at Pulsed Neutron Source

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Pulsed reactor IBR-2 in FLNP







Information on user policy on http://flnp.jinr.ru

What can we study? How to do this?



201°

-Huge penetration capability



The peak intensities give the information about an atomic structure (and texture) of a sample. Displacement of peaks on pattern - about symmetry and average parameters of an unit cell Peak widths – about average block sizes (crystal grains) and unit cell parameter dispersion (microstrains). Sample can be multiphase. Phase analysis.

In-situ study –investigation of electrodes in operating time



Study of battery materials by neutron diffraction



Figure 1

Cross section of the assembled device: (1) cell top, (2) spring with piston, (3) negative current collector, (4) cell body, (5) compartment for the active material and entry window for neutrons, (6) positive current collector.

A real power cell consists of many "duty" phases. A model cell emulates work of a real battery. It is ideal for experiments but it does not work one to one as real battery





C=2900mAh, U= 2.8-4.2V, m=46g



HRFD, Low Resolution mode, exp time is 5 minutes, ~C/10, ~C/5





Yamada et al. APL Mater. 1, 042110 (2013)

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Structural evolution in LiFePO₄-based battery materials: *In-situ* and *ex-situ* time-of-flight neutron diffraction study



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HIGHLIGHTS

GRAPHICAL ABSTRACT

- Time-of-flight *in-situ* neutron powder diffraction was applied to study commercial Li-ion batteries.
- Comparative study of the behavior of LiFePO₄- and V-added LiFePO₄-based batteries in charge—discharge cycling was carried out.
- Detailed tracing of the multistage process of Li-insertion into graphite





Vanadium Substitution of LiFePO₄ Cathode Materials To Enhance the Capacity of LiFePO₄-Based Lithium-Ion Batteries

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Electrochemical properties



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Nº2

LiFePO₄+V (shortly **LFPV**) V=1% Unknown displacement of V . (V is considered to substitute Fe.)

N1

Pure LiFePO₄ (shortly LFP)

Anode is graphite for both cells

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Experiments





HRFD station

IBR-2 neutron source

-~4 *10⁶ n/sm²/s

--2 back-scattering detectors;0.16 sr



Galvanstate KIKUSUI





MAPS and others programs for data processing



Phase content for cathodes

Weigh parts of $FePO_4$ and $LiFePO_4$ phases (in %) in batteries at different states of charge (SOC).

SOC, %	Battery №1 (LFP only, C=2Ah)		Battery №2 (LFPV, C=10Ah)	
	FePO ₄	LiFePO ₄	FePO ₄	LiFePO ₄
0	43(9)	57(5)	37(9)	63(9)
45(5)	66(9)	34(4)	68(8)	31(3)
100	93(13)	7(3)	100(11)	0

Cutoff voltage is the same for both cells – 2.5 and 3.8 V

Proportion between cathode and anode is the same for both cells (~2:1). And real capacity of cell№2 is ~11Ah



Anode -negative electrode. LiC_n phases.



Phase transitions in Li-intercalated phases (LiC_n)

Anode -negative electrode.LiC_n phases. **Evolution of graphite diffraction peak.**



(cell №1, where a cathode isLiFePO₄)

(cell No2, where there is $LiFePO_4+V$)

High intensive graphite peak (1, d = 3.35 Å), lithium-intercalated phases of graphite LiC₂₇ (2, d = 3.47 Å), LiC₁₂ (3, d = 3.52 Å)and LiC₆ (4, d = 3.70 Å)

Anode - negative electrode. LiC_n phases. 3D evolution of graphite diffraction peak.



Anode for cell №1, where cathode is pure LiFePO₄

Anode for cell №2, where cathode is LiFePO₄ +V

Anode -negative electrode. LiC_n phases



State of charge (%) 25 75 100 0 50 b Relative content 0.8 LiC₁₈, LiC₁₂ 0.6 LiC 0.4 LiC 0.2 2 10 0 8 time (hours)

Phase transitions in anode of cell with pureLiFePO₄ (battery N 01)

Phase transitions in anode of cell with V-added LiFePO₄ (battery N $^{\circ}2$)



ND investigation of cathode materials in ex-situ mode (stationary conditions)



ND investigation of cathode materials in *exsitu* mode (stationary conditions)



There are evidences of defects decreasing coherent block size (~crystallites)

Summary

From *in-situ*:

- 1) In general LFPV (LiFePO₄ with V) operates similar to LFP (pure LiFePO₄).
- 2) But LFPV works effectively LFP:
 more volume of cathode operates in LFPV battery,
 anode of LFPV battery has more Li-reached LiC₆ phase.
- 3) Addictive of V in LFP increase quantity of defects decreasing effective size of crystallites (from *ex-situ*).
- 4) Decreasing of the crystallite sizes helps to improve Li migration inside of LFP-like cathode.

General conclusions

- 1) TOF diffraction at the IBR-2 (HRFD station) is a promising technique for studying the materials that make up Li-batteries, as well as transition processes in them.
- 2) The acquired diffraction data allowed detailed tracing of the multistage process of Li insertion into graphite followed by the formation of several LiC_n phases. In the battery N^o2 based on the LFPV-cathode a ~10% larger part of the anode material passes into LiC₆ state if compared with LFP-based battery.
- LiFePO₄ ↔ FePO₄ transitions are clearly seen and quantifiable. From obtained data one can see that in cell with LFPV all volume of cathode works if compared with LFP-based battery.
- 4) Ex-situ study has shown that inserting vanadium into the LiFePO₄ structure, a significant (from a few thousand to about 400 Å) decrease in the typical size of coherent neutron scattering domains occurs. This effect can be interpreted as a considerable increase in the density of defects.

Right now

We do experiments with model cell. We have one model cell with vanadium windows (vanadium does not make neutron diffraction peaks).

We try to make another one with Si windows.



Thank you for your attention!



ND investigation of cathode materials in *ex-situ* mode (stationary conditions)



Фурье дифрактометр высокого разрешения











Исследование аккумуляторов на LiCoO₂



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Операции

-Суммирование

- -Нормировка на ванадий
- -Нормировка на мощность реактора

-Вычет некогерентного фона -Чистка по необходимости

-Суммирование по циклам

-Суммирование по времени для увеличения статистики

-Перевод в нужный формат -Первичный анализ (VM, FP, Origin...Surface)

-Обработка в Vmria (пока только одиночные)

-Обработка Ритвельдом в FullPro

(возможна циклическая обработка,

если хорошие данные.)





