

Thesis Changes Log

Name of Candidate: Natalia Katorova

PhD Program: Materials Science and Engineering

Title of Thesis: The effect of selected electrode-solution interactions on the potassium-ion battery electrochemical performance

Supervisor: Prof. Keith Stevenson

Co-advisor: Prof. Artem Abakumov

The thesis document includes the following changes in answer to the external review process.

Response to Professor Antipov

Dear Professor Antipov,

Thank you for your attention to my thesis and time you spent reading it, below you will find responses to your comments:

1) The papers № 3, 4 and 6 which are not related to the thesis topic should be removed from the list of publications.

These papers were removed.

2) Title for Fig. 2.1 should be placed on the bottom of this figure.

The figure caption was moved to the correct position.

3) How the composition of $K_{1.44}Mn(Fe[CN]_6)_{0.9} \cdot 0.4H_2O$ (KMFCN) was determined? What was the accuracy? What are the valences of transition metals?

The composition was determined using the Energy dispersive X-ray (EDX) spectroscopy and thermogravimetric analysis (TGA). The former technique manages to identify the elemental ratio of K, Mn and Fe. The content of C and N was identified due to the stoichiometric ratio. The latter allows to identify the water content. The resulted KMFCN composition is $K_{1.44 \pm 0.09}Mn(Fe[CN]_6)_{0.90 \pm 0.20} \cdot 0.4H_2O$.

The valences of transition metals were not identified during this study. However, Mn and Fe in $K_{1.44}Mn(Fe[CN]_6)_{0.9} \cdot 0.4H_2O$ are both should possess the valence of 2, since they were analyzed using Raman spectroscopy and measured temperature dependence of magnetic susceptibility in KMFCN material with the same monoclinic structure and similar lattice parameters obtained via the same co-precipitation synthesis

1. Xue, L., Li, Y., Gao, H., Zhou, W., Lü, X., Kaveevivitchai, W., Manthiram, A. and Goodenough, J.B., 2017. Low-cost high-energy potassium cathode. *Journal of the American Chemical Society*, 139(6), pp.2164-2167.

4) Why the only 60:30:10 mass ratio was used for the electrode preparation?

Various composite ratios of active material, conductive additive and binder (60:30:10; 65:25:10; 70:20:10; 75: 15:10; 80: 10:10 respectively) were probed to attain best electrochemical performance of KMFCN cathode in K half cell with [2.5M KPF₆/G2] electrolyte solution. The best combination of initial specific discharge capacity value of 105 mA·h·g⁻¹ (at 0.1C rate) and rate capability of 72 mA·h·g⁻¹ (at 1C rate) was observed for electrode composite with 60:30:10 mass ratio originating from the poor conductivity of PBA-

based cathode. Unfortunately, common implemented technique of carbon-coating to improve conductivity is unavailable to apply due to low thermal stability of KMFCN.

5) How it was proved that “...the peak at 3.87 V vs K+/K on cathodic scan corresponds to the Mn³⁺/Mn²⁺ redox”?

Operando X-ray absorption near edge structure (XANES) spectroscopy is the powerful tool to examine oxidation states of the transition metals in potassium manganese hexacyanoferrate structures depending on potential change. During discharge the Mn³⁺ ions are published reduced first and the average oxidation state of Mn changes towards ²⁺ in manganese hexacyanoferrate structure A_xMn[Fe(CN)₆]_y·zH₂O^{1,2}. Hence, the same assumption was applied in the study. Though the structural evolution of KMFCN cathode during K cell operation was not in the scope of the present study, it indeed raises important issues about the effect of Fe(CN)₆-vacancies and interstitial/structural water.

1. Sottmann, J., Bernal, F.L., Yusenko, K.V., Herrmann, M., Emerich, H., Wragg, D.S. and Margadonna, S., 2016. In operando Synchrotron XRD/XAS Investigation of Sodium Insertion into the Prussian Blue Analogue Cathode Material Na₁. 32Mn [Fe (CN) 6] 0.83 · z H₂O. *Electrochimica Acta*, 200, pp.305-313.

2. Mullaliu, A., Aquilanti, G., Conti, P., Giorgetti, M. and Passerini, S., 2020. Effect of Water and Alkali-Ion Content on the Structure of Manganese (II) Hexacyanoferrate (II) by a Joint Operando X-ray Absorption Spectroscopy and Chemometric Approach. *ChemSusChem*, 13(3), pp.608-615.

6) What is the origin of the reversible redox process for the KVOPO₄ below 3 V?

It might correspond to V⁴⁺/V³⁺ redox and, thus, enhance the content of intercalated K⁺-ions. The V⁴⁺/V³⁺ redox below 3V vs Na⁺/Na was observed and elucidated via XANES for the intercalation of Na⁺ ions in K_{0.36}VOPO₄ host¹. This issue was not checked for studied KVOPO₄ cathode structure since it exhibits smaller discharge capacity values.

1. Ding, J., Lin, Y.C., Liu, J., Rana, J., Zhang, H., Zhou, H., Chu, I.H., Wiaderek, K.M., Omenya, F., Chernova, N.A. and Chapman, K.W., 2018. KVOPO₄: A New High Capacity Multielectron Na-Ion Battery Cathode. *Advanced Energy Materials*, 8(21), p.1800221.

7) There are several misprints:

- p. 24 surface diffusion of **adion**
 - p. 67 **Thence** D-glucose-derived HC
 - p.113 in K-ion cells **umep** the highest electrolyte
- All typos were fixed

Response to Professor Komaba

Dear Professor Komaba,

Thank you for carefully studying my dissertation, below you will find answers to your comments.

-In the entire thesis, terms of “interface” and “interphase” should be used carefully and correctly. In particular, SEI is abbreviation of “solid electrolyte *interphase*” which was first proposed by Professor Peled.

All usages of these terms were checked and corrected within whole manuscript.

- P. 27, “The structure is stabilized due to charge ordering in the transition-metal slabs²⁸ and ordering of K⁺ ions and vacancies in the interslab space^{29–33}.” The references here are on sodium layered oxides, not potassium. In page 42, graphite in K cell is discussed by citing Li graphite papers. The description is required to be revised and modified properly.

The description was revised.

- P. 22 - 58, Chapter 2 is “Review of the Literature.” It is good at total understanding of the Kion chemistry, but it looks the simple gather of literatures without the candidate’s philosophy and research direction. After the very long description, “motivation and objective” are shown in only two pages. This is not attractive to the audience.

Chapter 2 was rewritten to emphasize the candidate’s philosophy and chosen research directions.

p.31 “PBAs possess several disadvantages: the low tap density, the low electronic conductivity due to their open 3D framework structure and chemical-bond character and insufficient thermal safety in case of a short circuit. The cyanide groups are released as toxic cyanides above 200 °C, which also exothermically react

with the electrolyte and cause the runaway⁶². However, the tap density value might be enhanced via spray drying within thermal stability of PBA material, the electronic conductivity might be increased via addition of carbon nanotubes to electrode composite and, finally, the suppression of CN groups emission might be attained via the utilization of additive acting as scavenger.”

p.52 “The analysis of published data indicates the attractive temperature range for HC powder annealing resides at 1100-1500°C¹. The decreased annealing temperature resulted in poor electrochemical performance in K cell. Further enhanced annealing temperature is undesirable owing to K⁺-ion battery development at affordable cost for the needs of stationary energy storage. Thus, 1200°C and 1500°C chosen to obtain a clue about best synthesis conditions of HC powder.”

- In Chapter 3, electrode loading (mg/cm²) is required for KMFCN, KVPO, HC electrodes used in every tests.

The following part was added to Chapter 3:

p.62 “The electrode loading for KVPO was in the range (1.4-1.8 mg·cm⁻²), for KMFCN - in the range (1.2-1.9 mg·cm⁻²); for HC – in the range (0.6-0.9 mg·cm⁻²) for electrochemical measurements in K half cells.”

- Position of Table 4.1 and Table 4.2 should be exchanged because Table 4.2 earlier appears than Table 4.1 in the text.

- P. 74, the last second line: Figure 4.7c is not found in the thesis.

- From Figure 4.6c, reversible capacity of the KMFCN electrode should be obtained.

- P. 75, the last fifth line: Figure 4.8 should be Figure 4.7.

- P. 85, main text, figure picture, and figure captions were fixed improperly.

All these comments were addressed and corrected.

- P. 88, discussion in Figure 5.11: at least, two closely related papers (DOI: 10.1021/acsami.0c08002, DOI: 10.1039/D0TA08851J) are missing, which may be described in Chapter 2 as well.

The following part was added to Chapter 2:

p.36 “Moreover, the binary-salt KFSI-KPF6 solutions could be implemented to attain both stable SEI on graphite negative electrode and Al current collector stability⁷⁸”

p.37” The use of highly concentrated electrolytes (>3 M) leads to the preferential formation of stable FSI--derived SEI^{57,74,85-87}”

The following part was added to Chapter 5:

p.88 ” The applied strategy to tune salt concentration in ether-based electrolyte solutions was also reported to attain the enhanced cycle stability of K full cell comprising graphite anode and K₂Mn[Fe(CN)₆] cathode¹⁶⁹. The utilization of highly concentrated [5.6 mol·kg⁻¹ KFSI/G3+0.5wt% VC] leads to the discharge capacity of 106 mAh·g⁻¹ of cathode after 100 cycles. Furthermore, the observed findings are in line with other studies on electrolyte composition optimization that enhances the stable cycling of K full cell delivering the initial discharge capacity value of 105 mAh·g⁻¹ of cathode^{170,171}”

- P. 98-99, in Figure 7.5, picture and caption are separated. And, the picture is very unclear to distinguish the bubble.

I’ve tried to make it more clearly. Now white arrow indicates the bubble.

-In Figure 7.7, three CV data are shown, but there is no anodic current of potassium extraction, i.e. no reversible potassium insertion for the CVs. The surface deposits observed with AFM is really SEI, K⁺ conducting solid electrolyte interphase? If the deposits consist of non-ion conducting byproducts of cathodic decomposition, it would not be SEI layer.

in situ AFM technique is successfully utilized to probe the surface layer formation on the electrodes in alkali metal-ion battery during last decades¹. The difference between measured CV curves in AFM cell configuration and coin cells was published for Li-ion cells². The location of the peak corresponding to Li⁺-ion extraction from HOPG is significantly shifted at the anodic scan compared to one observed at CV curve measured in the coin cell configuration. Moreover, the switch from HOPG material to hard carbon electrode results in the peak disappearance³. It might originate from the experiment geometry and small electrode size, since the utilization of ultramicroelectrode (with area ~0.002 mm²) results in vanishing the duck-shape peak at CV curve under slow scan⁴. In our experiment, the electrode area is about 0.071 mm². Besides, the ratio of the surface area through which intercalation occurs to the volume of particles in AFM cell configuration is much less than in a coin cell configuration. Furthermore, the effect of mechanical stresses on the diffusion

coefficient⁵ during K⁺-ion intercalation into electrode host arises, since HC particles are fixed in the epoxy and, hence, cannot expand freely in all dimensions during intercalation.

1. Alliaata, D., Kötzt, R., Novák, P. and Siegenthaler, H., 2000. Electrochemical SPM investigation of the solid electrolyte interphase film formed on HOPG electrodes. *Electrochemistry communications*, 2(6), pp.436-440.
2. Zhang, Z., Smith, K., Jervis, R., Shearing, P.R., Miller, T.S. and Brett, D.J., 2020. Operando electrochemical atomic force microscopy of solid–electrolyte interphase formation on graphite anodes: the evolution of SEI morphology and mechanical properties. *ACS applied materials & interfaces*, 12(31), pp.35132-35141.
3. Luchkin, S.Y., Lipovskikh, S.A., Katorova, N.S., Savina, A.A., Abakumov, A.M. and Stevenson, K.J., 2020. Solid-electrolyte interphase nucleation and growth on carbonaceous negative electrodes for Li-ion batteries visualized with in situ atomic force microscopy. *Scientific reports*, 10(1), pp.1-10.
4. Bard, Allen J.; Faulkner, Larry, R. *Electrochemical Methods: Fundamentals and Applications*. 2001, 1–833.
5. Zhang, X., Shyy, W. and Sastry, A.M., 2007. Numerical simulation of intercalation-induced stress in Li-ion battery electrode particles. *Journal of the Electrochemical Society*, 154(10), p.A910.

- P. 103, “washed in DEC during a couple of hours to remove traces of KPF6 from the HC surface.” Washing electrode is important, but dissolution into pure DEC solvent for hours may lead to possible loss of SEI. The candidate has to discuss the possibility of SEI dissolution in pure DEC.

Indeed, the insolubility of SEI components in DEC solvent is very important for high capacity retention, since the dissolution of SEI components might cause new SEI formation, thus, increasing the irreversible capacity loss during battery operation¹.

The following part was added to corresponding section:

p.103 ”This treatment is required despite it might partially dissolve organic components owing to higher solubilities of the potassium organic compounds (e.g., potassium alkyl carbonates and potassium alkoxides)^{17,34}.”

1. An, S.J., Li, J., Daniel, C., Mohanty, D., Nagpure, S. and Wood III, D.L., 2016. The state of understanding of the lithium-ion-battery graphite solid electrolyte interphase (SEI) and its relationship to formation cycling. *Carbon*, 105, pp.52-76.

- Figure 7.9 is highly interesting data to show direct evidence of potassium trapping. The referee is curious any chemical reaction between the K trapped HC and water/O₂ gas.

This issue was not examined in the present study. The possible interaction should be carefully addressed in future study since the K trapped in HC should be sensitive to water and O₂ in air in terms of thermodynamic potentials.

- In Chapter 8, a few Russian characters remain.

This typo was fixed.

- P. 113, to conclude the thesis, a description of “One may speculate that this presumably polymeric organic component improves the mechanical properties of the SEI making it more resistant towards fracturing and more effectively preventing the electrolyte decomposition process thus reducing ICL” is good point. The referee understands “One may speculate...” but does not understand “what the candidate expects/believes/hopes future perspective for next-generation battery.” I encourage the candidate to emphasize candidate’s personal idea and opinion in Chapter 8. For instance, details of any new additive and its rational design/selection can be commented for K-ion battery by the candidate.

The following part was added to Chapter 8:

p.114 “Apparently, the numerous issues should be addressed to organic electrolyte solution to design K full cell with prolonged cycle life and high energy density characteristics such as electrolyte oxidative stability, Al current collector corrosion and the ability to form the stable passivation layer that conducts K⁺-ions on both cathode and anode sides. Yet the electrolyte choice is unique for each pair of negative and positive electrodes. Indeed, the measurements in K half cell to examine intrinsic properties of electrode material should be conducted carefully with the respect to K metal as the capacity fade might originate from growing thick layer on its surface.

Regarding, the K full cell comprising KMFCN and HC electrodes, further development of ether-based electrolyte solution composition should contain the concentration optimization of electrolyte additive with the reduction potential preceding the solvent reduction like VC, ethylene sulfite (ES) or 4-chloromethyl-1,3,2-dioxathiolane-2-oxide (CMDO). Presumably, this approach facilitates the stable SEI formation on HC surface and, thus, preventing electrolyte decomposition and decreasing the irreversible capacity loss. Furthermore, safety issues arise concerning the emission of CN groups in the case of thermal runaway. Thereby, the electrolyte additive acting as CN gas scavenger must be developed to elaborate safe potassium-ion battery.

Furthermore, concentrated KFSI-based electrolyte benefits the electrochemical performance of K full cell comprising carbonaceous negative electrodes since it sufficiently passivates the anode surface and possess oxidative stability against Al current collector corrosion. However, high cost of KFSI salt does not approach the requirements from stationary storage market. Hence, future research should be focused on elaboration of KPF6/KFSI binary-salt solutions or artificial SEI design. The artificial thin SEI layer formation in concentrated KFSI-based electrolyte before cycling might be a proper compromise between the utilization of expensive KFSI salt and its profit in stable SEI formation on hard carbon anode.”

Response to Professor Myung

Dear Professor Myung,

I express my gratitude for the attention paid to the work. I am very glad to accept the invitation for publication. Below you will find reply to your comments

- **Please carefully check typos.**
- **K⁺-ion, K-ion, potassium-ion, and potassium ion were used in this thesis. It would be better to unify the wording.**

All typos were corrected and the uniform wording is introduced

Response to Professor Kosova

Dear Professor Kosova,

Thank you for your attention to my thesis, below you will find answers to your comments.

1. The section “Author’s Contribution” contains repetitions, e.g., items 1 and 5, 2 and 3, 4 and 6.

This issue was fixed

2. In section “Novelty”, I suggest to redistribute the contents of items 3 and 4. It would be better if item 3 would contain the reasons of irreversible capacity loss in PIBs with HC and the need to avoid the reduction of HC particles to nanoscale, while item 4 - the role of the VC additive.

The content of items 3 and 4 was reformulated according to the referee comments.

3. Some of the references given in the thesis contain inaccuracies in their design, e.g., #31, 47, 60, 68, 72, etc.

The references were corrected

Response to Professor Aksenov

Dear Professor Aksenov,

Thank you for carefully studying my dissertation, below you will find answers to your comments.

A summary for section "Effect of synthesis conditions on Hard Carbon properties" should be added at the end of the section.

The following part was added to Chapter 4:

p.74. ”Hence, HC powders with decreased content of nanosized particles and annealed at higher temperature of 1500°C deliver the best electrochemical properties. The best combination of synthesis conditions comprise the HTC of (D-glucose + pectin + citric acid, 180 ° C, 16 h) with the subsequent high-temperature annealing at T=1500 °C..”

- **What is the best combination of synthesis conditions for hard carbon? Please add in summary.**

The following part was added to Chapter 4:

p.74. “ The best combination of synthesis conditions comprise the HTC of (D-glucose + pectin + citric acid, 180 ° C, 16 h) with the subsequent high-temperature annealing at T=1500 °C..”

- Some conclusions or connection with the next section should be added for section "Aluminum current collector passivation" otherwise it is not clear for what reason the measurements were performed

The following part was added to Chapter 5:

p.79” Thus, [2.5 M KPF₆/G2] electrolyte solution can be utilized with positive electrodes and, hence, in K full cells. The origin of the improved electrolyte stability against Al current collector oxidation with salt concentration increase should be identified. So, Raman measurements to examine the spatial organization of the ions and molecules in the solution were performed.”

- What is the solubility of KPF₆ in diglyme-based electrolytes?

To the best of our knowledge, the attained highest concentration of KPF₆ salt in diglyme was published to be 2.8 M¹. Nevertheless, in my experiments an increase of the KPF₆ concentration over 2.5 M resulted in nontransparent solutions even after stirring overnight, indicating a solubility limit for KPF₆ in diglyme at around 2.5 M.

1. Mohammadiroudbari, M., Qin, K. and Luo, C., 2022. Multi-Functionalized Polymers as Organic Cathodes for Sustainable Sodium/Potassium-Ion Batteries. *Batteries & Supercaps*, p.e202200021.

- The performance of electrodes in high-concentrated electrolytes is improved, but what about the conductivity of such electrolyte and its performance at lower temperatures?

The additional experiments were conducted. The electrolyte solution resistance increased to 332 Ω·cm² according to PEIS measurements in symmetric K cells under thermal conditions of -1±2°C until electrolyte was completely frozen. The ether-based electrolyte was not published to improve low temperature performance despite the low melting point of diglyme. However, the K cell with conventional carbonate-based electrolyte also degraded under 0°C- -10°C.

- Fig. 5.11 What was the c-rate during cycling?

Current density value was added to the caption of Figure 5.11

- p 76. The KVOPO₄ cathode, exhibiting the KTiOPO₄ -type structure, could serve as the cathode in K cells. The capacity of this cathode is 50 mAh/g. It is too small for realistic cells, please rewrite.

This part was rewritten as following:

p.76-77 “The synthesized KVOPO₄ compound, exhibiting the KTiOPO₄-type structure, could not compete with other cathodes for K cells in terms of specific discharge capacity values. However, it could still serve as the positive electrode with polyanionic structure to examine various electrolyte compositions.”

- p89. - However, the specific reasons for the observed HC behavior in the concentrated electrolytes should be clarified in the future research. What kind of specific reasons? Please clarify.

The following part was added to Chapter 5:

p.91” Albeit, the similar performance of HC electrode in all [x M KPF₆/G2] solutions, the outstanding performance of full K cell with HC negative electrode is attained in more concentrated electrolyte compositions”

Response to Professor Drozhzhin

Dear Professor Drozhzhin,

Thank you for your careful consideration of my dissertation and questions, below you will find the answers to them.

1) The author explains the reduced capacity of KVOPO₄ cathode material compared to the literature data by a specific morphology caused by the use of a different method of synthesis. In this regard, the question arises why the author chose this particular method of synthesis.

Hydrothermal synthesis allows adjusting synthesis conditions to tune particle properties (for example, particle size and morphology). Hence, it's beneficial technique to prepare electrode materials. The resulted particles agglomerate with average size of 20 μm indeed exceeds the particle size of 2-10 μm obtained in another study¹. However, the enhanced specific capacity value might stem from the extended upper cutoff potential to 5 V vs K⁺/K (as it was also mentioned on p.82). This is not applicable for full K cell elaboration owing to the oxidative stability of utilized electrolytes. Yet 80 mA·h·g⁻¹ is lower compared to the specific discharge capacity of potassium manganese hexacyanoferrate positive electrode being 105 mA·h·g⁻¹. Thus, the main efforts were focused to elaborate and optimize the composition of K_xMn[Fe(CN)₆]_y·zH₂O compound as positive electrode for K full cell.

1. Chihara, K., Katogi, A., Kubota, K. and Komaba, S., 2017. KVPO 4 F and KVOPO 4 toward 4 volt-class potassium-ion batteries. *Chemical Communications*, 53(37), pp.5208-5211.

2) Similar question regarding Prussian blue cathode. The author explains the low value of the capacity by a different composition, both in cation and in crystal water. The question arises why the author studied this particular composition of KMFCN cathode.

As the research is dedicated to the development of full K-ion battery with long cycle life and affordable cost, the easily scalable and inexpensive co-precipitation synthesis technique is utilized. Further research aiming the KMFCN material optimization is under the progress.

3) The author mentioned that the presence of the VC-based polymer SEI layer of the surface of the anode has a positive effect on the stability of the electrode during expansion and contraction of the anode material. The question is whether there are any numerical data on the magnitude of such expansion and contraction of HC in K-ion cells.

The volume expansion of hard carbon particles could achieve the value of 44%¹. In present study, the variation in interlayer distance between graphene sheets were estimated via HR-TEM. The initial interlayer distance of 0.38 nm did not change after cycling of HC electrode in K half cell with [0.5M KPF₆/EC:DEC(1:1, v:v) + 4%wtVC] electrolyte. While cycling of HC electrode in K half cell with [1M KPF₆/G2] and [2.5M KPF₆/G2] with results in the increased interlayer distance up to 0.52 nm and 0.41 nm respectively.

1. Lei, H., Li, J., Zhang, X., Ma, L., Ji, Z., Wang, Z., Pan, L., Tan, S. and Mai, W., 2022. A review of hard carbon anode: Rational design and advanced characterization in potassium ion batteries. *InfoMat*, 4(2), p.e12272.

4) As disadvantages of the Prussian blue cathode materials, the author noted the low conductivity and low tap density of the material. However, there is not a word about its safety. Is there any data on the thermal stability of PB-based materials and on the danger of processes that can occur during the heating of a battery (e.g. due to a short circuit) with such a type of cathode material?

The thermal safety issues of PBA cathodes can be attributed to both thermal failure and toxic cyanide evolution¹. The cyanide groups are released as toxic cyanides above 200 °C, which also exothermically react with the electrolyte and cause the runaway. Nevertheless, the degradation of SEI layer on carbonaceous negative electrode occurs at lower value of temperatures. The galvanostatic measurements of full K cell comprising KMFCN positive electrode, hard carbon negative electrode and carbonate-based electrolyte were conducted at 60°C at current rate of 15 mA·g⁻¹. The initial discharge capacity value of cathode of 99 mA·h·g⁻¹ decreased to 92 mA·h·g⁻¹ upon 40 cycles.

The following part was added to Literature review section:

p.31” PBAs possess several disadvantages: the low tap density, the low electronic conductivity due to their open 3D framework structure and chemical-bond character and insufficient thermal safety in case of a short circuit. The cyanide groups are released as toxic cyanides above 200 °C, which also exothermically react with the electrolyte and cause the runaway⁶².”

1. Li, Z., Dadsetan, M., Gao, J., Zhang, S., Cai, L., Naseri, A., Jimenez-Castaneda, M.E., Filley, T., Miller, J.T., Thomson, M.J. and Pol, V.G., 2021. Revealing the Thermal Safety of Prussian Blue Cathode for Safer Nonaqueous Batteries. *Advanced Energy Materials*, 11(42), p.2101764.

5) What is the relevance of articles 4 and 6 (Page 5) to the presented work?

These papers were removed.

6) Why did the author choose temperatures of 1200 and 1500 C for annealing of the HC?

The published data indicates the attractive temperature range for HC powder annealing resides at 1100-1500°C¹. The decreased annealing temperature resulted in poor electrochemical performance in K cell. Further enhanced annealing temperature is undesirable owing to K⁺-ion battery development at affordable cost for the needs of stationary energy storage. Thus, 1200°C and 1500°C chosen to obtain a clue about best synthesis conditions of HC powder.

1. Yamamoto, H.; Muratsubaki, S.; Kubota, K.; Fukunishi, M.; Watanabe, H.; Kim, J.; Komaba, S. Synthesizing Higher-Capacity Hard-Carbons from Cellulose for Na- and K-Ion Batteries. *J. Mater. Chem. A* 2018, 6 (35), 16844–16848. <https://doi.org/10.1039/C8TA05203D>.

7) **What is the first cycle Coulombic efficiency for HC-based anode in 2.5 M diglyme-based electrolyte? In figure 5.10.c it looks close to 100% which is doubtful.**

The data were corrected.

8) **Why is the initial capacity of KMFCN cathode in carbonate-based electrolyte higher than in diglyme-based electrolyte?**

The observed variation of capacity values could originate from the formation of different SEI layers on HC exhibiting different resistance as it occurs with reactive potassium metal counter electrode with carbonate-based and diglyme-based electrolytes^{1,2}

1. Xiao, N.; McCulloch, W. D.; Wu, Y. Reversible Dendrite-Free Potassium Plating and Stripping Electrochemistry for Potassium Secondary Batteries. *J. Am. Chem. Soc.* 2017, 139 (28), 9475–9478. <https://doi.org/10.1021/jacs.7b04945>.
2. Hosaka, T.; Muratsubaki, S.; Kubota, K.; Onuma, H.; Komaba, S. Potassium Metal as Reliable Reference Electrodes of Nonaqueous Potassium Cells. *J. Phys. Chem. Lett.* 2019, 10 (12), 3296–3300. <https://doi.org/10.1021/ACS.JPCLETT.9B00711>.

9) **Why VC additive was tested on electrolytes based on carbonates and not on glymes?**

The logical consequence of study is to probe [2.5M KPF₆/G2+4wt% VC] electrolyte solution that has been done. The HC surface covering by SEI film was indeed evidenced using HR TEM combined with EDX mapping. However, the electrochemical performance was not obtained in K full cell that might stem from large amount of VC additive. Further research is required to optimize VC concentration.

Response to Professor Itkis

Dear Professor Itkis,

Thank you for carefully studying my dissertation, below you will find answers to your comments

• **In this work cyclic voltammetry is typically performed in two-electrode cell configuration. That can be acceptable for illustration purposes. However, it is not correct to analyze the peak shapes, peak-to-peak separation and such parameters (e.g. see p. 75) without correct potential measurements (reference electrode, ohmic drop compensation). Why was voltammetry not performed in three-electrode configuration?**

Indeed, the two-electrode cell configuration is inappropriate choice to extract parameters such as charge-transfer resistance, apparent diffusion coefficients, etc. from CV, PEIS or GITT data. Herein, the peak-to-peak separation was mentioned only to highlight the polarization owing the formation of thick and resistive surface films. The main challenge arises from the reference electrode that must keep the constant potential during the measurements. Since the simple choice of the potassium metal does not satisfy this requirement as its potential varies. The suitable alternative could be the electrode material which undergoes two-phase transition during K⁺-ion de(intercalation) within wide potential range. After charging up to corresponding plateau it might keep the constant potential and, hence, could be utilized as reference electrode. This issue will be addressed in future study.

• **Even worse idea, in my opinion, is to analyzed current collector corrosion in such a way (voltammetry in two-electrode cell, fig. 5.1). Especially is we look at fig. 5.1b we see current onset at higher voltages for higher electrolyte concentrations. This however is not directly indicative for corrosion stability, as this effect can be simply due to higher solution resistivity for concentrated system.**

The solution resistivity was measured to decline with the enhanced KPF₆ salt concentration. The utilized technique is applied in the number of studies^{1,2}. The main purpose was to identify if Al current collector surface passivates or not.

1. Hosaka, T.; Kubota, K.; Kojima, H.; Komaba, S. Highly Concentrated Electrolyte Solutions for 4 v Class Potassium-Ion Batteries. *Chem. Commun.* 2018, 54 (60), 8387–8390. <https://doi.org/10.1039/c8cc04433c>.
2. Hosaka, T.; Matsuyama, T.; Kubota, K.; Yasuno, S.; Komaba, S. Development of KPF₆/KFSA Binary-Salt Solutions for Long-Life and High-Voltage K-Ion Batteries. *ACS Appl. Mater.*

- **For Raman spectra analysis (table 5.1) we see that even 1M solution of KPF₆ in diglyme the fraction of unperturbed solvent molecules is only 25%. Can the author compare these results with other studies (e.g. for lithium or sodium ions in ether solvents)?**

The amounts of free solvent molecules were measured for KFSA/G1; KFSA/G2 and KFSA/G3 electrolyte solutions¹. In the most dilute electrolyte the fraction of unperturbed solvent molecules reaches 50-60 that exceeds 25% we have obtained in our study. But this amount is still enough to destroy cell performance if no stable SEI film is formed.

1. Hosaka, T.; Matsuyama, T.; Kubota, K.; Tatara, R.; Komaba, S. KFSA/Glyme Electrolytes for 4 V-Class K-Ion Batteries. *J. Mater. Chem. A* 2020, 8 (45), 23766–23771. <https://doi.org/10.1039/D0TA08851J>.

- **The description of impedance spectra (p. 83) is given in definitive and non-convincing way. For example, the author claims that high-frequency intercept in Nyquist plot is the solution resistance. I'm pretty much sure that it's true, however, the methodology of AC impedance analysis should be described (and ideally compared to conductometry measurements).**

Symmetric cells are utilized as EIS does not give us the reliable data in two-electrode cells with two electrodes being different to each other. Since no potential is applied there is no faradaic reaction. Only processes that might occur is the spontaneous formation of surface layer and the double layer charging. Each of them is represented by corresponding elements in the modelling scheme. The utilized technique was applied in number of studies¹.

1. Single, F., Horstmann, B. and Latz, A., 2019. Theory of impedance spectroscopy for lithium batteries. *The Journal of Physical Chemistry C*, 123(45), pp.27327-27343.

- **In the same part, the author shows that SEI resistance dependence on concentration has a minimum at 2.0 M. What is the experimental error and what is reproducibility of R_{SEI} estimation?**

The experiment in K symmetric cells were reproduced 3 times and electrolytes were prepared again for each time. The diglyme-electrolyte solutions with KPF₆ salt concentrations corresponding to 1M; 1.5M; 2V and 2.5M. The deviation values were added to the Table 5.2. The largest variation was observed for 1M KPF₆/G2 electrolyte solution.

- **In all the work the author uses molar concentrations for electrolyte solutions. Are they truly mols per liter? Were the densities of solutions measured?**

This issue was not checked during the study a couple years ago. The solution densities were measured due to the reviewer request. The molar concentrations were calculated to be slightly different (“1M” – 0.97M; “1.5M” – 1.54M; “2M” – 1.91M; 2.5M- 2.45M). The differences may occur due to the prolonged storage time of G2 and KPF₆ salt in the glovebox.

- **The XPS data for cycled HC electrodes look strange. While in the F 1s spectrum there is distinctive peak for C-F bond, there is not counter-part in C 1s spectrum. Can the author comment on that?**

The data were reanalyzed and this peak is assigned to K_xPO_yF_z according to the published literature¹.

1. Wu, Z.; Zou, J.; Shabaniyan, S.; Golovin, K.; Liu, J. The Roles of Electrolyte Chemistry in Hard Carbon Anode for Potassium-Ion Batteries. *Chem. Eng. J.* 2022, 427, 130972. <https://doi.org/10.1016/J.CEJ.2021.130972>.

- **One more question on XPS analysis: was any actions performed to compensate the sample charging (SEI is insulating)?**

The dual beam charge neutralization method was applied at PHI VersaProbe II spectrometer. It uses a low energy ion beam to eliminate the samples static charge allowing the low energy electron beam to reach the sample and neutralize the localized positive charge created by the x-ray beam

- **In fig. 6.3 it is not clear what does band color intensity mean? Do they show different spectral components? Which ones?**

Yes, it demonstrated the distribution of elements with different chemical bonding\environment. But Figure 6.3 was removed from the manuscript as it does not deliver any important information.

- **To be honest, I cannot see the potassium trapped in the “cages” in fig. 7.9.**

Figure 7.9c illustrates that C-K EELS edges in HC electrode after 30 cycles exhibit two clear peaks at 297.5 and 300.1 eV belonging to the K-L_{2,3} edge compared to pristine HC electrode.

- **There are some typos (e.g. Russian letters in conclusion #2). Some figures and captions are poorly formatted: e.g. figs. 3.1, 4.5, 5.1, and others are single-column but have two-column captions. Fig. 5.6c (equivalent scheme) is of a poor quality (low resolution).**

Figure 5.6 was added with high resolution. Other figures were also formatted and all typos were corrected