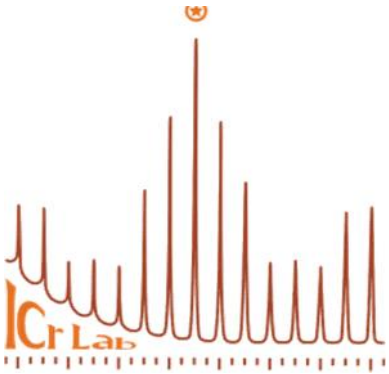


(Li,K)VPO_4F: новый 4В катодный материал для высокомощных металл-ионных аккумуляторов

Станислав Федотов

Аспирант 4 г.о.

S. S. Fedotov, N. R. Khasanova, A. S. Samarin, O. A. Drozhzhin, D. Batuk, O. M. Karakulina, J. Hadermann, A. M. Abakumov, E. V. Antipov. $AVPO_4F$ (A = Li, K): A 4 V Cathode Material for High-Power Rechargeable Batteries. *Chem. Mater.*, 2016, **28**, 411-415)

40-е Фрумкинские чтения, 28 октября 2016

План

I. Интеркаляционные процессы в аккумуляторах

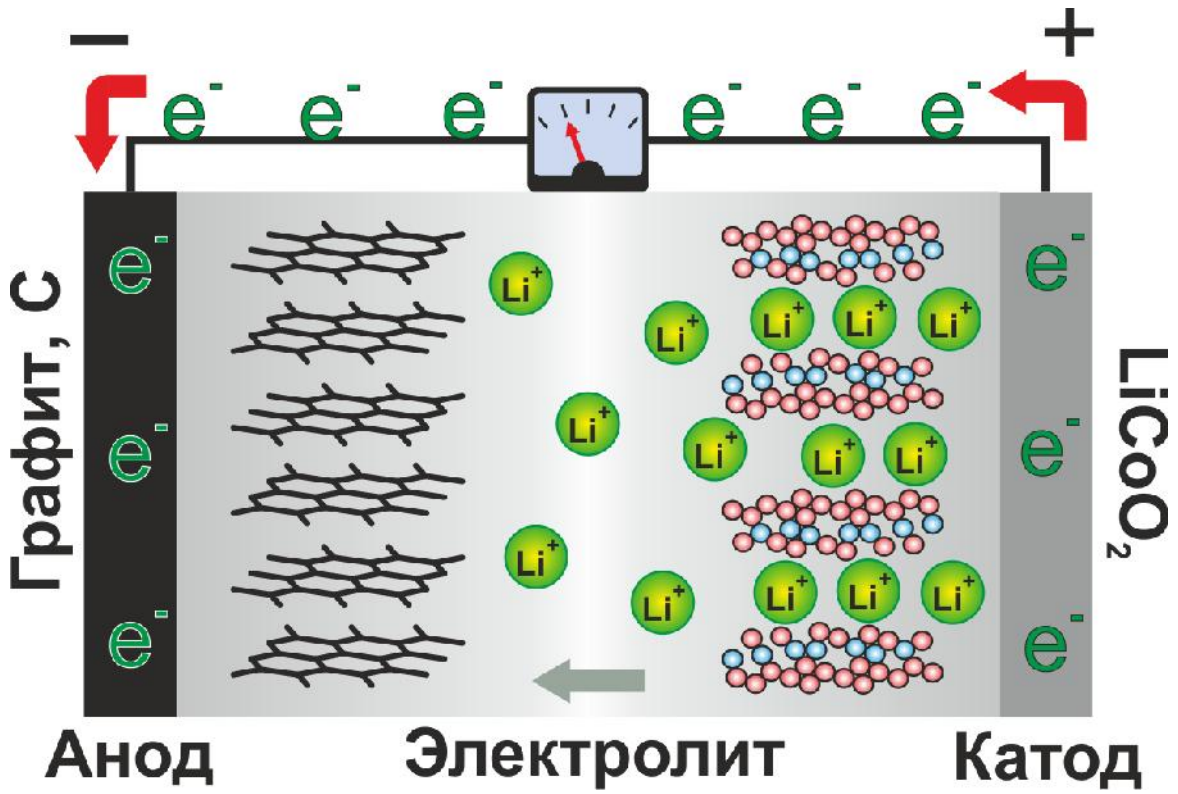
II. (Li,K)VPO_4F: синтез и ф/х исследование

III. (Li,K)VPO_4F: э/х исследование

IV. Диффузия ионов ЩМ в (Li,K)VPO_4F

V. Выводы

Аккумуляторы и интеркаляция

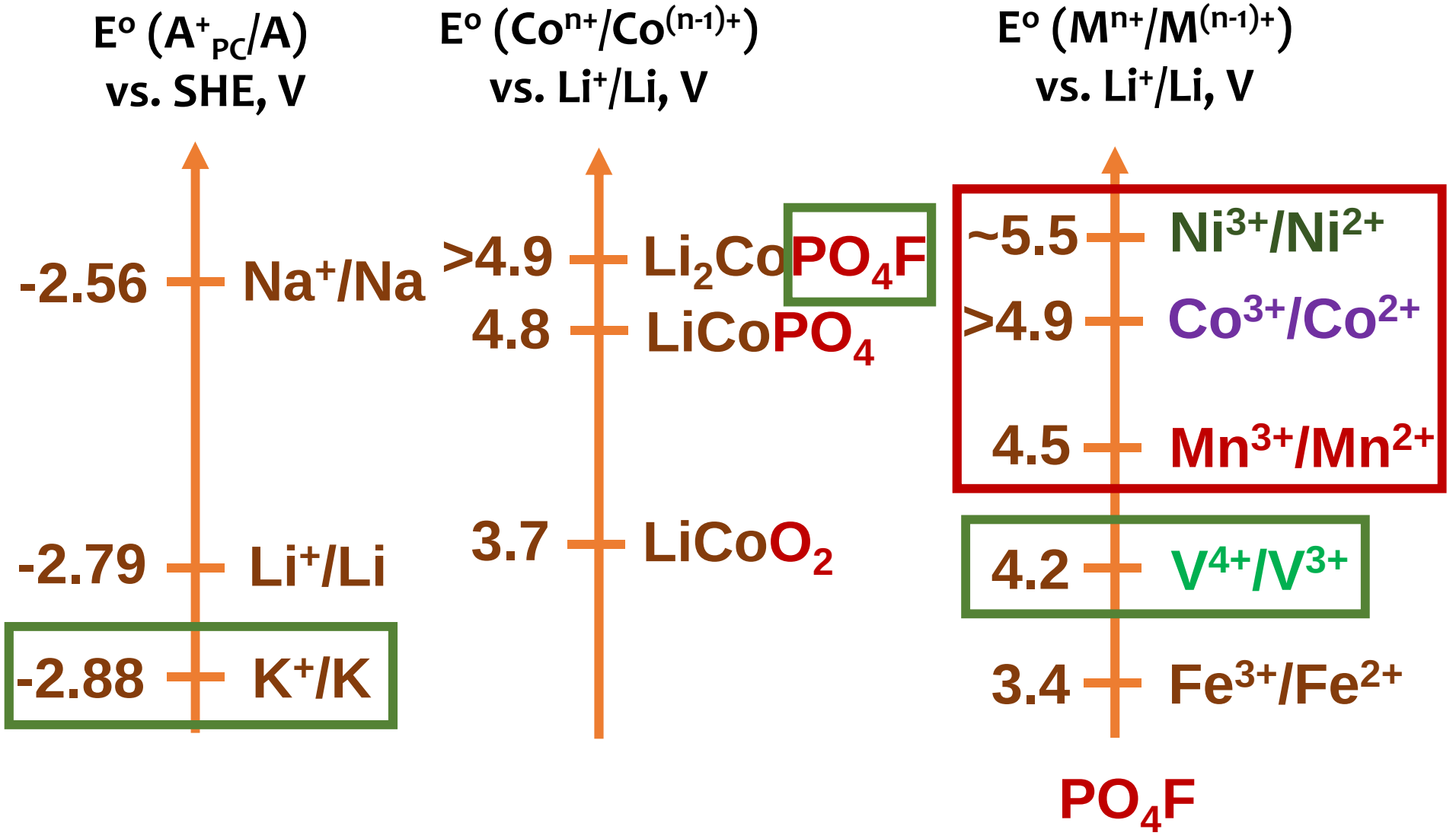


Удельная энергоемкость = Рабочий потенциал × Удельная емкость

Вт·ч·кг$^{-1}$ В А·ч·кг$^{-1}$

$$E = E_K - E_A$$

Потенциал vs химический состав



На пути к новому материалу

$K^{3+}V P O_4 F^{1-}$

Синтез:

Двухстадийный криохимический метод

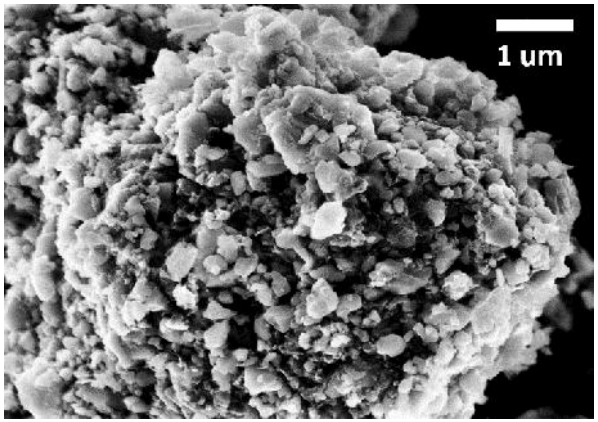
1) VPO_4/C (800℃, Ar-поток)

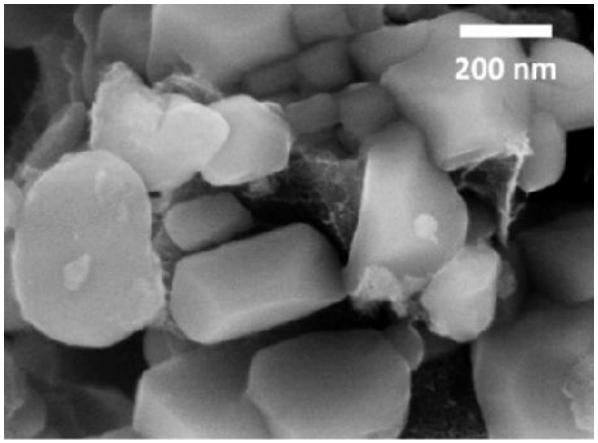
2) $VPO_4/C + KF \rightarrow KVPO_4F/C$
(600℃, Ar-поток, закаливание)

СЭМ: 200–400 нм

ИСП-АЭС K:V:P
0.38(2):0.42(3):0.43(2)

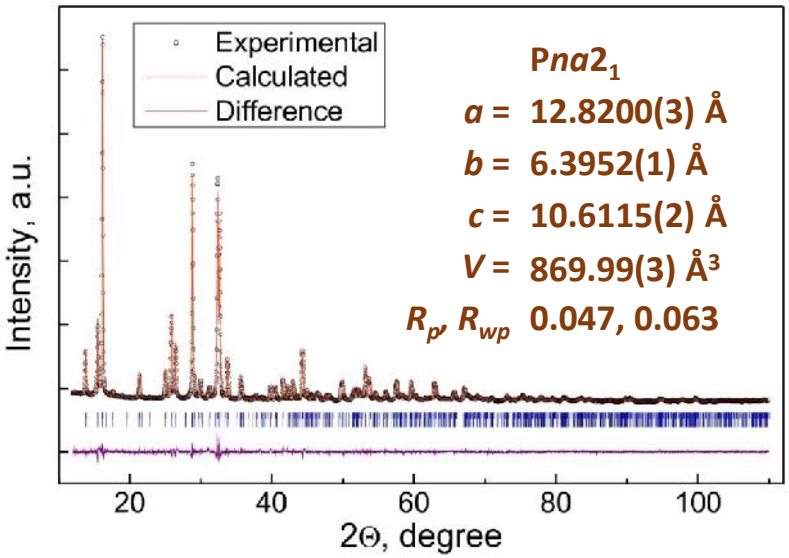
ТЭМ-ЛРСА K:V:P
0.33(1):0.32(1):0.35(2)





Fedotov S.S. et al, *Chem. Mater.* *28* (2016) 411-415

$KVPO_4F$: кристаллическая структура



$Pna2_1$

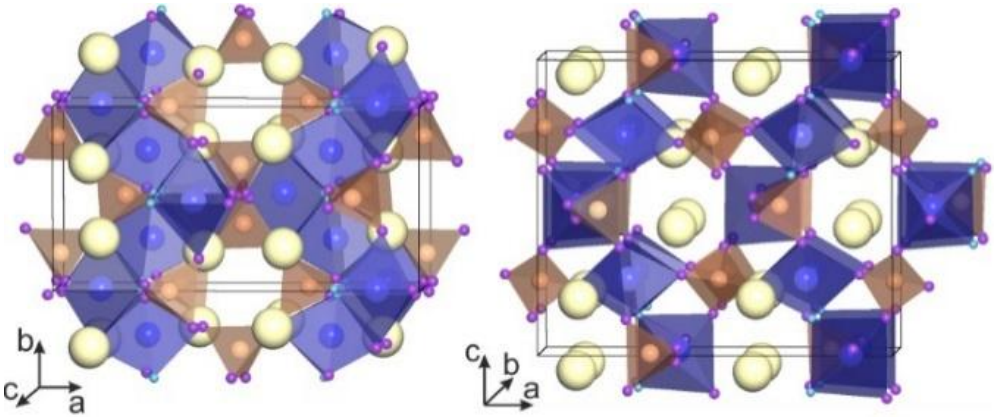
a = 12.8200(3) Å

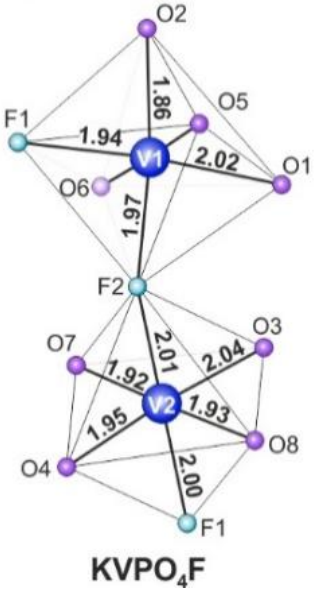
b = 6.3952(1) Å

c = 10.6115(2) Å

V = 869.99(3) Å^3

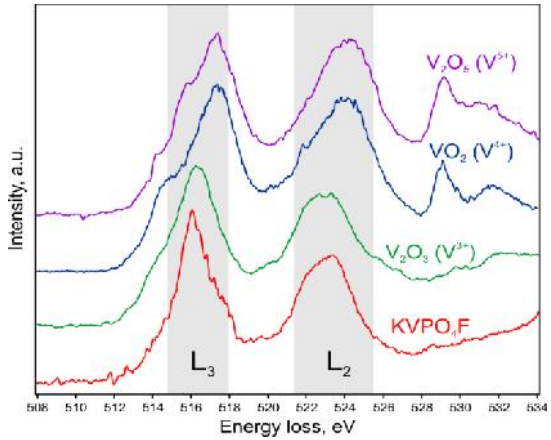
R_p, R_{wp} 0.047, 0.063

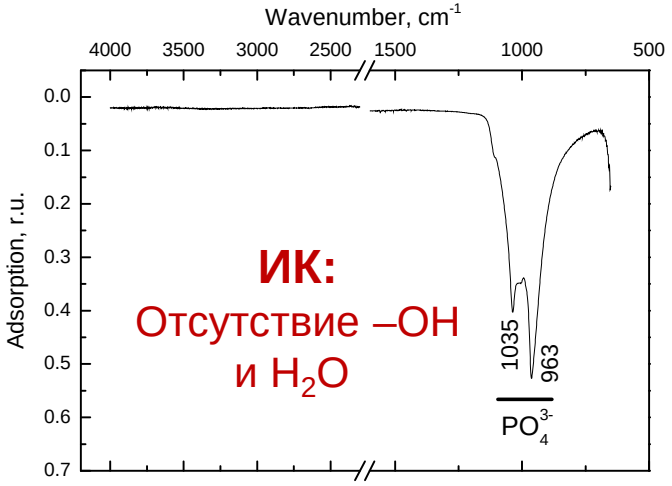




$KVPO_4F$

СХПЭЭ





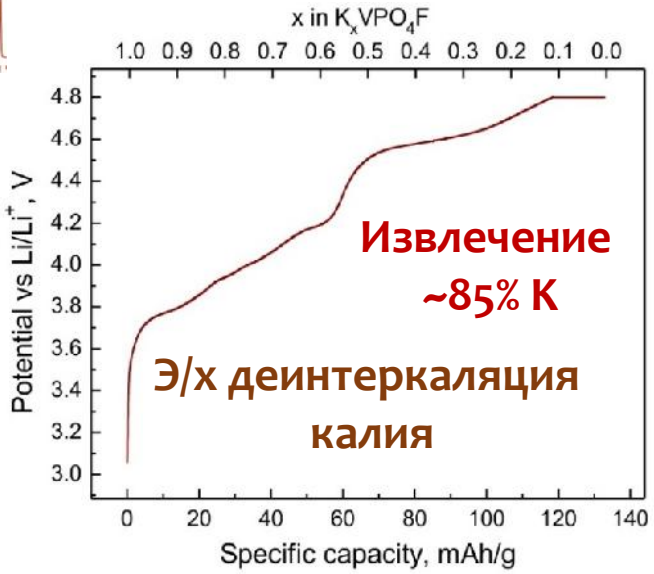
ИК:

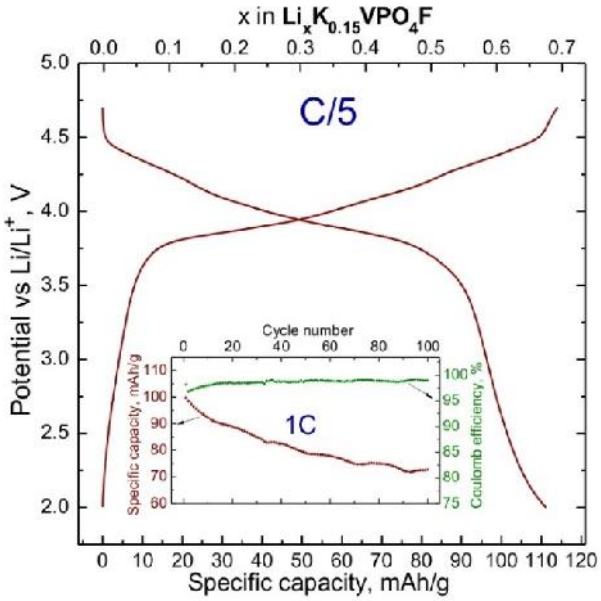
Отсутствие –OH и H_2O

Межатомные расстояния :

среднее V–X расстояние **1.98** Å

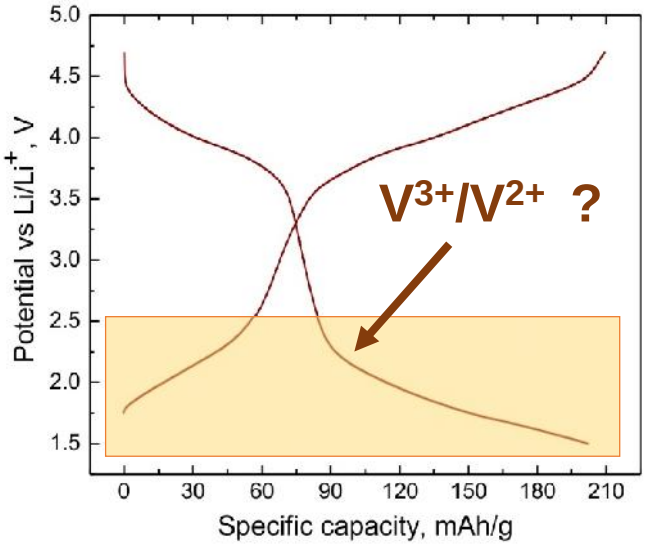
Электрохимическое исследование

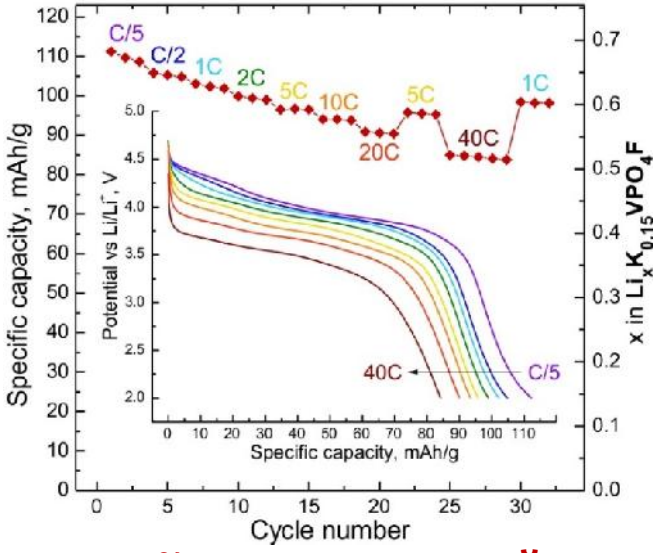




~4 В

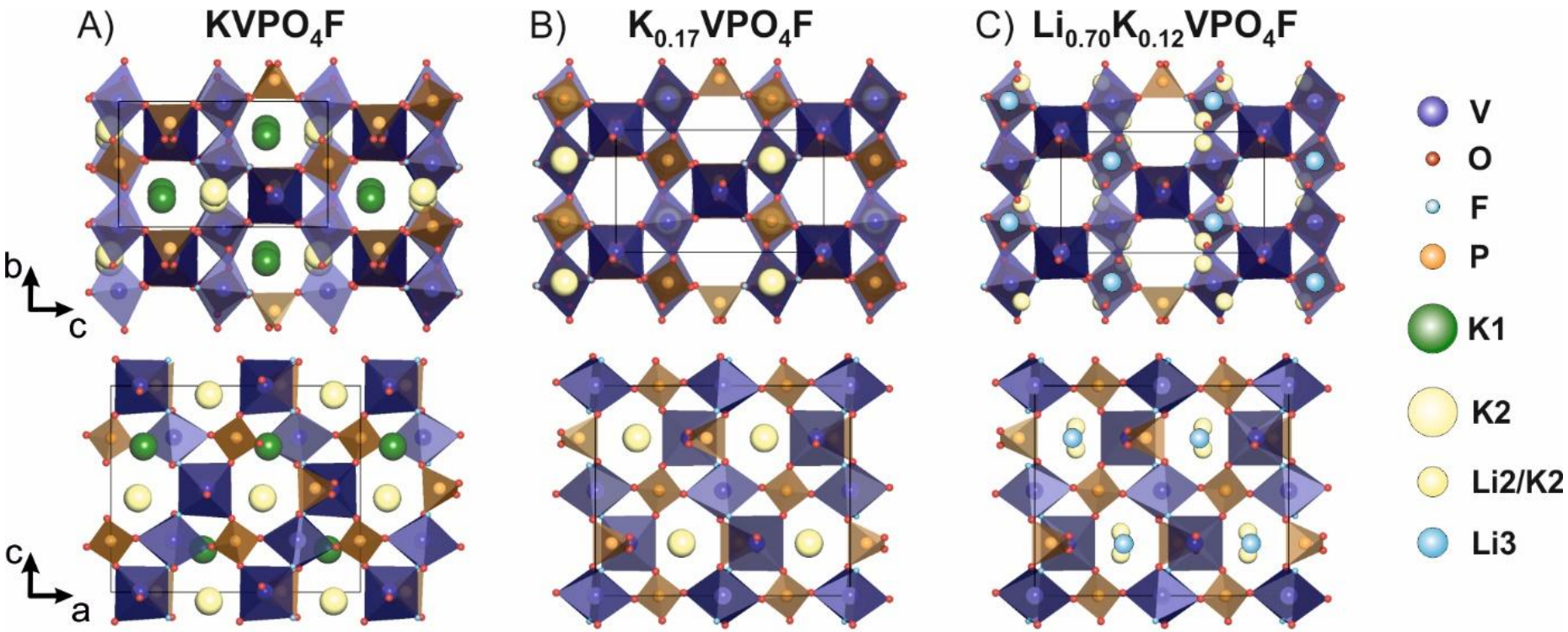
1.5 – 4.7 V vs Li/Li^+





75% первоначальной емкости при 40С!

Кристаллическая структура э/х модифицированных фаз

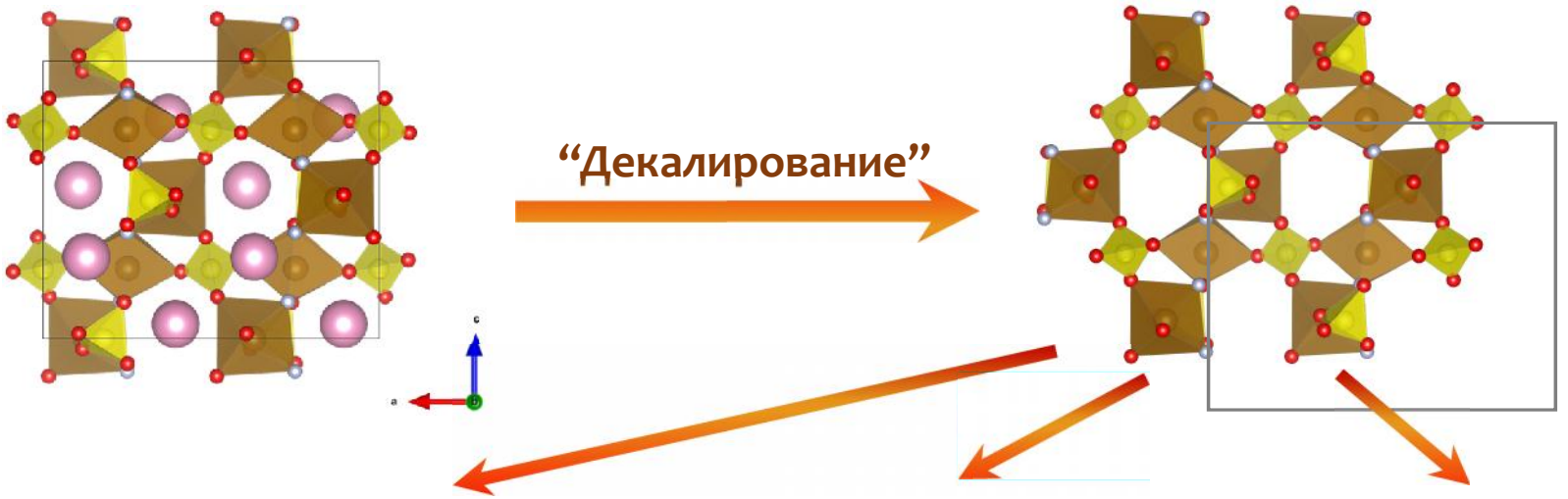


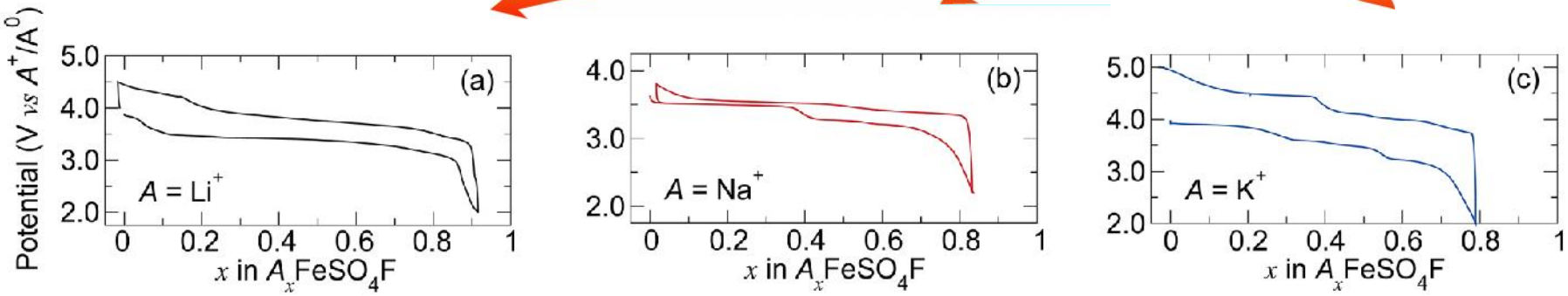
$Pna2_1$ **Pnan** **Pnan**

КТР и обратимая де/интеркаляция ЩМ

Recham, N. et al *Chem. Mater.* 2012, 24, 4363–4370.

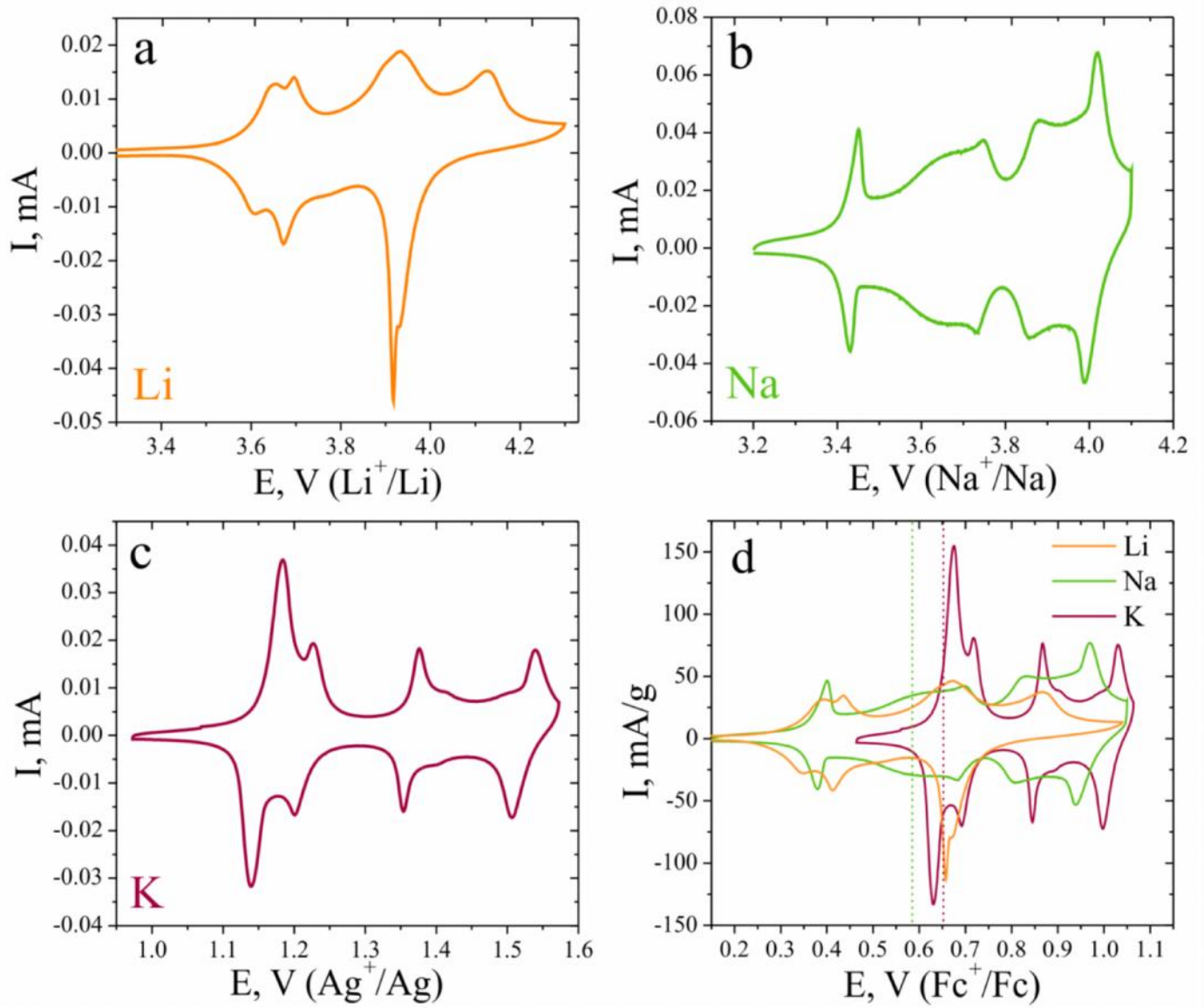
$KFeSO_4F$ Tarascon's group $FeSO_4F$





«Универсальность» каркаса КТР

$KVPO_4F$ vs Li, Na и K

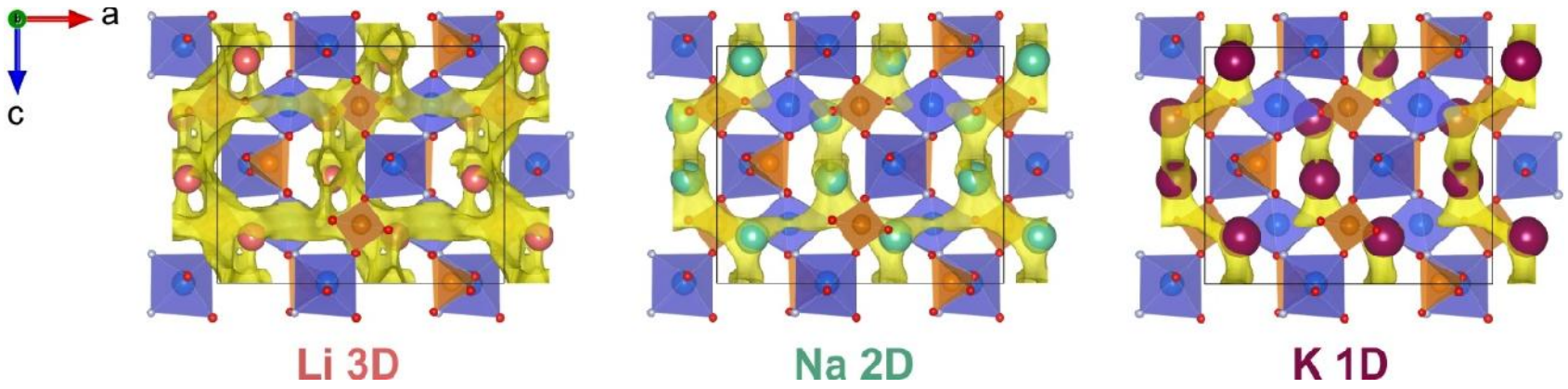


3-электродные ячейки
Электролит:
1M APF_6 или $ACIO_4$ в EC/DEC

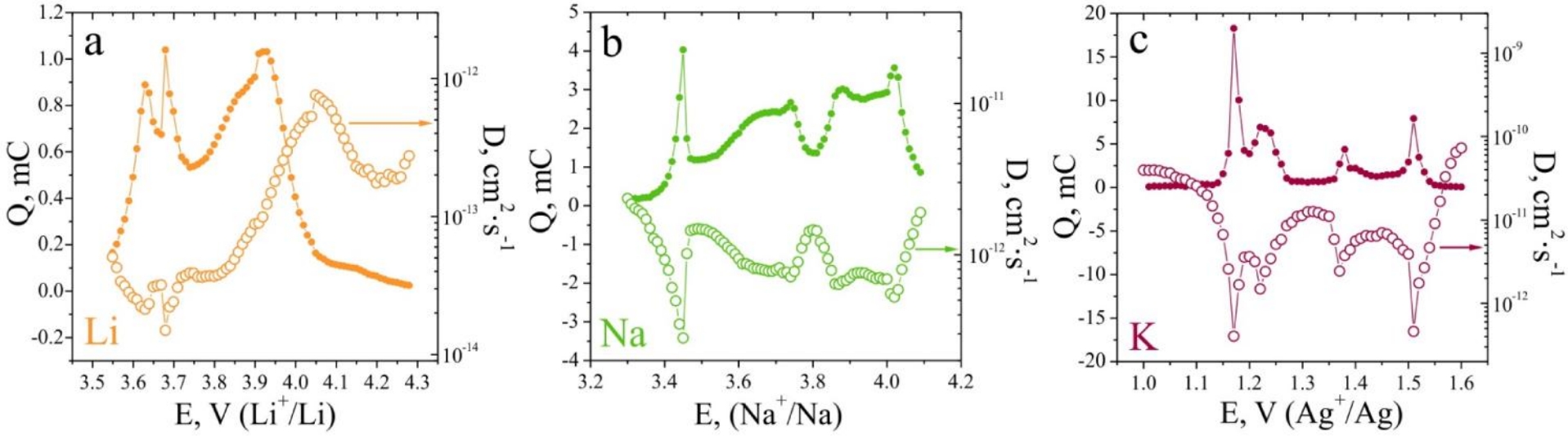
Эл-д сравнения:
Li, Na или Ag^+/Ag

Диффузия ионов щелочных металлов

BVEL (Bond Valence Energy Landscapes)



Коэффициенты диффузии Li^+ (PITT)



Выводы

I. A novel $KVPO_4F$ fluoride-phosphate is synthesized and characterized. It complements a series of KTP-type $KMPO_4F$ compounds (M = Al, Cr, Fe). According to the Rietveld refinement, $KVPO_4F$ crystallizes in the orthorhombic symmetry (P*na*21 space group, a = 12.8200(3) Å, b = 6.3952(1) Å, c = 10.6115(2) Å, V = 869.99(3) Å^3)

II. After the "depotassiation", the obtained cathode material indeed reveals the attractive electrochemical properties in a Li-anode cell capable to operate at 40C preserving a substantial capacity level and retention (>50% of theo. capacity at 40C).

III. Alkali ion diffusion coefficients in AVPO4F are found using PITT techniques. Diffusion coefficients are one or two order of magnitude higher for Na and K respectively than Li.

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Skoltech

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Andriy Zhugayevych

Natalia Katorova

Keith Stevenson

Thank you for your attention!

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