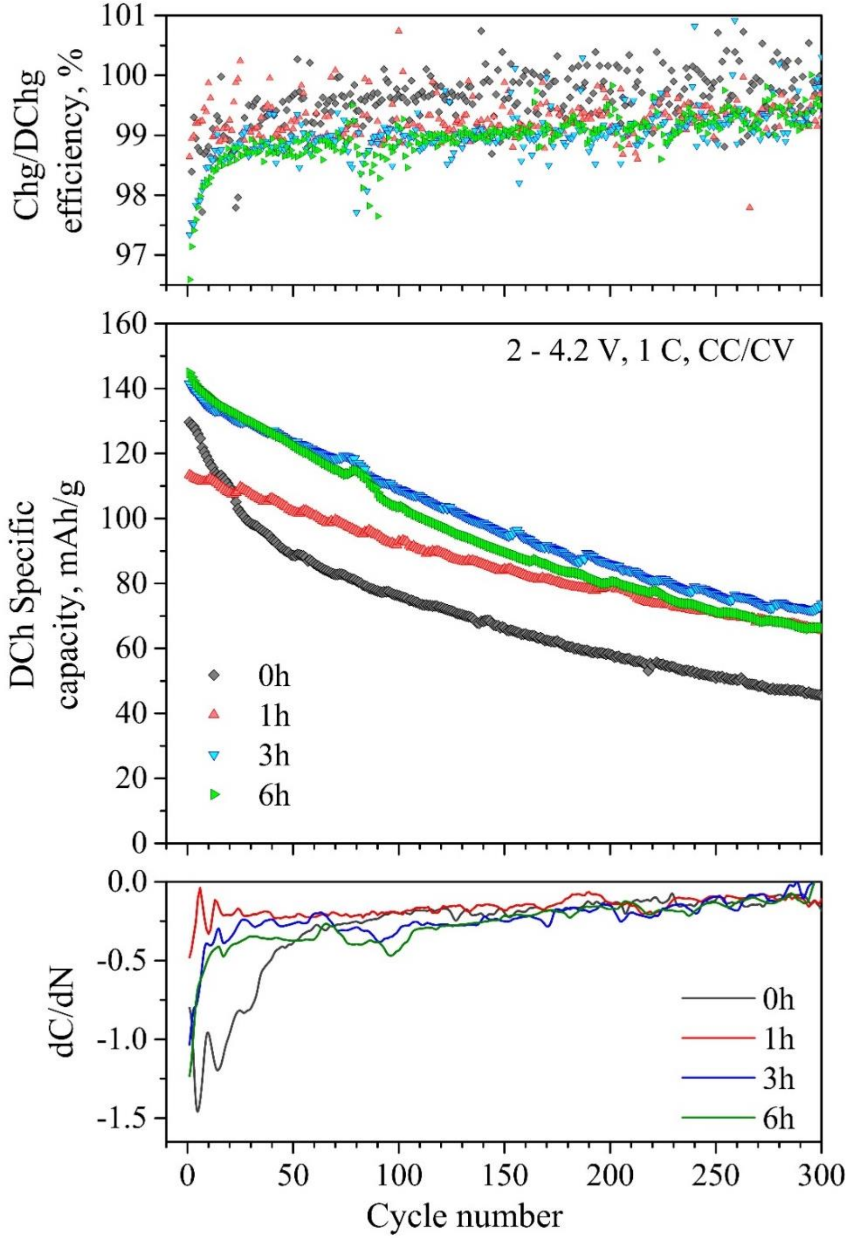
(b)– 80/10/10

(c)– 70/15/15









Results and conclusions

Samoylova NY, Donets ME, Vasin RN, et al. Correlation between structure, microstructure and electrochemical properties of Prussian white cathode material for sodium-ion batteries. *Nano Research*, 2025, 18(4): 94907280. https://doi.org/10.26599/NR.2025.94907280

1. The original PW contains several structural phases:
   rhombohedral phase (“R”) ~ 55%
   cubic phase ~40%
   small amount of another rhombohedral phase (dehydrated “d-R”) ~ 4%

2. d-R phase fraction: $\begin{cases} \approx 52\% \text{ for 1h and 3h of milling} \\ \approx 65\% \text{ for 6h of milling} \end{cases}$

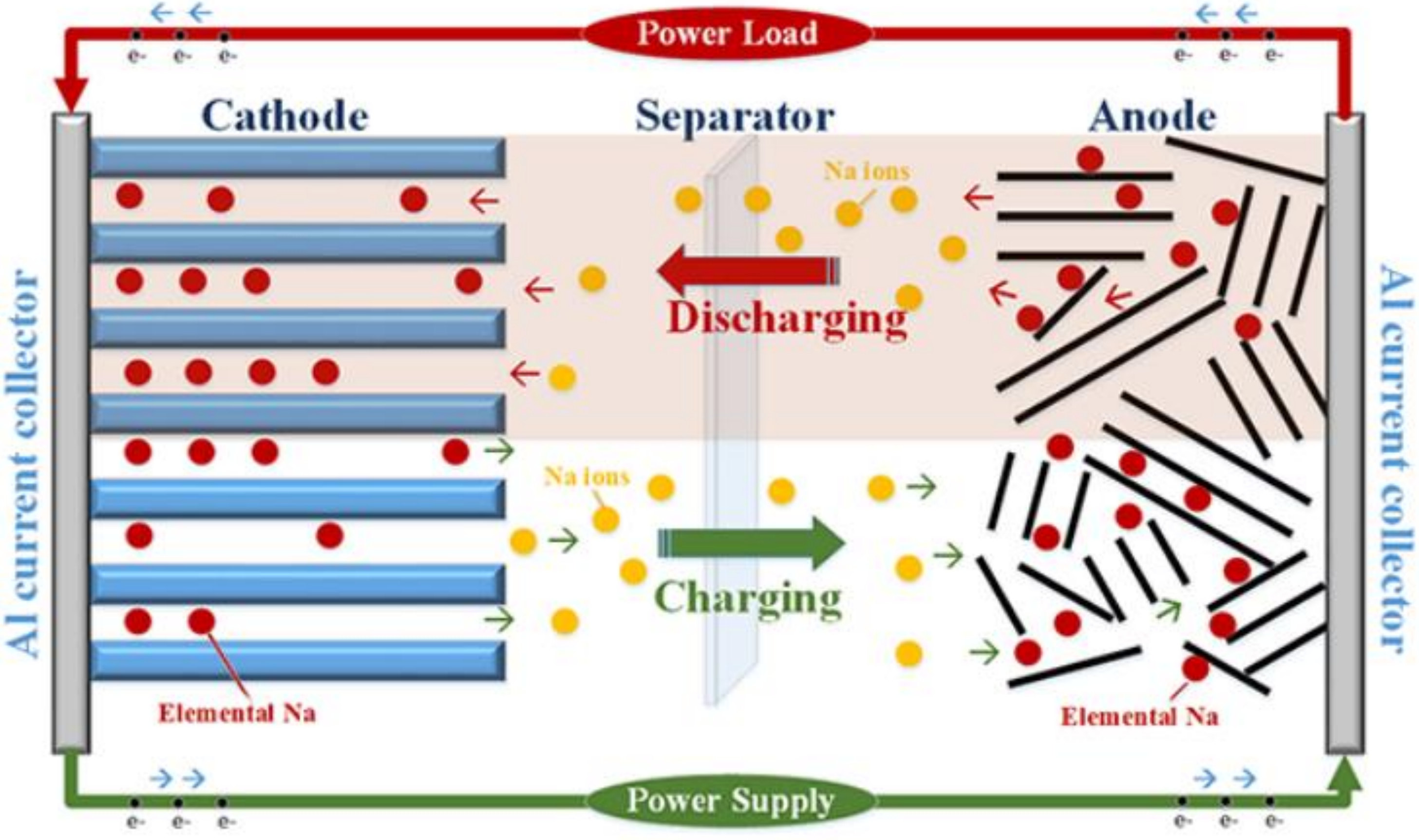
3. As a result of the release of water from the structure, the cubic phase transforms into the dehydrated rhombohedral phase.

4. The initial capacity of an electrode based on PW 0h at a rate of 0.1C is 150 mAh/g, compared to a theoretical capacity of 170.8 mAh/g.

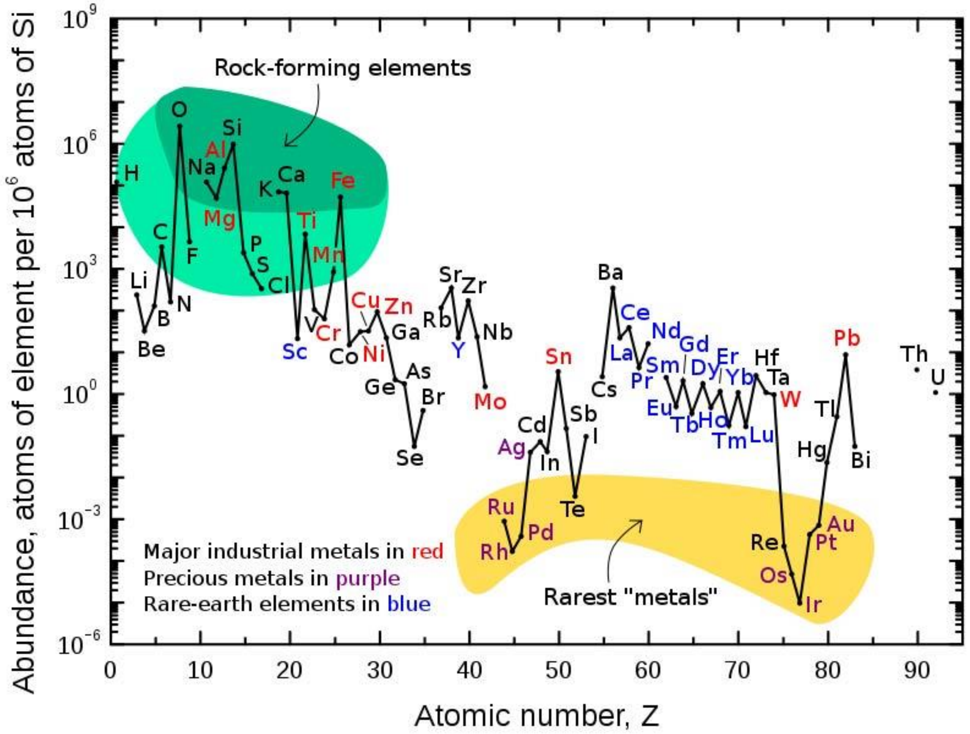
5. 0.1C – 2C: electrodes based on milled PW powders show a capacity slightly lower than the capacity of the original, irregularly depending on the grinding time.
   5C, 10C: milled PW electrodes show a consistently higher capacity compared to the original PW electrode - the longer the milling time, the higher the capacity.

Thank you for your kind attention!

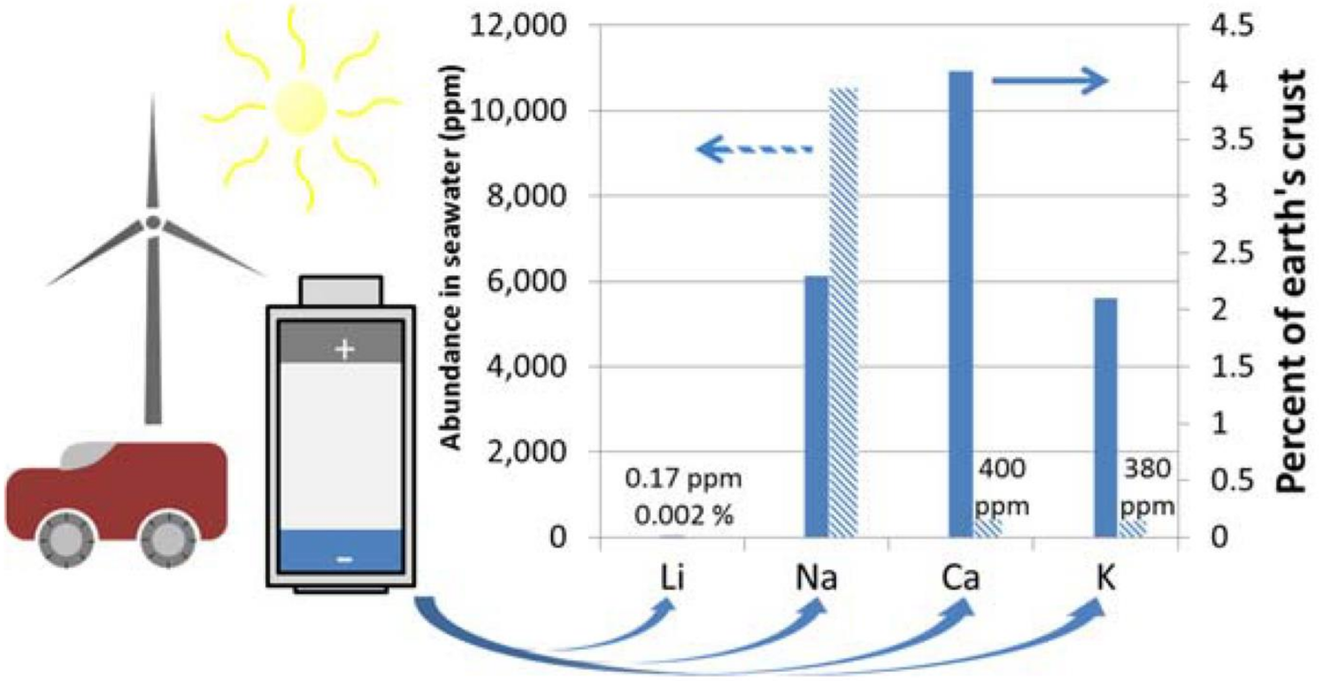
Na-ion battery working principle



Terrestrial abundance of elements



DOI: 10.1093/nsr/nwab050

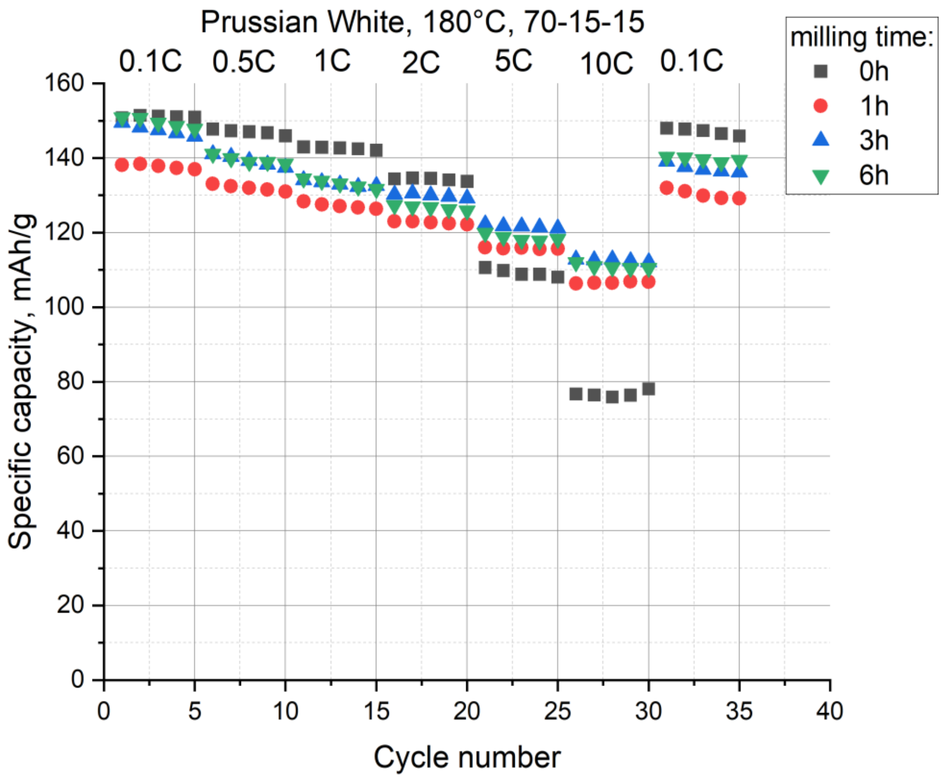


DOI: 10.3390/batteries6010011

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.

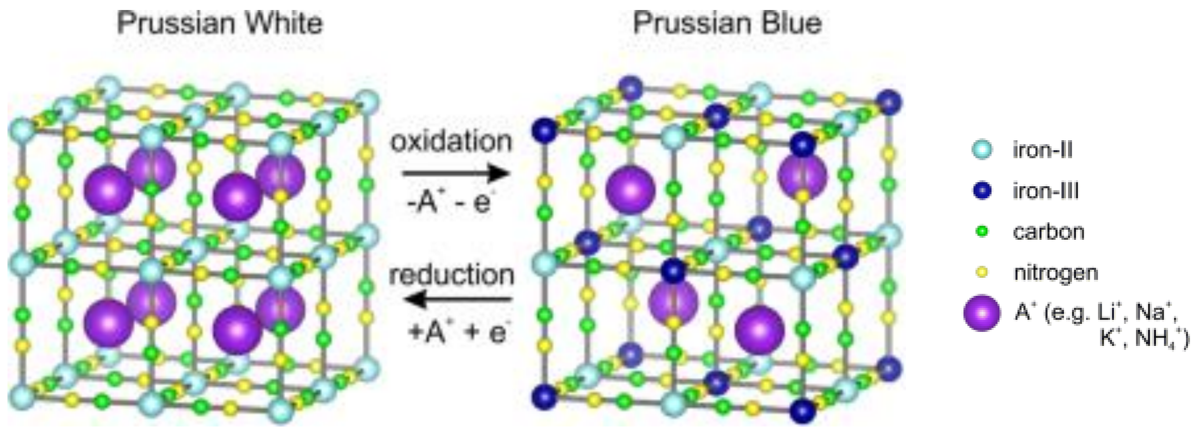


Prussian Blue and analogues

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

$\square$ - $Fe(CN)_6$ vacancies

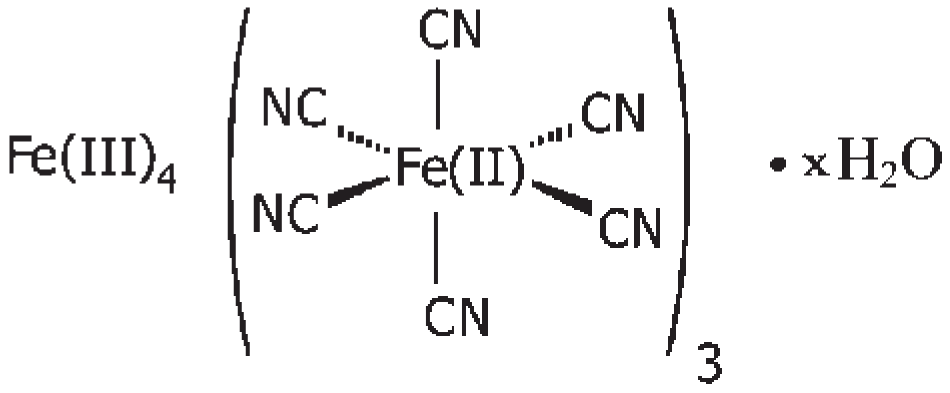
y – number of $Fe(CN)_6$ vacancies



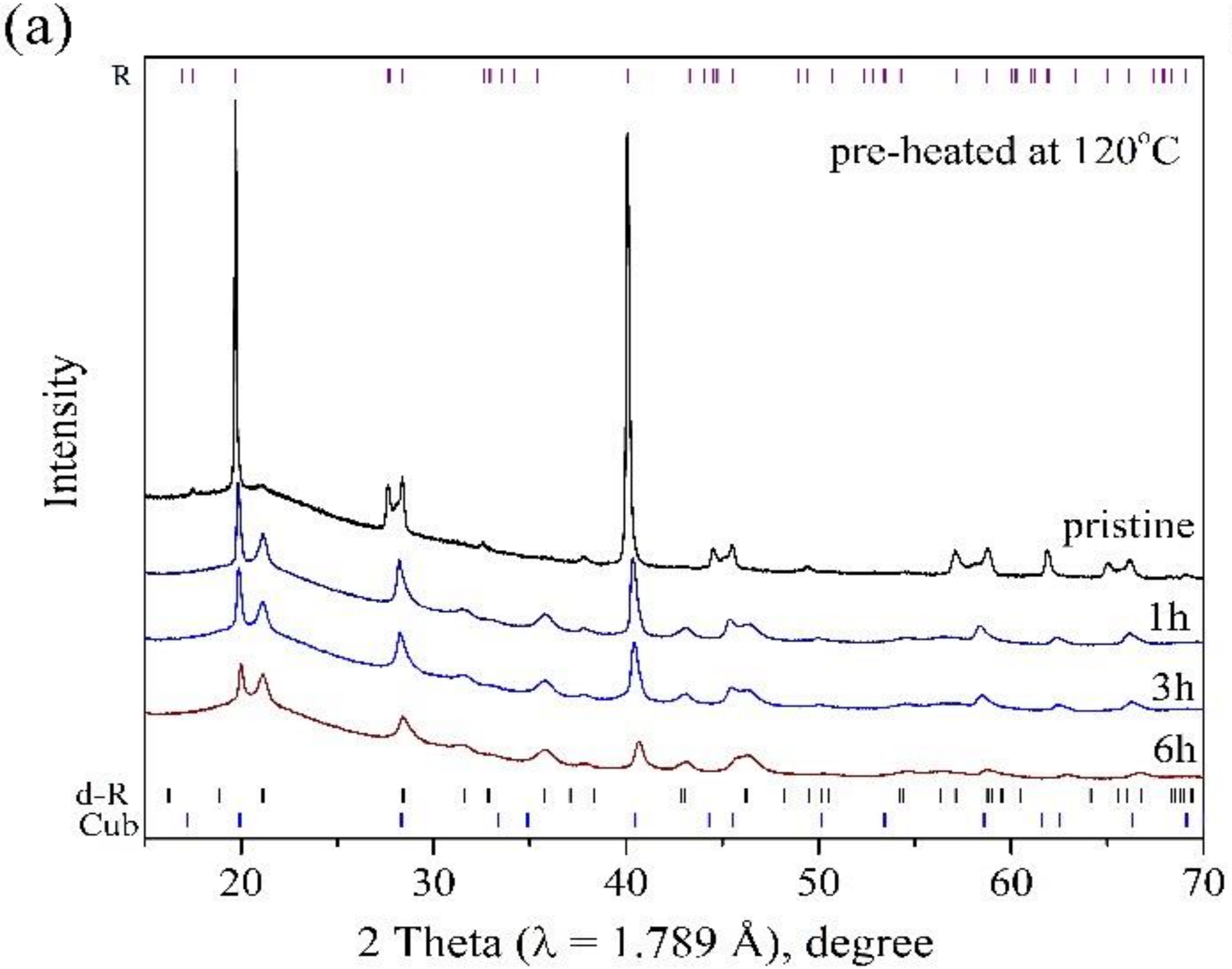
PBAs are a class of transition metal cyanides, and their general chemical formula can be expressed as $A_xM[M'(CN)_6]_{y\square 1-y}\cdot mH_2O$ ($0 \leq x \leq 2$, $y < 1$), where A is an alkali metal element (Li, Na, and K); M is a transition metal element such as Fe, Mn, Co, Ni, and Cu; M′ is usually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

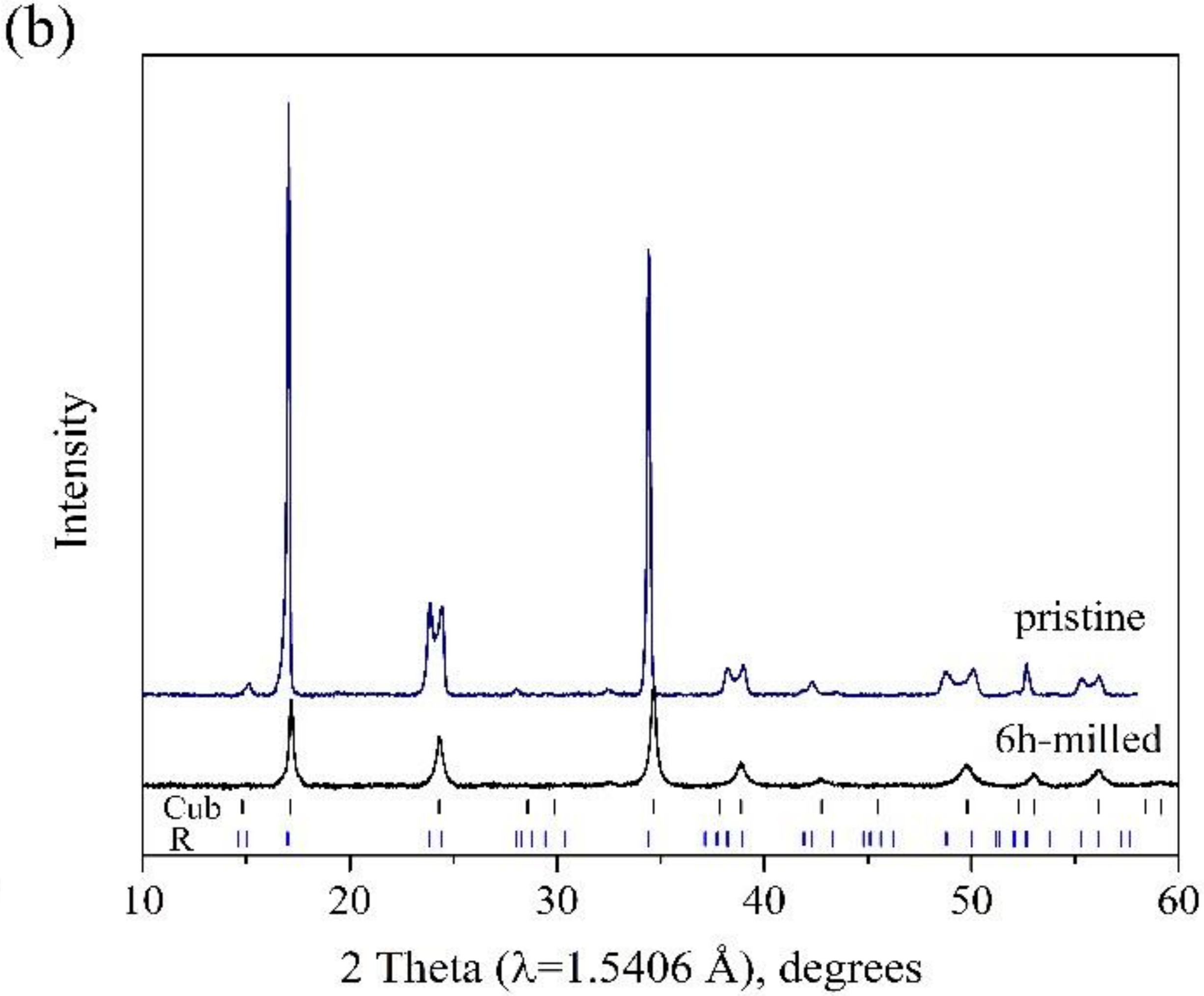
$Fe_4[Fe(CN)_6]_3\cdot x\,H_2O$

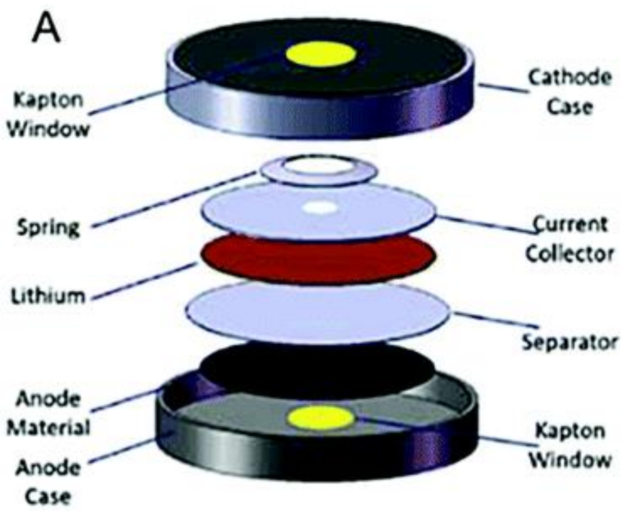
Prussian blue is an inorganic complex salt containing two differently charged iron ions Fe^{2+} and Fe^{3+} and the negatively charged hexacyanoferrate ions $[Fe(CN)_6]^{4-}$

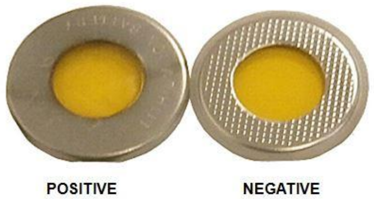


Structural study. XRD spectra of pristine and milled PW samples. Phase analysis.





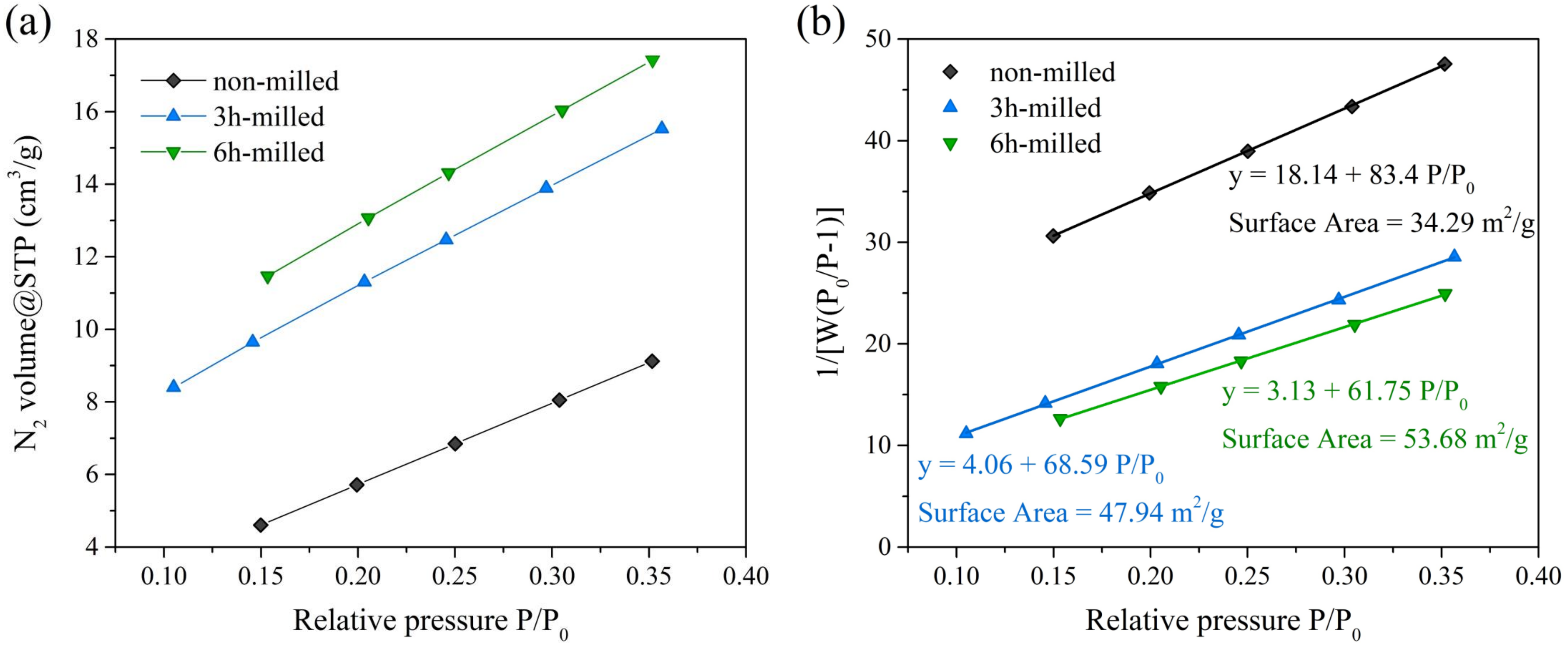

A
Kapton Window
Cathode Case
Spring
Current Collector
Lithium
Separator
Anode Material
Anode Case
Kapton Window


POSITIVE
NEGATIVE

Results of Rietveld analysis for the pristine, 1h-milled, 3h-milled, 6h-milled amd 6h-milled PW.

	PW powders				
	Pristine, dried	1h-milled, dried	3h-milled, dried	6h-milled, dried	6h-milled, not dried
“R” phase, sp. gr. $R\bar{3}$					
Vol. content, %	67.2±2.4				
a, Å	7.474±0.001				
c, Å	17.647±0.002				
<Cryst. size>, Å	> 2000				
“d-R” phase, sp. gr. $R\bar{3}$					
Vol. content, %		41.4±1.1	36.0±1.1	47.3±1.2	
a, Å		6.560±0.002	6.565±0.002	6.567±0.001	
c, Å		18.928±0.008	18.956±0.009	18.911±0.007	
<Cryst. size>, Å		344±12	341±5	350±8	
First cubic phase, sp. gr. $Fm\bar{3}m$					
Vol. content, %	28.8±1.0	37.3±1.0	29.8±1.8	19.7±0.9	36.4±4.0
a, Å	10.415±0.001	10.391±0.001	10.360±0.001	10.348±0.001	10.374±0.002
<Cryst. size>, Å	> 2000	> 2000	1620±110	1670±210	1630±410
Second cubic phase, sp. gr. $Fm\bar{3}m$					
Vol. content, %		18.9±1.2	32.1±1.9	31.6±1.4	61.3±6.7
a, Å		10.323±0.003	10.346±0.003	10.314±0.003	10.399±0.003
<Cryst. size>, Å		469±17	190±7	173±15	250±20
Impurity NaO_2, sp. gr. $Fm\bar{3}m$					
Vol. content, %	4.0±0.4	2.4±0.3	2.1±0.3	1.4±0.3	2.3±0.8
a, Å	5.510±0.003	5.515±0.004	5.519±0.005	5.502±0.005	5.502±0.005
Overall refinement quality					
R[illegible], %	1.37	1.03	1.04	1.03	1.55

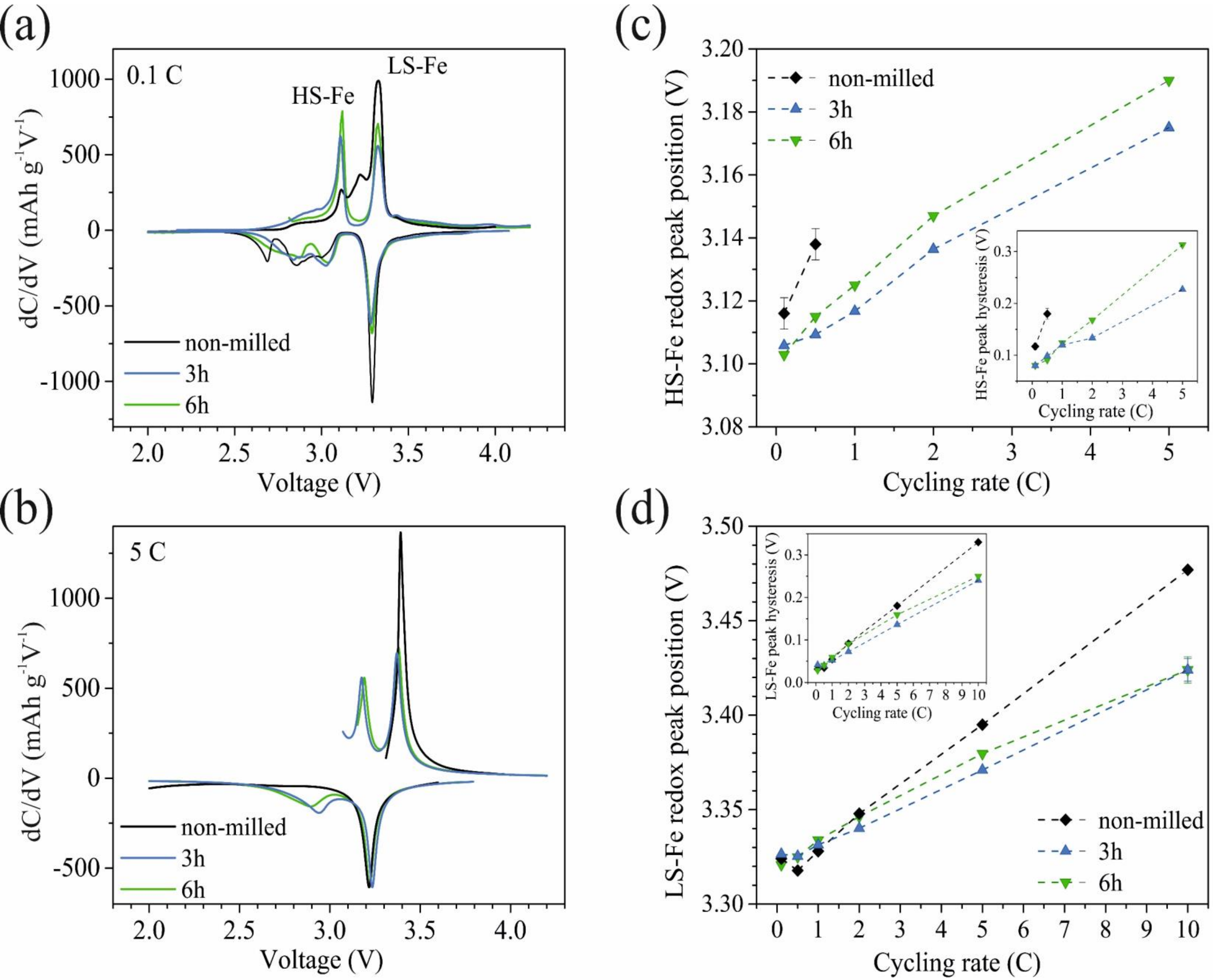
(a) Volume of nitrogen absorbed on the PW samples' surface vs. relative pressure P/P_0.
(b) BET plots with the linear fits for the non-milled and milled PW samples.

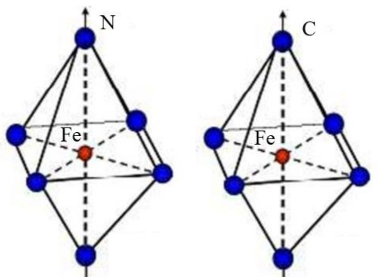


The surface area of the pristine and milled samples was determined from gas absorption experiments using BET analysis.

The ball milling increases the surface area of the powder from 34.29 m^2/g for the non-milled sample to 47.94 and 53.68 m^2/g for the 3h- and 6h-milled samples, respectively.

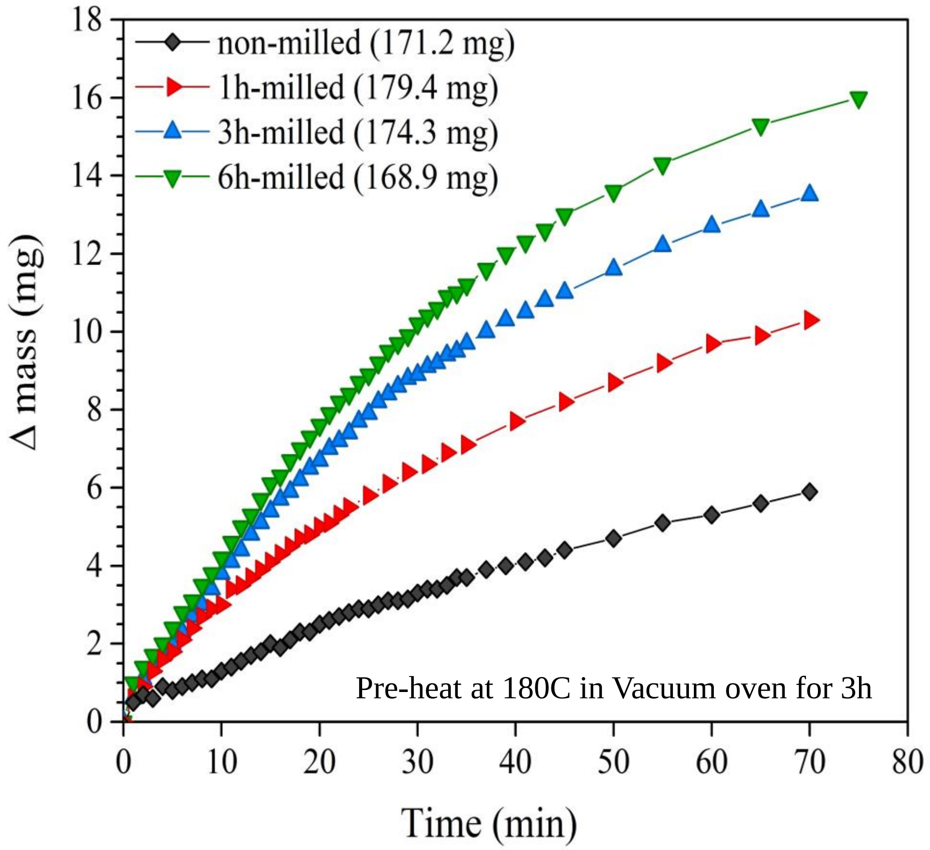
dC/dV для электродов 70/15/15 во время циклирования, положения HS-Fe и LS-Fe пиков





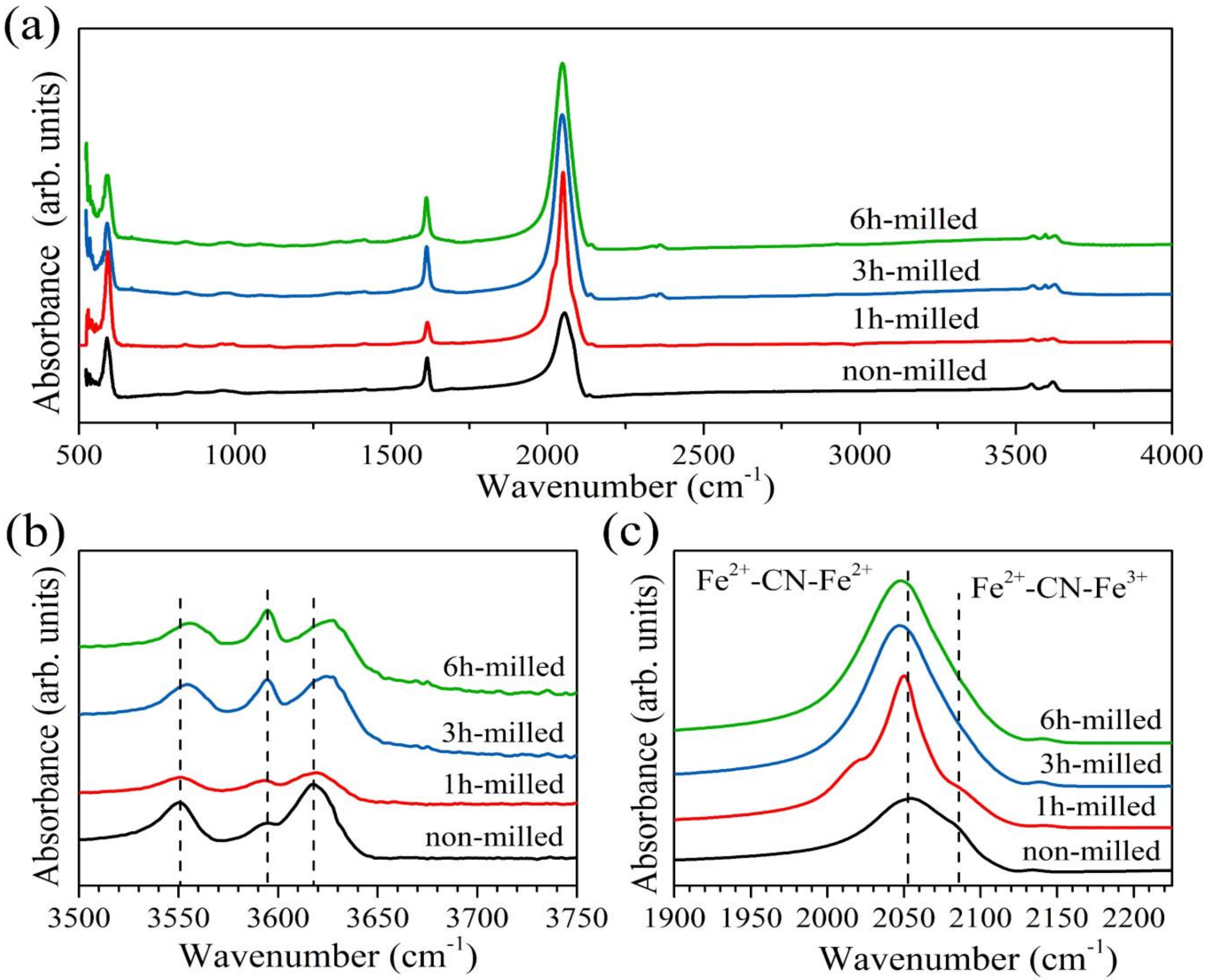
- 2 стадии интеркаляции Na+ в структуру: ~3.1V низковольтное плато, ОВР HS-Fe2+/3+ в октаэдрах FeN_6 ~3.3V высоковольтное платно, ОВР LS-Fe2+/3+ в октаэдрах FeC_6
- Большая разница м/у исходным и перемолотыми PW в интенсивностях пика HS-Fe
- Мех. перемол: 1) облегчает диффузию Na+; 2) увеличивает площадь поверхности с не окисленным HS-Fe → интенсивный пик ОВ потенциала во время электрохим. циклирования.
- Псевдоемкостной эфф-т (накопление зарядов катионов от фарадеевских процессов на поверхности) контролирует ОВ процесс LS-Fe, способствует лучшему циклированию перемолотого материала на высоких скоростях.

Поглощение воды порошками PW



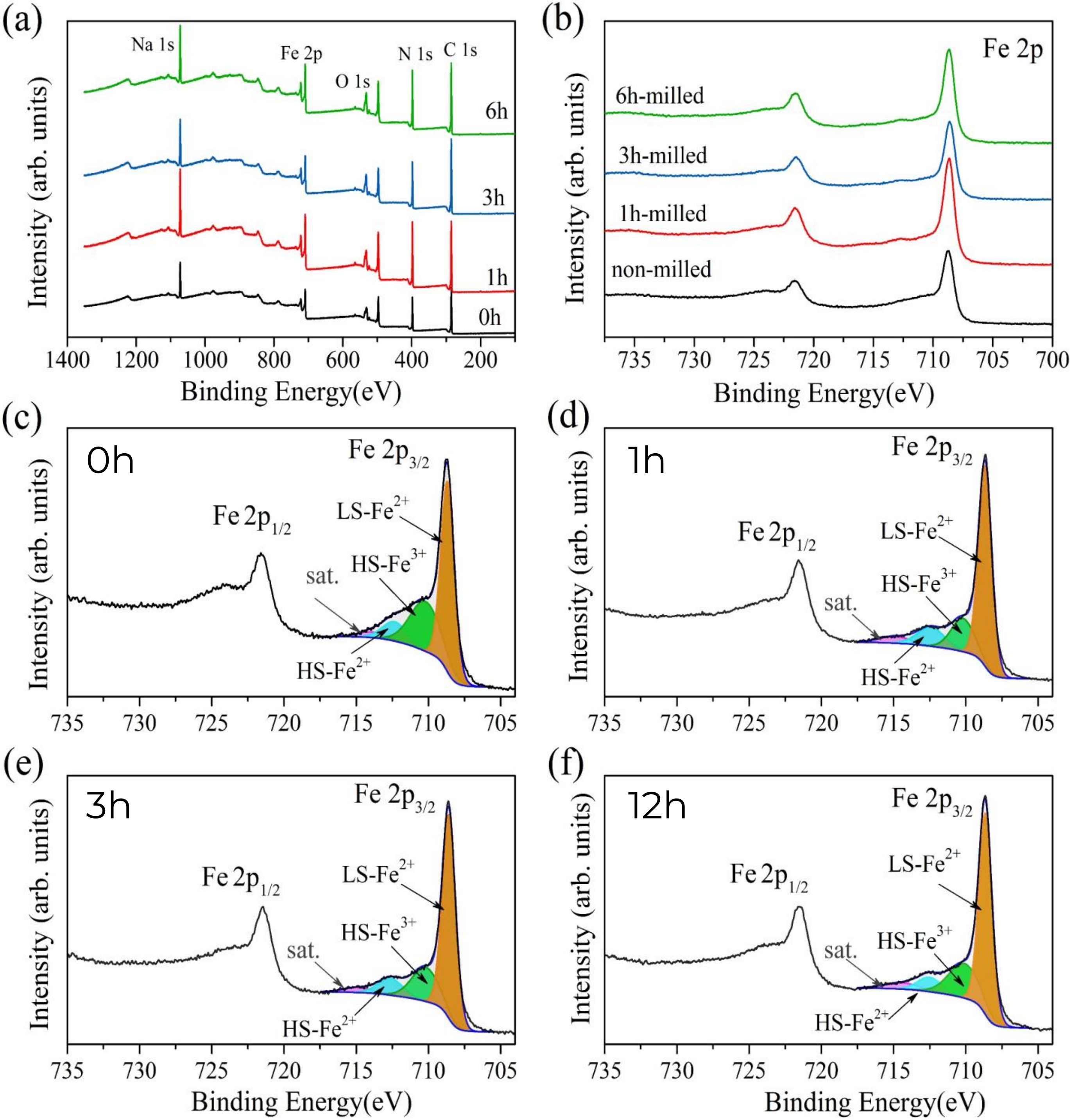
Масса поглощенной воды различными образцами порошка PW
при комнатной температуре и относительной влажности ≈ 30%

FTIR спектры исходного и перемолотых образцов PW при комнатной температуре



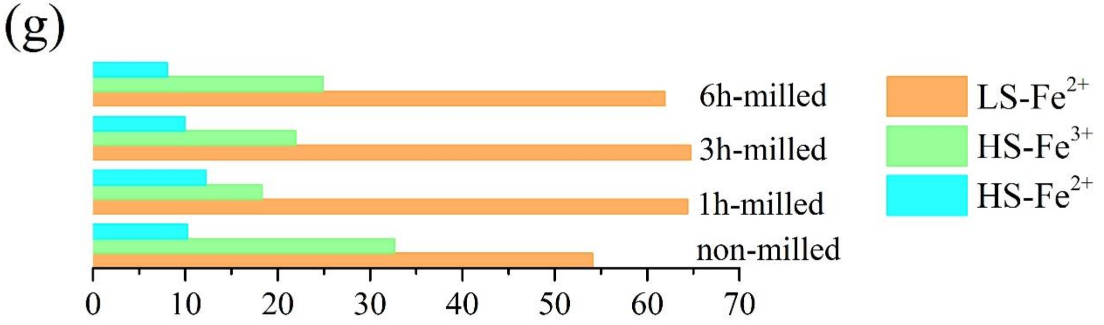
- Поглощение воды в процессе перемола → полоса поглощения υ(O─H) при 3500-3700 $см^{-1}$
- (b): Интенсивность υ(O─H) при 3595 $см^{-1}$ ↑ при t ↑
- Для PW 1ч, 3ч полосы 3551 $см^{-1}$ и 3618 $см^{-1}$, наблюдаемые в спектре PW 0ч, смещаются в сторону больших волновых чисел. => снижение степени окисления катионов Fe в системе.
- (c): υ(C≡N) при 2000-2100: характеристика эл. состояния PW, т.к. C≡N чувствителен к ст. ок. катионов Fe.
- Max. на 2050 $см^{-1}$ и плечо около 2080 $см^{-1}$ для PW 0ч – колебания υ(C≡N) => частичное окисление поверхности при длит. хранении.
- υ(C≡N) смещается в сторону меньших волновых чисел по мере t ↑ => восстановление Fe.

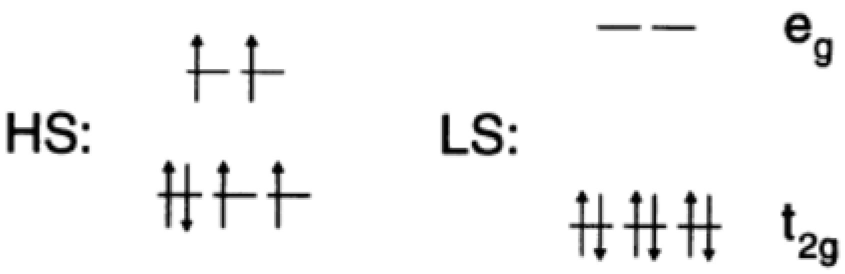
Перемол разрушает частицы PW, обнажая не окисленную поверхность, и => средняя степень окисления активной поверхности уменьшается.



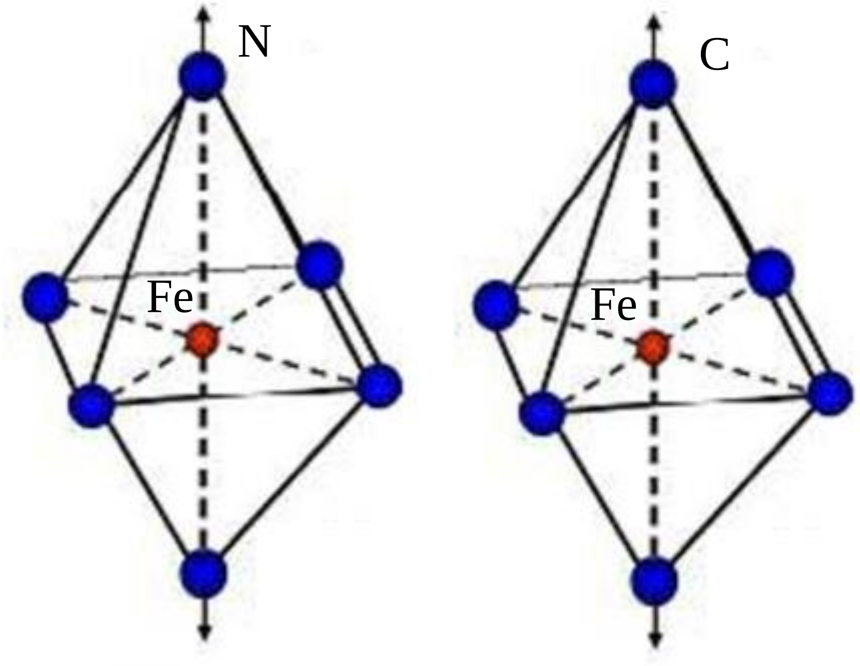
Спектры XPS порошков PW.

- **~708.6 эВ LS-Fe2+, ~710.5 эВ HS-Fe3+; ~712.5 эВ HS-Fe2+, ~714-714.9 эВ оксид железа.**
- **PW 0ч**: более высокое содержание HS-Fe3+ и более низкое LS-Fe2+ по сравнению с перемолотыми образцами.
- **Перемолотые PW**: доля HS-Fe3+ ↑ при ↑ t перемола.
- Диапазон энергий связи 710-716 эВ может быть отнесен к мультиплетам оксида железа.
- Оксиды железа могут существовать на поверхности частиц и вносить значительный вклад в сигнал XPS (зонд. ~10 нм) в то время, как на XRD и не было выявлено существенное количество оксидов железа в поверхностном слое (10-20 мкм).



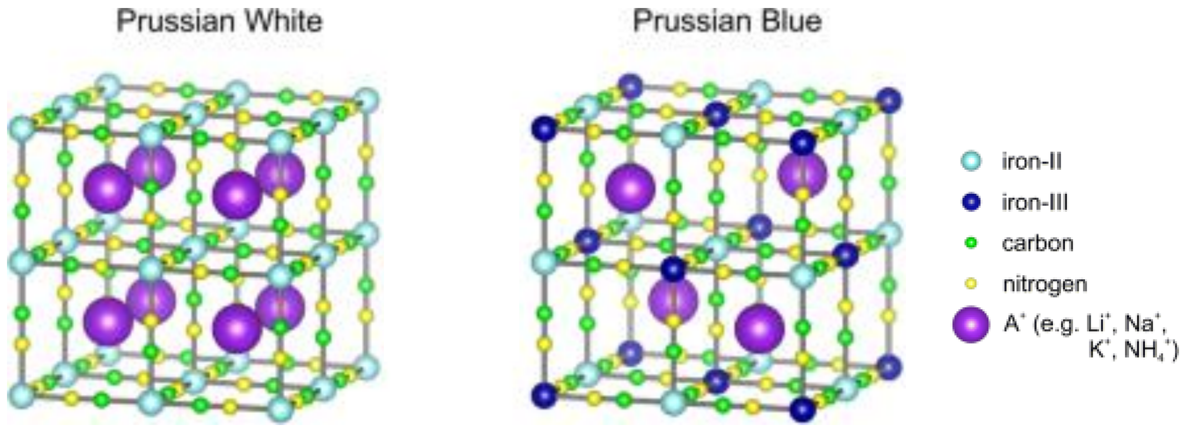


HS and LS configurations of a $3d^6$ system.



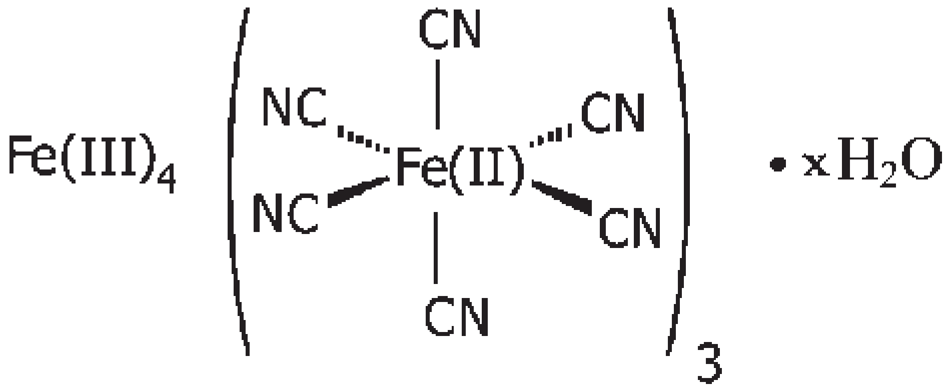
Prussian White and Prussian Blue

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

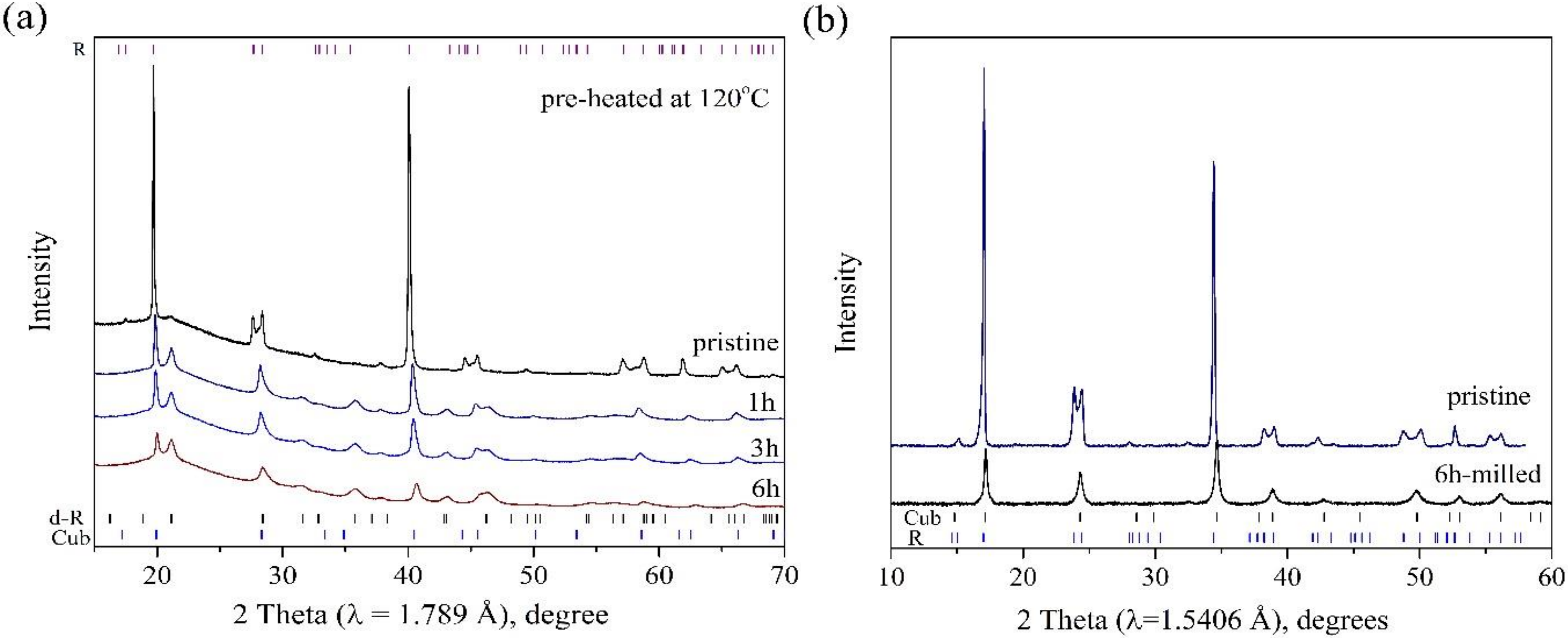


$Fe_4[Fe(CN)_6]_3\cdot x\,H_2O$

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



Structural study. XRD spectra of pristine and milled PW samples. Phase analysis.



Results of Le Bail analysis for the pristine and milled PW powders

	milling time			
	0 h	1h	3h	6h
"R" phase, sp. gr. R-3				
Vol. fraction	0.546(12)			
a, Å	7.487(1)			
c, Å	17.651(2)			
<Cryst. size>, Å	~10000			
"d-R" phase, sp. gr. R-3				
Vol. fraction	0.043(4)	0.524(60)	0.519(58)	0.645(127)
a, Å	≈6.57(fixed!)	6.560(2)	6.565(2)	6.573(2)
c, Å	≈19.04(fixed!)	18.980(8)	18.996(8)	18.915(7)
<Cryst. size>, Å	≈200(fixed!)	128(2)	126(2)	121(2)
"1st cubic phase", sp. gr. Fm-3m				
Vol. fraction	0.402(10)	0.208(43)	0.102(14)	0.086(23)
a, Å	10.428(1)	10.384(1)	10.379(2)	10.319(4)
<Cryst. size>, Å	576(26)	1086(101)	970(62)	1048(312)
"2nd cubic phase", sp. gr. Fm-3m				
Vol. fraction		0.255(53)	0.368(51)	0.256(67)
a, Å		10.341(4)	10.344(2)	10.284(4)
<Cryst. size>, Å		458(19)	296(9)	211(12)
impurity NaCl, sp. gr. Fm-3m				
Vol. fraction	0.009(1)	0.013(3)	0.011(2)	0.013(3)
a, Å	5.522(2)	5.507(3)	5.510(4)	5.513(3)
<Cryst. size>, Å	388(78)	211(51)	196(50)	217(50)
Overall fit quality				
Rwp, %	3.46	2.07	1.81	1.74

Charge-discharge curves of pristine and milled PW