Evaluation of submitted dissertation by Ms. Claudia Janeth Limachi Nina, with the title "Sustainable and green batteries: Fluorine-free Lithium-ion cells"
Evaluation done by prof. RNDr. Petr Vanýsek, CSc, Brno University of Technology

In the following I will throughout the evaluation show that the PhD candidate presents general knowledge in the field of battery electrochemistry, that the presented work shows ability of the candidate to work independently and that the results obtained are original solution to existing problems in battery electrochemistry.

The presented dissertation deals with very timely topic related to lithium-ion cells. Lithium-ion cells are currently the most used type of rechargeable electrochemical power sources and it can be expected that the operating concept and the chemistry fundamentals will drive the technology of storage batteries in foreseeable future. With that in mind, one concern is utilization of fluorine containing compounds throughout the manufacture, a problematic issue as use of these compounds has potential of adverse effect on the environment. Thus, the work in this field aims to address this by probing and evaluating ways of eliminating on lowering the use of fluorine-containing compounds.

The dissertation follows the now-standard approach of assembling the background information, followed by the experimental part. The experimental part begins on page 117 and the body of the text ends on page 247, so approximately half of the dissertation is the background. In a journal publication, where introduction with a background from literature is also a norm, the proportion of the foreword would certainly be much shorter. In dissertation, this can be longer, but even here one might suggest to keep it shorted part in the body of the text. For example, discussion about nickel and cobalt being environmental hazards and main cost drivers in the cells, since the dissertation does not deal with these issues, is redundant. However, it is already written, so how well does it convey the written information? It is an excellent piece of a review that in fact will be, no doubt, a source of reference to those who will be lucky to come across this dissertation. The list of references has 406 items, which certainly can be source of future study material. However, with so many references used in text it should be ensured that their choices are appropriately contextualized and in some instances elaboration of key studies or findings from these citations should be used to add depth and originality.

The writing style is quite formal and polished. Still, the transitions between sections could be more seamless. Consider for example explicitly connecting the discussion of the fluorinated compounds in the introduction to the broader environmental and regulatory concerns and then to the technological advancements being proposed. The writing style might have been influenced by reliance on external aids which might have affected the choice of vernacular that a chemist would otherwise use, which in turn would make the text style more comfortable to the practitioner of science and technology. There are few errors. For example in the legend for Fig. 12 we read about analitycal instead of analytical balance. An error easily done by a non-native writer; this makes the otherwise polished writing stand out even more so.

The experimental part is reporting in a systematic way on various tasks. It characterizes the electrolyte, then the cathode fabrication, then the anode fabrication, then characterization of the cathode and then the same of the anode. All this written first for the coin cell assembly, followed by description of similar tasks for the pouch cell. This sequential approach works fine for dissertation text. In a publication, a more concise approach, with treating the procedures or results in parallel and highlighting the similarities and differences would be more welcome.

The work is not only systematic in studying the modifications in the electrolytes. It is equally systematic and comprehensive in the study of rate capacities for various compositions and assemblies of no fewer than seven variations. The volume of the work done throughout the dissertation work is commendable. The candidate shows ability to work independently in her research area.

The following chapter again in similarly systematic way presents outcome of the work with aqueous-processed electrodes, lithium iron phosphate, synthetic graphite and silicon oxide composite. Again, this is driven by the pursuit of a cell composition that would not rely on fluorine based materials.

In addition to the purely fundamental electrochemical studies of complete cells (capacity and current voltage characteristics), other experimental techniques and methodologies had to be learned to be incorporated in the study. Rheology of the slurries for preparation of the electrodes had to be studied. This may not be important for a coin cell, but it is a critical parameter for a large scale assembly of viable cells, which is certainly one the goals of this dissertation. The electrode materials were also characterized by scanning electron microscopy to gain further insight on the granularity and surface makeup as electrochemistry inherently relies on surfaces, or rather, interfaces. Thus, their investigation is tantamount to understanding what is going on the electrodes. As one of the obstacles in preparing the electrodes, observed by this method, was cracking of the slurries upon drying. These observations were used as a feedback for further experimentations with some future elimination of this cracking in sight.

The electrochemical characterization of the studied materials demonstrated that fluorine-free lithium-ion cells not only hold immense promise but also pave the way for a transformative shift in battery technology. At both laboratory and pre-pilot scales, these cells indicate remarkable promise in their performance, possibly at some point standing shoulder-to-shoulder with their fluorinated counterparts. This meticulous work marks a milestone as a comprehensive exploration of the feasibility and scalability of fluorine-free lithium-ion cells. By prioritizing sustainability and environmental stewardship, this work highlights the potential to revolutionize energy storage, enabling greener, safer, and more sustainable batteries. Additionally, the enhanced recyclability of these cells further amplifies their appeal, positioning them as a game-changing solution to the challenges of modern energy demands.

With such a large body of work, some errors are expected and there certainly are some to pint out. In Table In Table A.1. symbol for kilogram is Kg with K as a capital letter. It must have come as a transcription form another source, as it does not repeat elsewhere. On more serious note

is the fact that in Fig. 47 conductivity is given to five significant figures. The question a candidate might be asked at the defense would be about the proper reporting of significant figures for experimental date. This can go for example for Table 57 with milliamperhours given for four significant figures. I suspect that the candidate learned from older colleagues about a screen printing according to a person named Dr. Blade. This seems to be propagated myth. The name come from using a sharp edge, i.e. a blade, dragged, "ducted" over the surface. Later 'ductor' became a doctor. While in it not necessary to know this history, it explains why the name should not have abbreviation Dr. and why blade should to be capitalized.

In compilation of the background text there is a statement conflict on page 21. In the first paragraph we read that synthetic graphite is energy-intensive, contributing to a large energy footprint, a statement basically dismissing synthetic graphite as a viable material. The following paragraph states that synthetic graphite (and also silicon oxide offer an advanced solution to "these" challenges. The "these" is unfortunate here as it is not really clear what challenges are being addressed and thus the two paragraphs really do not go together.

In summary, even though some negatives and errors are in the text, no problems are found in the dissertation or in the work that was the basis for this text. The candidate demonstrated ability to work on a research problem and conclude it in a well written text. The dissertation contents indicates that the author has general knowledge in the battery field. The candidate benefits from this just as does the laboratory where the work was performed.

"In my opinion the presented doctoral dissertation of Ms. Claudia Janeth Limachi Nina meets the requirements for doctoral dissertations in the light of the applicable regulations and therefore I hereby request that the Scientific Council for the Chemical Sciences Discipline admits the PhD candidate to the next stages of the doctoral procedure.

In Brno
5 February 2025

prof. RNDr. Petr Vanýsek, CSc.