Prénom NOM
Intitulé

Institut des Matériaux Jean Rouxel
UMR 6502
Site de Polytech Nantes
rue Christian Pauc BP 50609
44306 Nantes Cedex 03, France
Tel. 02 40 68 31 98
Fax 02 40 68 31 99

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Report on the PhD manuscript of Xuexue Pan

The PhD work of M. Xuexue Pan deals with the strategies for designing high performance sodium-ion capacitors (NIC). More precisely, these strategies are divided in two categories: the use of alternative negative electrode material to replace standard hard carbons, and the use of sacrificial compounds for the pre-sodiation of the negative electrode instead of standard sacrificial metallic sodium electrode.

The manuscript is properly organized and written in a good scientific English. It begins with a chapter dedicated to an overview of the recent literature on electrical double-layer capacitors (EDLCs) and their components before going deeper into the topic of sodium-ion batteries. A dedicated emphasis is given to the review of materials for the negative electrode. This state-of-the-art chapter is ending with the detailed review of sodium-ion capacitors, especially with regards to the pre-sodiation strategies. The main papers on the different fields are cited and analyzed, together with very recent advances published upon the last 2-3 years. The pros and cons of NICs are carefully detailed and the different concepts are illustrated through interesting figures.

Chapter 2 presents the design of a NIC using tin phosphide as negative electrode. The discussion is based on the related published paper "High performance hybrid sodium-ion capacitor with tin phosphide used as battery-type negative electrode" published in Energy Storage Materials in 2019 with the candidate as second author. It focuses on the synthesis and electrochemical behavior of Sn_4P_3 as the negative electrode of a full cell using activated carbon as the positive. The understanding of the charge storage mechanism and the balance of the electrodes for designing the full cell are well presented, but the most impressive point is the performance with a specific energy of 39 Wh/kg at a power density of 1 kW/kg over 6500 cycles. These are among the highest reported values in the literature data. Although some specific hazard could have been depicted especially during the ball-milling synthesis and during the pre-sodiation of Sn_4P_3 using metallic sodium, the chapter is fully documented and appears as an original contribution to the field.

Chapter 3 reports on the pre-sodiation strategy using Na_2S as sacrificial cathodic material that replaces metallic sodium for this crucial step of the fabrication process. It is also based on a paper published in Electrochimica Acta in 2019 with the candidate as first author of this interesting article. A very careful description of the pre-sodiation process is conducted in this chapter. The method proposed by Kötz to determine the limit of stability for the potential window is very nicely applied to the electrochemical data collected by the candidate. Moreover, this is one of the few applications of such rigorous technique in the literature. A detailed analysis of the changes occurring to the sacrificial material, the positive electrode and the full device is provided. Some questions can be raised with regards to the formation of polysulfides that should act as redox shuttle between the two electrodes or regarding the chemical changes of the electrolyte after the first sodiation step and during further cycling.

Chapter 4 is somehow a genuine combination of the different advances obtained in the previous chapters. It is also a main contribution to the pre-sodiation strategies with an insight on a new sacrificial compound: $Na_2C_4O_4$. The paper entitled "Advantageous carbon black deposition during the irreversible electrochemical oxidation of $Na_2C_4O_4$ used as presodiation source for the anode of sodium-ion systems" (published in Energy Storage Materials in 2021) serves as a guideline for this chapter with M. Pan as the main author. Apart from its novelty, the main interesting result is the deposition of carbon on the positive electrode while the sacrificial material is oxidized. The candidate has coupled many techniques to come to this conclusion and this is the most detailed report in the literature up to now. From what was a hypothesis in previous literature reports, the candidate succeeded in getting strong experimental evidences that this phenomenon occurs. It can be also mentioned that the negative electrode depicted in chapter 2 is used to design the cell in this chapter, which emphasizes the strength and the originality of the project of the team from Poznan University of Technology working on NICs.

The last chapter focuses toward "A strategy for designing more durable sodium-ion capacitors with optimized output energy", which is currently submitted to the very high impact factor journal Energy & Environmental Science. The limitation in cycling ability of the cell is the main topic of this work. The major guideline is the use of composite negative electrode, coupling Sn_4P_3 with spherical hard carbon particles in order to moderate the volume change upon cycling the negative electrode, thus preventing/limiting capacity fade. This clever strategy is investigated using different ratio of positive to negative electrode which in turn affect the cell performance. The pre-sodiation is achieved using a metallic sodium sacrificial electrode. The results obtained with the sacrificial compounds presented in Chapters 3 and 4 could have been of interest to compare with the standard method. However, the reported results are quite impressive with an improved cycling ability of the device (up to 9000 cycles) which is also a major keystone for NIC technology.

A summary of the PhD work is proposed and some perspectives are given at the end of the manuscript. The bibliography section shows more than 219 pertinent references. The candidate should probably think of other original development that can be triggered by his research work and this could be further emphasized during the oral defense.

Although this PhD work was disturbed by Covid-19 crisis and its consequence, the approaches presented in the manuscript are quite interesting and the reported results open the way for future improvements of real life NIC devices. Overall, the manuscript reflects the good scientific level and experimental skills of M. Xuexue Pan. It is illustrated by many figures that support the discussion. The 4 chapters dedicated to materials synthesis and characterizations are bright illustrations that M. Pan can manage complex scientific projects. All the content of the manuscript reveals the scientific maturity of the candidate who has successfully based his scientific project on the expertise of the lab and of his supervisors. M. Xuexue Pan has also published 4 papers in high impact factor scientific journals (first author for two of them) and one more is under reviewing process. He gave 6 oral communications mostly at International meetings, and presented 3 posters.

In summary, M. Pan is presenting in a rigorous manner a large number of results and he succeeded in organizing the discussion in a clear way. The major point of this discussion is the preparation and the characterizations of NIC full cell implementing new negative electrode materials and new sacrificial pre-sodiation compounds. Moreover, all these data allow the candidate to formulate some requirements for the optimization of NICs. The influence of full devices and the tests performed at fast cycling rates also denote the interest of the candidate for practical applications of his work.

All the reasons detailed above lead me to express a positive opinion about the PhD work of M. Xuexue Pan and I strongly support the oral defense of this work by the candidate for the attribution of the title of Doctor of Philosophy.

Prof. Thierry Brousse

IMN - UMR 6502
Polytech Nantes
Rue Christian Pauc - BP 50609
F44306 NANTES Cedex 3
Tél. : 33(0) 240 683 198
Fax : 33(0) 240 683 199

Below is a non-limited list of questions that can be addressed during the public defense of the PhD thesis.

Chapters 1 & 2

1/ It seems that Sb combined with Sn gives the most favorable cycling ability as negative electrode in Na-ion batteries. Furthermore, this alloy exhibits high electronic conductivity. So what motivated the choice of a much more isolationg and hazardous electrode based on tin phosphide ?

2/ What is the limiting component of metal-ion capacitors ?

3/ Which range of time constant is expected for a metal-ion capacitors ?

Chapter 3

4/ What happens to the electrolyte when Na_2S irreversibly reacts with sodium ?

5/ What is the role of polysulfides after thi first sodiation step ?

6/ Is there any possibility of sulfur incorporation in carbon at the positive electrode ?

Chapter 4

7/ Which pressure can be reached inside the cell upon first sodiation step ?

8/ Is there any evidence of the residual reaction occuring at the positive elctrode upon cycling (after the pre-sodiation step) ?

9/ Is there any reactivity between the sacrificial molecule and other components of the cell such as the separator ?

Chapter 5

10/ Is there any strategy to further improve the cycling ability of the negative electrode (use of different binders, of alternative electrolytes,etc…) ?