

Thesis Changes Log

Name of Candidate: Vahid Ramezankhani

PhD Program: Materials Science and Engineering

Title of Thesis: Characterization and Optimization of Organic Redox-Active Electrode Materials for Potassium-Ion Batteries

Supervisor: Dr. Stanislav S. Fedotov

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

I appreciate the feedback provided by the members of the jury on my dissertation.

Response to Prof. Mohammadhossein Safari

Page 21 (end of page): this is not a convincing reason for not choosing the inorganic electrodes...I assume that you wanted to mention that the in-depth investigation of such electrodes requires advanced techniques not available in the conventional research labs.

Response. It is edited as “conducting an in-depth investigation of electrodes of this nature necessitates the utilization of advanced techniques that are not typically accessible in conventional research laboratories.

Page 23: there are some typos in this page. Please carefully check the English.

Response: Grammar is checked and edited.

Page 24: a more negative potential (remove 'cell').

Response: It is removed.

Page 25: replace ‘metal-ion transportation’ by ‘charge transport’. Charge transport is a better term as the electrolytes mostly have a transference number for the metal ions which is far less than one. ‘transport’ is the right term instead of ‘transportation’.

Response: It is replaced.

Page 25 (last paragraph): in the text both ‘cathode/anode’ and ‘positive/negative’ has been used to distinguish between the electrodes. This can be confusing. Please stick into one terminology.

Response: Changed to cathode and anode.

Page 26 (end of page): I suggest the following rephrasing: this method is based on the application of a constant current and following the evolution of the cell voltage. The capacity delivered by coulomb counting when normalized to the mass or volume of the electrode can determine the specific capacity of the electrode under study.

Response: It is edited to what you suggest.

Page 27: eq.1: provide the dimension of the variables I assume that C is in mAh/g

Response: The dimension for C-rate is mA g⁻¹. However, for capacity mAh g⁻¹ is applicable.

Page 27: end of page: mAh cm⁻²

Response: It is corrected. Thanks!

Page 28: average reduction discharge potential

Response: There is no difference between average reduction potential and average discharge potential. However, I switched to the discharge potential.

Some figures seem to be reproduced from the literature. Please make sure to cite the appropriate references in the figure captions.

Response: Around 97% of Figs in this dissertation is my own design except where I included references.

Page 33: you mention ‘mechanical stability of the liquid electrolyte’. It is not clear what is meant

by the mechanical stability in the context of a liquid electrolyte.

Response: It is edited as “the mechanical stability of SEI (homogeneity and integrity) of the KFSI-containing electrolyte”.

Figure 2.7: in subplot(c): at right end of the schematics, 'k+' should be replace by 'A-' ?

Response:

Thanks! It is corrected.

Page 39: mention the reference electrode in reporting the half-cell electrode potentials 0.8-3.2V vs. ? (K, SHE, or Li,...) This seems to be a general remark in the remainder of the text as well.

Response: It is added as “vs. K⁺/K”. All experiments are in a half-cell scheme.

Page 44: better to replace the ‘assayed’ term throughout the whole manuscript by something like 'investigated

Response: The word assayed is replaced.

In section 2.13: more details about the problems with the K metallic anode could have been included. particularly compared to the Li and Na metallic electrodes.

Response: This paragraph is added to the section 2.13. The outer layer of alkali metals, such as lithium Li, Na, and K, is known to develop an oxide coating, primarily composed of K₂O with a layer of KO₂ on top. Notably, the oxide layer on K is more porous compared to that on Li and Na, even when potassium is handled with care within an argon (Ar)-filled glove box. An additional challenge associated with using metallic potassium is its strong propensity to develop dendrites when it comes into contact with the electrolyte. This is particularly concerning as the onset of dendrite formation occurs at a remarkably low crossover current, as low as 0.2 mA cm⁻². This behavior is likely attributed to the relatively high self-diffusion coefficient of potassium compared to Li and Na.

Chapter 3 (page 58): here more details can be provided about the type of materials to be seen in the following chapters (at least a list of names) - also a paragraph could be added to motivate the thesis objective in the perspective of the discussions in the previous chapter... a kind of knowledge gap analysis to substantiate the contribution of this thesis. Also, P1-P9 polymers better to be introduced in some detail. For instance, which category of polymers they belong to, etc.

Response: The following paragraph is added to the dissertation. For an extended period, the integration of organic materials into metal-ion battery technology has posed substantial challenges. Organic materials are prone to dissolution in carbonate and ether-based electrolytes, with carbonyl-containing organic materials being particularly susceptible. Their performance is hindered by lower tap energy density, reduced conductivity, capacity degradation, and suboptimal ICE. In this context, we introduce 11 novel organic redox-active materials within the carbonyl-containing family, widely recognized as one of the most formidable classes of organic materials. Our goal is to address the longstanding challenges that have persisted since the 1980s. To achieve this, we have established the following research objectives:

Section 4.2: here, you better start the section by briefly mentioning that for some of the electrode materials besides the tape casting, the spray coating method was tried as well for the coating of the electrodes. You might also briefly motivate it.

Response: The following paragraph is added. “For OHTAP, we are exploring spray coating to control thickness, uniformity, and adhesion to the Al current collector. However, for the other materials, we are exclusively investigating tape casting.”

Section 4.3: again, some short motivation is helpful to explain the need for this step and the materials.

Response: The following paragraph is added. “Solution-based pre-potassiation is a straightforward technique used to investigate the uptake of metallic potassium by functional groups. In this method, the composite is treated with potassium naphthalene, leading to a discernible change in the solution's color as the reaction progresses. Subsequently, the reacted electrodes are examined using FTIR to compare their spectra with those of pristine organic materials. This approach offers the advantage of bypassing the arduous process of extracting electrodes from cycled coin-type cells.”

Figure 5.2: it is helpful to state or restate the formulation of the electrodes and also the electrolyte formulation in the figure captions. At the end, it is important to have an idea about the gravimetric capacity of the electrodes considering the extra weight of the binder and conductive additives. This can simplify the comparison of the results of this research with the SOA Li-ion and other technologies.

Response: The text is added as “The composite electrode formulations used in both deposition techniques are 50:40:10 wt. % of OHTAP: Carbon super P: PVDF and the electrolyte formulation is 1 M (KTFSI) in (DOL:DME = 1:1 v/v).”

During battery programming on a battery tester to apply a specific current rate, only the weight of the active mass is taken into account. Furthermore, in the text, it is mentioned that the inclusion of carbon in the capacity yields approximately 25 mAh g⁻¹.

Table 5.1: I think it is useful to add an extra column to list the normalized energy density of the samples including the weight of the binder and carbon.

Response. Following text “. The last column corresponds to the normalized energy density, considering the weight of carbon and binder” and table 1 are added.

Table 1 Overview of the electrochemical performance of polymers **P1-P6**.

Polymer	Theoretical specific capacity (mAh g ⁻¹)	Current density (A g ⁻¹)	Cycle number	The initial capacity (mAh g ⁻¹)	The final capacity (mAh g ⁻¹)	Average discharge potentials (V)	Energy density (Wh kg ⁻¹)	Normalized energy density (Wh kg ⁻¹)
P1	518	0.5	400	388	422	1.65	696	348
P2	686	0.6	500	254	274	1.84	504	252
P3	468	0.4	50	190	207	1.56	322	161
P4	669	0.55	1400	208	216	1.8	392	196
P5	515	0.38	150	243	246	1.7	418	209
P6	418	0.3	1000	204	214	1.77	379	189.5

It is better to locate the figures as close as possible to the place where they are discussed for the first time in the text. So you might improve on this aspect.

Thanks a lot! It is revised.

Response to Prof. Evgeny V. Antipov

Firstly, the rationale behind the selection of a G₂-based electrolyte with a concentration of 2.2 M warrants clarification, as understanding the choice of electrolyte concentration is pivotal to the overall research context

Response: Here are some reasons for choosing the electrolyte with this formulation. Firstly, I had to think about high viscosity to suppress the dissolution of organic redox active materials. The second reason is the issue with metallic potassium. The outer layer of alkali metals, such as lithium Li, Na, and K, is known to develop an oxide coating, primarily composed of K₂O with a layer of KO₂ on top. Notably, the oxide layer on K is more porous compared to that on Li and Na, even when potassium is handled with care within an argon (Ar)-filled glove box. An additional challenge associated with using metallic potassium is its strong propensity to develop dendrites when it comes into contact with the electrolyte. This is particularly concerning as the onset of dendrite formation occurs at a remarkably low crossover current, as low as 0.2 mA cm⁻². This behavior is likely attributed to the relatively high self-diffusion coefficient of potassium compared to Li and Na.

Secondly, it would be valuable to explore the possibility of crystallization of the polymers investigated throughout the dissertation, as this could significantly impact their performance and applications.

Response: Some reports indicate that organic potassium salt materials exhibit a crystalline structure. For instance, Ni-based coordination polymers and organic potassium salts demonstrate crystallinity (1,2). An effective method for assessing the crystallinity of an organic electrode material is through cyclic voltammetry and galvanostatic charge and discharge profiles. Materials with a certain level of crystallinity typically display a plateau in their charge-discharge profiles, while investigated polymers tend to exhibit smooth charge and discharge curves. XRD measurements were conducted on materials with the rigid back-bonding polymer P9, which showed an amorphous structure. I was confident that materials containing pyrazine rings do not possess a crystal structure, as evident from the XRD pattern in Figure 1c. However, when thiophene and dioxin rings are combined with benzoquinone, a minor degree of crystallinity emerged, although the predominant structure in polymers P7 and P8 remained amorphous. As shown in Fig. 1a,b, small peaks are apparent in the XRD pattern of P7 and P8. Probably, To further investigate the crystallinity, I must examine it with an XRD system with a shorter wavelength since I had access to a Cu source with a wavelength of ~ 1.5406 Å.

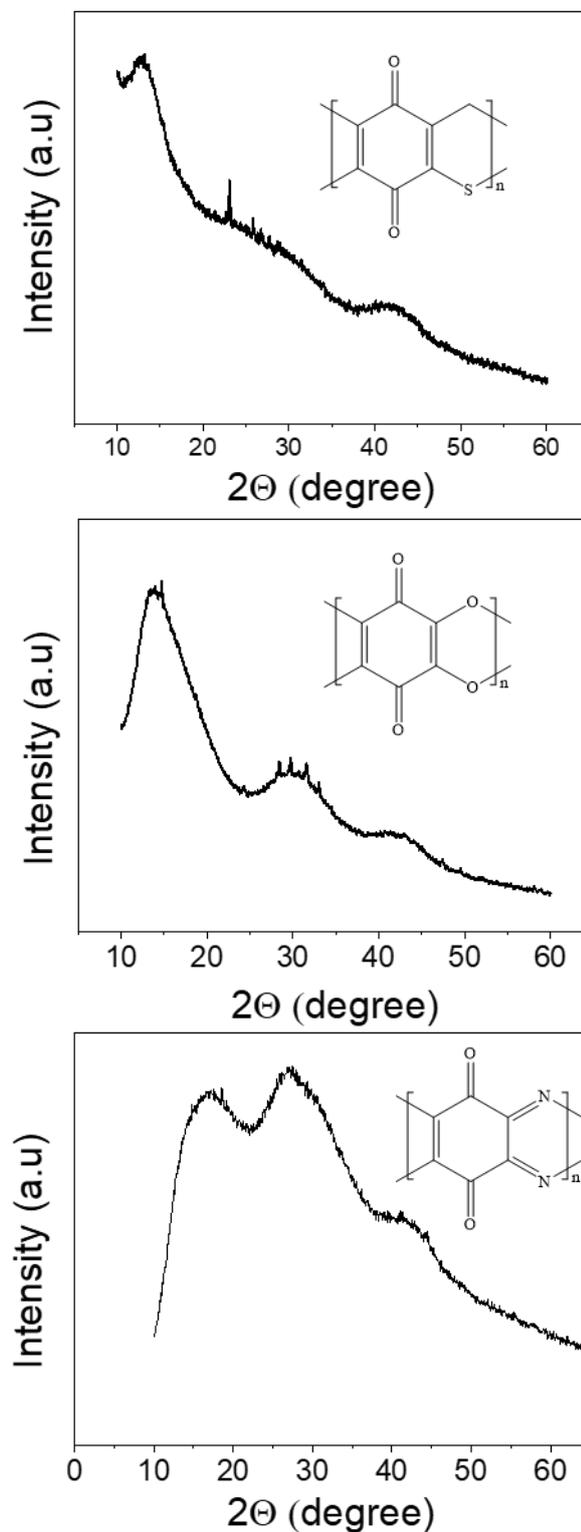


Fig. 1. XRD patterns of polymers P7 (a) P8 (b) and P9 (c).

Lastly, addressing the question of whether OHTAP operates effectively when implemented as a cathode in a real full-cell battery is crucial.

Response.

No. For this purpose it is required we prepare OHTAP-K salt or pre-potassiated **OHTAP** with K-naphtalene.

Response to Prof. Radostina Stoyanova

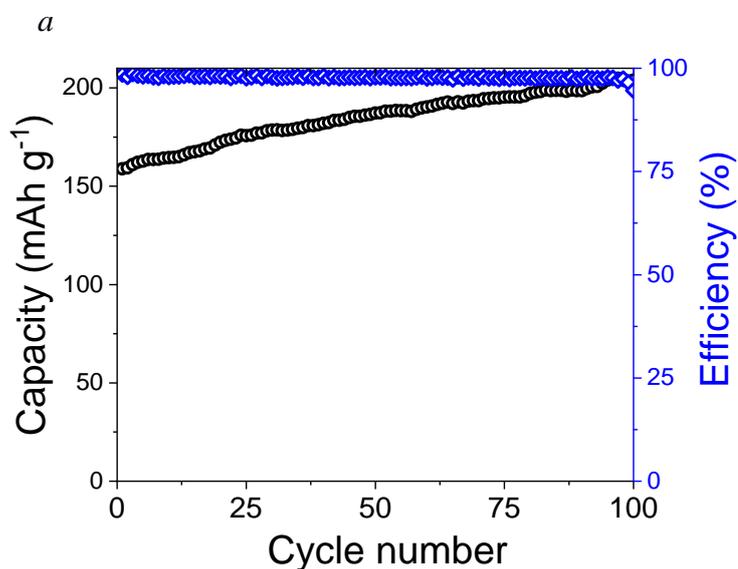
1. In half K-ion cell, the highly reactive K metal initiates a series of electrolyte decomposition reactions, which on its turn affect the overall cell performance. In this context, whether this issue is of importance for model K-ion cells fabricated in this thesis.

Response: Yes. the issue with metallic potassium. The outer layer of alkali metals, such as lithium Li, Na, and K, is known to develop an oxide coating, primarily composed of K_2O with a layer of KO_2 on top. Notably, the oxide layer on K is more porous compared to that on Li and Na, even when potassium is handled with care within an argon (Ar)-filled glove box. An additional challenge associated with using metallic potassium is its strong propensity to develop dendrites when it comes into contact with the electrolyte. This is particularly concerning as the onset of dendrite formation occurs at a remarkably low crossover current, as low as 0.2 mA cm^{-2} . This behavior is likely attributed to the relatively high self-diffusion coefficient of potassium compared to Li and Na. For example, I assembled half-cells, using OHTAPQ as active materials. I used electrolyte with formulation as 1 M KTFSI in (DOL: DME 1:1, v/v). As shown in Fig. 2, after cycle # 70 dendrite is initiated to form. Hence, I used concentrated electrolyte with formulation 2.2 M KPF_6 in diglyme.

2. Because of the low electrical conductivity, the electrode compositions are prepared by using a high amount of conductive carbon additives (or MWCNT). To what extent the carbon additives are passive in K-ion cells.

Response: The electrical conductivity of organic materials depends on their molecular structure. Small molecules and polymers containing pyrazin rings exhibit poor conductivity and require a 40 wt. % carbon nanofiller. On the other hand, there are a couple of polymers that contain benzoquinone as the building block, dioxin (**P8**), and thiophene rings (**P9**). Among these, **P7** exhibits better conductivity than **P8**, allowing for the use of 20 wt. % carbon super P (Fig. 2a). However, **P8**, with the same amount of carbon additive, demonstrates inferior performance (Fig. 2b).

In summary, a 40 wt. % carbon nanofiller is the upper limit for **OHTAP**, **OHTAPQ**, **P1-6**, and **P9**. On the other hand, the highest acceptable limit for **P7** is 20 wt. %.



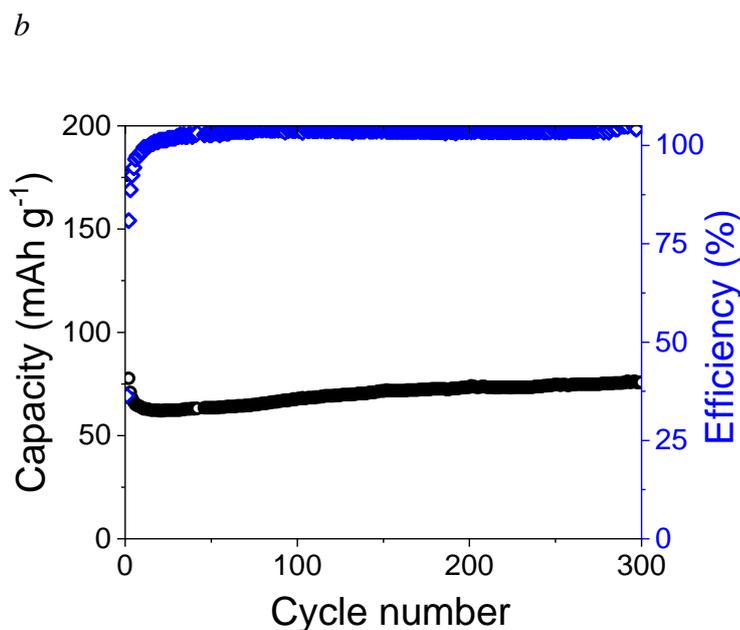


Figure 2. Cycle performance of P7 (a) and P8 (b), using 20 wt. % carbon nanofiller.

3. Concerning the mechanism of the electrochemical reaction, it appears that Faradaic and/or capacitive reactions contribute to the K-storage by organic materials. Is it possible to make a comparison between the different types of organic electrodes in respect of Faradaic/capacitive reactions?

Response: Yes. We can compare materials based on their specific surface area (SSA). As indicated in Table 2, P8 exhibits the highest surface area, making this polymer particularly suitable for supercapacitor applications. Among other polymers, P1, P2, and P7 possess surface areas of approximately 21.3, 27.2, and 26 m²/g, respectively, placing them in a range that exhibits characteristics bridging between battery materials and supercapacitors. For instance, P1 has a b-value of approximately 0.77, and its surface area of 21.3 suggests some capacitive characteristics.

To minimize non-Faradic reactions, the lowest tested voltage for half-cell experiments was maintained at 0.7 V.

Table 2. Surface area of investigated polymers

Polymers	P1	P2	P3	P4	P5	P6	P7	P8	P9
SSA ¹⁾	21.3	27.2	4.87	3.79	11.6	6.98	26	236	17
m ² g ⁻¹									

Response to Prof. Alexander M. Korsunsky

I would replace “design” in the chapter title with “characterization and optimization”, as it may be a better description

Response: The title changed to “Characterization and Optimization of Organic Redox-Active Electrode Materials for Potassium-Ion Batteries”.

I prefer to point out here that, in my opinion, the Objectives chapter needs re-thinking and revising.

Response. Chapter 3 is totally revised as

Chapter 3

For an extended period, the integration of organic materials into metal-ion battery technology has posed substantial challenges. Organic materials are prone to dissolution in carbonate and ether-based electrolytes, with carbonyl-containing organic materials being particularly susceptible. Their performance is hindered by lower tap energy density, reduced conductivity, capacity degradation, and suboptimal ICE. In this context, we introduce 11 novel organic redox-active materials within the carbonyl-containing family, widely recognized as one of the most formidable classes of organic materials. Our goal is to address the longstanding challenges that have persisted since the 1980s. To achieve this, we have established the following research objectives and detailed research flow chart (Fig 3.1):

3. Thesis objectives

Aim: Design of advanced K-ion batteries using organic redox-active materials.

Objectives:

- Characterization of the organic carbonyl-containing small molecules and polymers;
 - Tetraazapentacene-based redox-active materials;
 - Polymers derived from triquionoyl;
 - Rigid backbone quinone-based polymers
- Electrochemical characterization of the materials in half-cells with K-anode (cyclic voltammetry, galvanostatic charge/discharge, etc.);
- Investigation of proper electrolyte formulation to match well with metallic potassium;
- Exploring K-ion storage mechanism of carbonyl-containing materials by means of:
 - X-ray photoelectron spectroscopy (XPS);
 - Fourier Transform Infrared Spectroscopy (FTIR).
- Optimization of the electrodes in order to reach the highest capacity and the best charge-discharge cycling stability.
- Optimization of the electrode composition and mass-loading.
 - Replacing carbon super P with MWCNT.

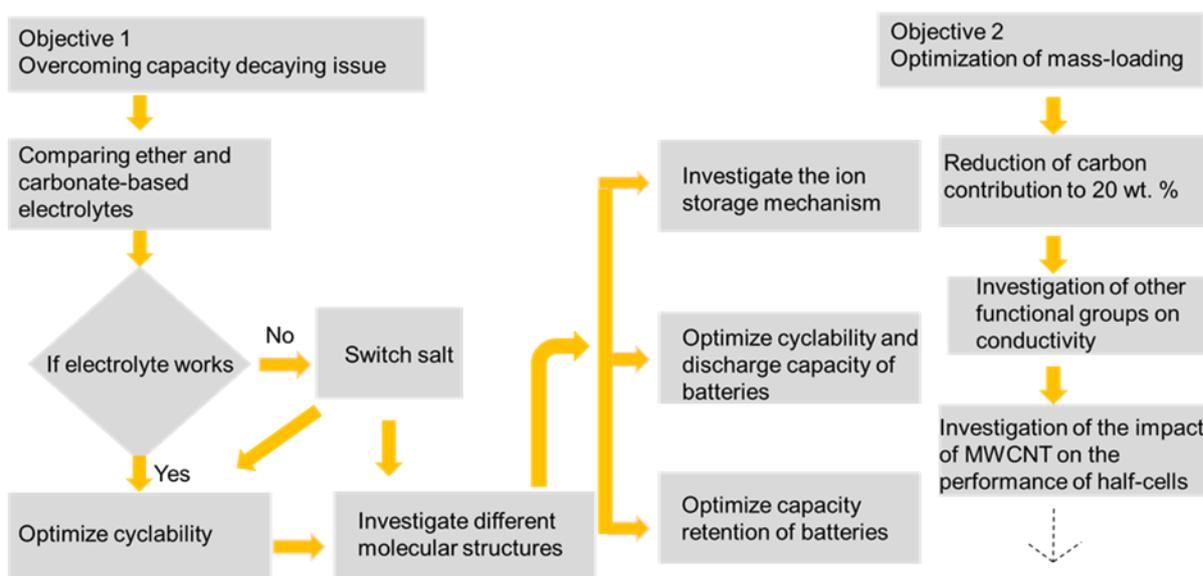
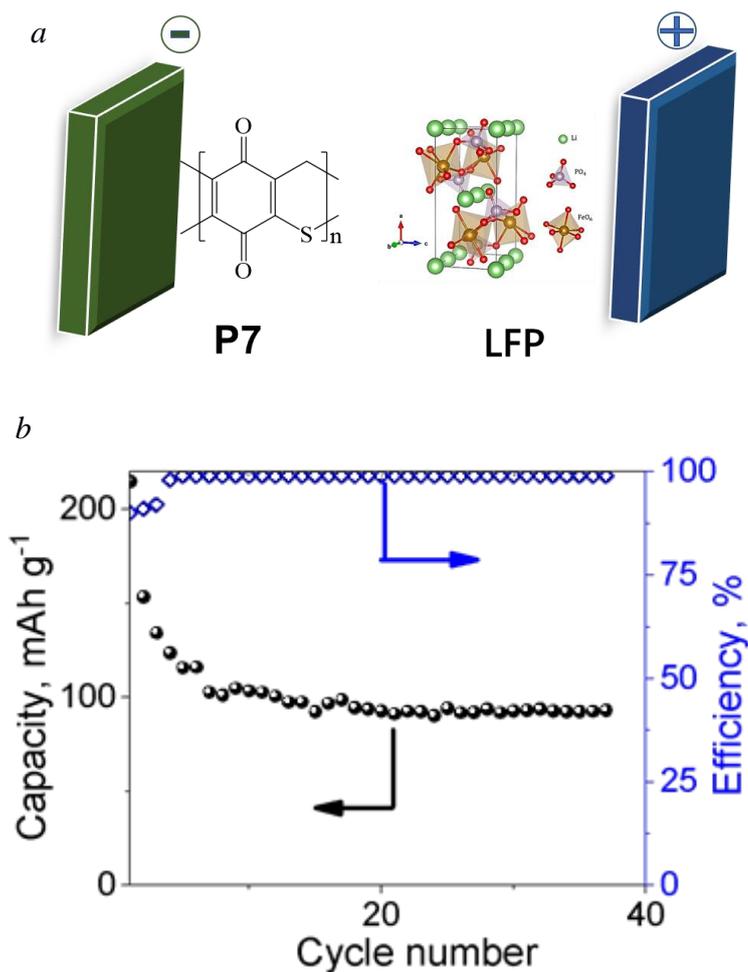


Fig 3 Research methodology flow chart

Response to Dr. Smagul Karazhanov

Have you tested the concept of pairing **P7** with high-potential inorganic materials, possibly in lithium-full cells?

Response: The full cell was constructed using LiFePO_4 (LFP) as the cathode and **P7** polymer as the anode (Fig. 4a), comprising a composition of 90% **P7**, 5% CNT, and 5% PVDF, with a mass-loading of approximately 6.3 mg cm^{-2} . At a current density of 30 mA g^{-1} , the half-cell demonstrated a capacity of approximately 100 mAh g^{-1} (Fig 4b). In the process of assembling a full cell, LFP underwent testing in a half-cell configuration at a C/10 rate, exhibiting a capacity of 159 mAh g^{-1} within the voltage range of 2.5-4.2 V (Fig. 4c). The full cell was prepared with a mass ratio of **P7** to LFP at 1:10. The initial results revealed an initial capacity of $\sim 133 \text{ mAh g}^{-1}$, instilling considerable optimism regarding the potential application of **P7** as electrode material in full lithium batteries (Fig. 4d).



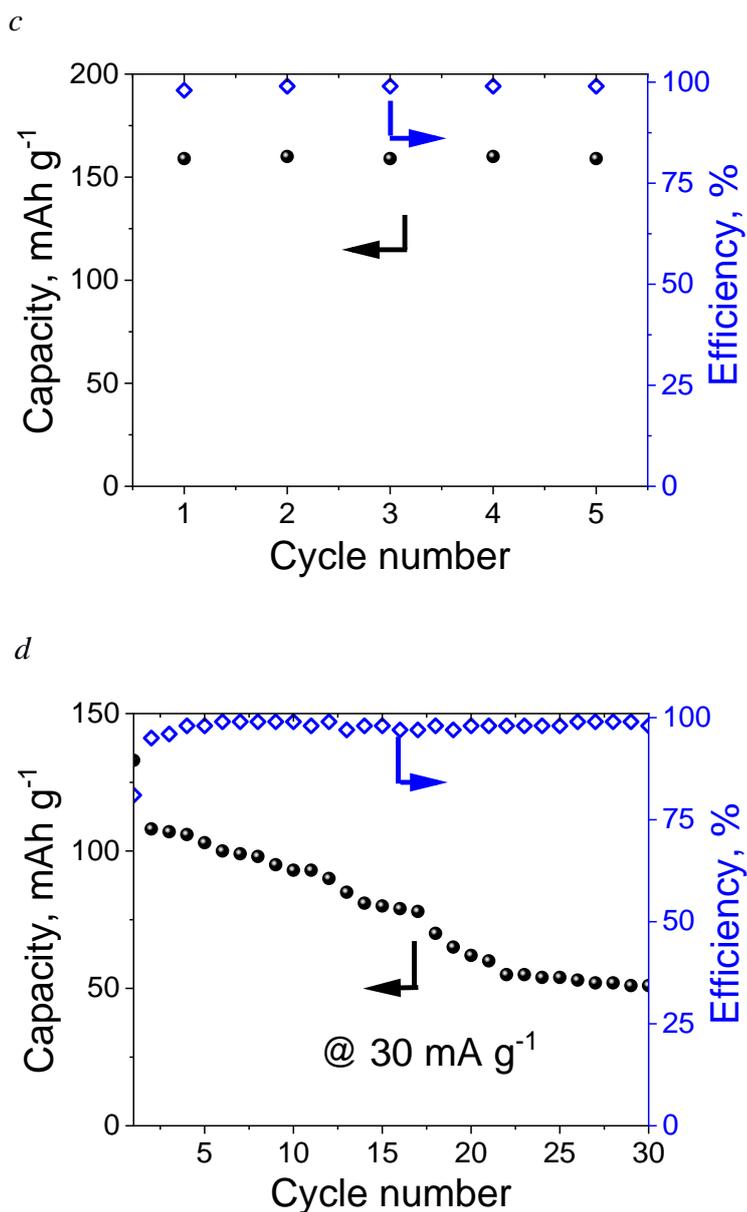


Fig. 4 Schematic of full Li battery (a), P7||Li half-cell at 30 mA g⁻¹(b), LFP||Li half-cell at C/10 rate (c) and LFP||P7 full cell (d).

References

1. Qijiu Deng, Congcong Tian, Zongbin Luo, Yangyang Zhou, Bo Gou, Haixuan Liu, Yingchun Ding and Rong Yang. Organic 2,5-dihydroxy-1,4-benzoquinone potassium salt with ultrahigh initial coulombic efficiency for potassium-ion batteries. *Chem. Commun.*, 2020, 56, 12234.
2. Roman R. Kapaev, Ivan S. Zhidkov, Ernst Z. Kurmaev, Keith J. Stevenson, and Pavel A. Troshin. A nickel coordination polymer derived from 1,2,4,5-tetraaminobenzene for fast and stable potassium battery anodes. *Chem. Commun.*, 2020,56, 1541-1544.