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Thesis Changes Log

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PhD Program: Materials Science and Engineering

Title of Thesis: Advanced characterization methods of materials and redox mechanisms in flow batteries

Supervisor: Prof. Keith Stevenson

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

Review of Professor Evgeny Antipov

All mistypes were corrected.

p. 24 Lithium-ion batteries were introduced into the market in 1991

p. 27 On the other side, the scientific community proposes new perspective materials for the cathode side and new high-voltage electrolytes to enhance battery power and specific capacity.

p. 27 At the nanoscale level, materials with advanced morphology are developed, which are capable of fast and reversible redox processes, e.g. graphene-based ones.

p. 29 Titan-based components, like sulfides, NASICON-type $NaTi_2(PO_4)_3$, and …

p. 30 These materials typically are cycled within two voltage plateaus.

p. 35 The electrochemical cell consists of two independent compartments through …

p. 39 $VO_2^+ + 2H^+ + e^- \rightleftarrows VO^{2+} + H_2O$ E_0 = 1.00 V vs. SHE

p. 39 The battery operates with an energy efficiency of >75% at current densities …

p. 75 Firstly, materials properties were monitored during aging in 0, 20, 80 and 100% SOCs …

p. 77 1.6 Summary from the literature review

Page numbers were added to the section 2.3

p. 100 50 ml of commercial electrolyte solution (1.6M of vanadium ions (V(III/IV) in 3M H_2SO_4) is used each time.

p. 102 The cell was charged with 100 mA cm^{-2} current density.

p. 111 The complex reaction of V(V) → V(IV) goes slower than the V(IV) → V(V) with …

Review of Professor Zhumabay Bakenov

1. *Clearly state the reason of studying the redox-active colloids based on LiMn2O4 nanoparticles along with the main object, the vanadium based RFB.*

p. 77 More detailed explanation was added to the Section 1.6 and 1.7.

p. 134 $LiMn_2O_4$ material was used as a model due to its high electronic conductivity, comparing to other cathode materials. Theoretical volumetric capacity of such systems significantly exceeds standard values of soluble species. However, both cases require understating of limiting reaction stages for further system development.

2. Add some discussions on the Author's vision of possible ways to enhance the V-RFB kinetics, and further enhancement of these RFBs implementation.

p. 113 In the case of vanadium RFB, additional improvements imply boosting of the $V^{3+/2+}$ pair kinetics, which can be done by an increase of surface area, conductivity enhancement, and introduction of stable active sites on the electrode surface. Moreover, balancing of the electrolyte flow rate, internal resistance of the cell and the real surface area of the electrodes can effectively extend the operation regimes without kinetics limitations.

3. It would be great if the Author added the DOI links in the Publications part of the Thesis (page 5) for ease referring.

p. 5 DOI links to the publications were added.

4. The Author participated in the INESS-2022 Conference in Kazakhstan in August 2022. This should be added to the list of Conferences (page 6)

I did not attend the Conference.

Review of Professor Oleg Levin

1. The research, described in the Ph.D. thesis, covers several systems for redox-flow batteries with different chemistries. What governed the choice of these systems? Are there any common properties, justifying the combined investigation of them?

p. 77 The explanation was added to the Section 1.6 and 1.7.

2. Chapter 2.2. According to the findings, described in the chapter, the structure of the surface of carbon materials influence the kinetics of vanadium redox processes on it. Based on you results, can you provide

any hints for choosing the better electrode materials for vanadium ORBs? Can the findings of Chapter 2.2 be somehow correlated with carbon composites design, presented in the Chapters 3.2 and 3.3?

p. 113 To sum up, both developed methods are useful tools for the elucidation of the problems with sluggish kinetics of any redox-active species at different electrode materials utilized in RFB. In the case of vanadium RFB, additional improvements imply boosting of the $V^{3+/2+}$ pair kinetics. Selection of the optimal electrode material is based on balancing of several factors: high active electrochemical surface area with many active sites and good transport properties for the electrolyte flow. Based on Raman studies, it occurs that high surface conductivity is an essential element for reaction rate acceleration. Therefore, a carbon material, like carbon paper or felt, modified by nanoparticles with pronounced catalytic effect, good stability in under operation conditions of the battery and high conductivity seems to be the best choice. Moreover, the additional attention must be paid to the suppression of hydrogen evolution reaction and stability of active sites on the anolyte side of the cell. Furthermore, balancing of the electrolyte flow rate, internal resistance of the cell, and the real surface area of the electrodes can effectively extend the operation regimes without kinetics limitations.

p. 132 The requirement for high conductivity is crucial as insufficient conductivity leads to high contact resistance between electrodes and current collectors, and, hence, to poor battery performance. The importance of high surface conductivity and no its reduction during long-term operation of the battery became evident based on the previous research.

Review of Professor Dmitry Shchukin

1. Introduction part. The hot topic in battery research is to replace one-electron battery to two-electron battery thus doubling the theoretical battery capacity. The candidate should comment this new direction comparing to the RFB approach.

p. 31-32 The discussion was added.

2. Why did RFBs get low attention from industry? What are the current difficulties for their application? Is it possible to use this concept for e-vehicle recharging (like petrol station with energy tanks)?

Main reason for slow RFB market growth was a synergy of two factors: low number of industrial installation due to poorly developed legislative framework and a system of standards and operation rules. The successful cooperation work of the leading companies has shifted the process, and the market is growing now. The most relevant directions now remain stationary grid energy applications, however, several projects were proposed using the electrolytes regeneration system for port marine boats [1].

1. *PESO: Port Energy Systems Optimisation | Maritime UK*. (n.d.). Retrieved October 8, 2022, from https://www.maritimeuk.org/priorities/environment/netzeromaritime-showcase/PESO-Ports-Energy-systems-Optimisation/

3. What is the influence of flow speed on the RFB performance?

p. 96-97 The flow of the electrolyte determines the mass-transport of redox species to the electrode, thus the limiting current for the flow rate can be derived. This type of losses is called concentration losses, as it increases the overpotential. Typical operation conditions of the flow battery are selected so that other types of losses (activation and ohmic) dominate, hence, flow speed is adjusted. Influence of concentration losses

is significant at high current densities. Numerical evaluation of dependence of a cell voltage on flow rate is described on pages 96-97.

4. Developed analytical methods should be compared to the existing ones.

Since each of the methods is discussed in a separate article, a comparison with exciting methods was given in the introduction to each article. In an addition, the literature review sections 1.4.5, 1.4.6, 1.5.3, and 1.5.4 highlight the existing methods. Comparison of Raman spectra decoding with literature data was done the article. Extracted numerical values of the apparent rate constants for the vanadium reactions were compared with the literature data also (p. 95). Methods for bipolar plates stability test were based on the similar ideas from fuel-cell science. I made the attempt to make the universal protocol, so that test results from different materials can be compared. Since the redox active colloids are the new class, no systematic studies on properties investigation were done. Moreover, sensing the electrochemical response from the suspension required new analytical models and methods. I adopted the basic method from catalysis to make fast screening redox response tests of the colloid materials and applied single particle collision experiment probing the colloid system without constant electrode contact.

5. Why vanadium-based RFBs have been selected; why not other and similar? I have found plenty of publications in WoS describing other redox pairs.

We selected vanadium for two reasons:

1) Based on the literature review, I demonstrated that vanadium chemistry is at the commercialization level in several companies and scientific knowledge of this system is impressive. Thus, developing the universal method for in situ materials characterization based on the model vanadium system would be straightforward in results interpretation.
2) Despite the many reported methods of the electrode modification, the origins of the performance improvements were unclear, hence, the developed technique could shed light on the important features of the reaction pathways.

p. 78 The vanadium-based system was chosen as a model RFB, due to a great accumulated scientific experience of this system and the VRFB suitability for a commercialization in Russia. Thus, developed characterization methods can be directly applied in the field.

6. What is biologic potentiostat (page 96)? I know Galvani's experiments (already published); is it similar?

p. 99 Testing is performed by BioLogic potentiostat VMP-3 with 10A booster. It is the name of the company and the model of the research-grade potentiostat device.

7. Why are bipolar materials important? What is about shortcuts?

p. 63 Bipolar plate provides electron shortcuts from a porous electrode to a current collector. It serves as the electrode made of impermeable, dense material with high conductivity. Moreover, the plates allow a serial

connection of the cells: one bipolar plate serves as a negative electrode for the first cell and as a positive electrode for the second cell.

8. Did you account for capillary effects in your model? Any charge/discharge effect is about interface and the delivery of the material to it.

We did not account for the capillary effect in the model. The volume of each compartment of the cell was represented as 10% of porous electrode material and 90% of the electrolyte, which is pumped at a constant speed through the cell under laminar regime (percentage was derived from the carbon felt porosity). We had an empirical mass transfer coefficients as a function of flow rate, that derives the rate of bring new portions of the electrolyte to the interface (p. 96).

Review of Professor Stanislav Fedotov

I would like to thank Professor Stanislav Fedotov for his constructive criticism of the work and valuable comments on the coherence lack. I tried to improve the thesis according to his comments and justify my position.

1. I strongly suggest to reformulate the thesis title since the work presents not only the characterization methods, but also the experimental approaches and numerical/modeling techniques aimed at the improvement of the RFB performance. The thesis includes a substantial part dedicated to the methods of capacity improvement which should not be neglected in the thesis or excluded if the current one remains.

The title of the thesis is selected as the generalization of my research findings and includes the proposed the experimental approaches and numerical/modeling techniques. Each paper is devoted to the material investigation as an object, but the developed methods are the most applied part of the works.

2. The miscomprehension of the title and request to correct it possibly originate from the absence of clearly written aims and goals of the thesis. I could not find a corresponding section in the thesis stating the idea, setting the goal and tasks for the work. This section should be added to disclose the reasoning behind the thesis proposal and assembling.

p. 79 The goals and objectives were added to the Section 1.7.

3. The thesis is composed as a compilation of research papers co-authored by the applicant. Generally, this form of thesis defense is appropriate if the series of papers presented is reasonably united by a common topic and is principally led by the applicant (the applicant is a first author mainly), not speaking of the scientific novelty and significance of the whole work that should be immediate and clear. In the current case, the work done consists of various projects that are attempted to be stitched into a single story but, in fact, are hardly glued without sufficient justification and detailization. Moreover, the applicant's input in most of the co-authored papers is not clear, nor properly explicated. A conventional form of a thesis manuscript might have been more appropriate for this case to give the committee/juries/readers a comprehensive description and understanding of its contents.

The author's contribution to each article is specified under the title of each article. The thesis format was approved at the pre-defense. Probably a not-standard thesis format confuses, as instead of considering different materials in each chapter of the thesis, a description of different methods is given.

4. The literature review should normally be designed to supplement the contents of the thesis. If the key idea of this thesis is the development of characterization methods and capacity improvement techniques then the overview should definitely reveal some useful information as to what other or similar methods of characterization are known and developed previously, their advantages/drawbacks and processes/parameters to be characterized, and what capacity boosting methods are currently available to further emphasize the advancement of the newly proposed improvement methods. The literature review currently is huge though incomplete since it does not comprise the necessary information which would help to understand the novelty, significance and advancement of all the work done.

The literature review is built as a general materials overview, followed by a detailed discussion of characterization methods and conclusions from each of the section for keeping the coherence.

p. 77 Summary from the literature review was expended to illustrate the logic in the Section 1.7.

5. Chapter 5 that summarizes the results and draws conclusions starts with the phrase "the development of tools that can be applied for materials characterization in the scope of RFB applications". As follows from the thesis, the characterization methods are simply a half of the proposed thesis. The other substantial part that is dedicated to the capacity improvement approaches is missing. Redox-active colloids and conductive additives cannot be considered as characterization methods. These are RFB properties improvement methods.

Main challenge in redox active materials studies was development of characterization methods, using with this system can be studied. Both studied materials do not have outstanding energy/capacity characteristics, I rather used them as model objects for testing methods.

p. 150 I characterized two redox-active colloids in terms of available capacity. The effect of the carbon nanotubes addition to the colloid was demonstrated by the nano-impact technique, demonstrating the necessity of electronic conductivity to achieve maximum capacity.

Provisional