POLITECHNIKA GDAŃSKA
WYDZIAŁ CHEMICZNY

KATEDRA CHEMII I TECHNOLOGII MATERIAŁÓW FUNKCJONALNYCH

dr hab. inż. Andrzej Nowak
Prof. PG

Gdańsk, 14.09.2021

Review

of the doctoral dissertation of Mr. Xuexue Pan titled "*Strategies for designing high performance sodium-ion capacitors*"

The mentioned above doctoral dissertation was conducted under the supervision of Prof. François Béguin and dr Agnieszka Chojnacka at the Institute of Chemistry and Technical Electrochemistry, Faculty of Chemical Technology of Poznan University of Technology. The main topic of the PhD thesis is focused on the utilization of thin phosphide (Sn_4P_3) as anode material in sodium-ion capacitor (NIC) followed by optimization of the NIC system in terms of the cycle life, capacitance and specific energy output.

Electric energy is one of the most important factors in today live. It is a heart of modern economies. Global energy demand is growing very rapidly and is one of the key reasons why CO_2 emissions is also very high. It affects climate change and pollution. Decarbonisation of electricity could provide a platform for reducing carbon dioxide emissions. Moreover, renewable energy may provide the access to electricity for all.

Renewables are expanding quickly, but not enough to fulfil requirements of the global electricity demand. It is predicted that fossil fuel-based electricity generation will cover 40% of additional demand in 2022, while the rest is attributed to nuclear power. Thus, carbon emissions from the electricity sector is expected to increase by 2.5% in 2022. Although, renewable power is growing impressively the problem is that it still is not where it needs to be put to reach net-zero emissions.

Among renewable energy sources the most common are solar, hydro, wind, biomass, geothermal and tidal. The utilization of them is mainly in stationary large-scale energy storage. However, in our daily activity there is a need for some other system that could be easily applied in mobile systems. The batteries and capacitors are the most suitable for such application. The former exhibit high specific energy, while the latter show high specific power. Among many different battery systems, metal-ion battery seems to be the right choice. It is due fact that it exhibits high energy conversion efficiency. Commercialized in 1991, and awarded to John B.

Nh

Goodenough, M. Stanley Whittingham and Akira Yoshino by the Nobel Prize in Chemistry in 2019, lithium-ion batteries (LIBs) are in common use as an energy storage. Rapid growth in mobile electrical devices is crucial in development alternative for LIBs mainly due to politician issues. Thus, utilization of sodium that is abundant on Earth, seems to be a natural choice.

Currently, many laboratories around the world are conducting research on the development of metal-ion capacitors. Such system exhibits the high voltage originating from battery, and high power capability attributed do electrochemical capacitor.

Doctoral dissertation of Mr. Xuexue Pan is a set of published articles devoted to three main issues: 1. finding a suitable anode material for NICs, 2. finding a solution for host presodiation and 3. optimizing the cyclability performance of NICs. It shows that the PhD thesis itself was very deeply and logically planned. By going step-by-step through all publications one my learn how to prepare NIC for practical application. It is very valuable approach as in most cases scientists at universities do not work on the optimization of the investigated system but are focus on publishing results of single experiment only.

The dissertation was split into five main chapters. The first is a literature review describing electrochemical energy storage systems, such us electrical double-layer capacitors (EDLCs), Na-ions batteries (NIBs) or Na-ion capacitors (NICs). The reader may gain knowledge regarding principles and properties of those systems including chemicals used for manufacturing (electrode materials, solvents, electrolytes etc.). This part is clear and explain the scope of the thesis. I would like to mention that the "star" symbol is no a multiplication symbol (ε_0, page 16).

The chapters from 2 to 5 are devoted to the published (2-4) or already submitted (5) papers while the chapter 5 is a submitted manuscript that are the core of the concept of "paper publication".

The first work (Chapter II) *High performance hybrid sodium-ion capacitor with tin phosphide used as battery type negative electrode* is devoted to finding a proper material to act as negative electrode in hybrid NICs. The selection of tin phosphide (Sn_4P_3) as an electrode material is due to its high theoretical specific capacity (1132 mAh g^{-1}) and insertion potential (0.3V vs. Na/Na^+) preventing sodium plating during reduction process. The detailed process of material synthesis, cell assembly and electrochemical tests is given. This works seems to be the most important for the further investigations regarding host presodiation and optimizing cyclability performance. The presented results show that Sn_4P_3 electrode material is suitable as a negative electrode in NICs with very high specific energy of 39 Wh/kg at 1 kW/kg after 6500

Nch

cycles. At that time it was the highest value among other NICs reported in the literature. Moreover, the capacity fading after the cycles was only 6%. It is very low assuming that no optimization was performed.

The second work (Chapter III) *Na_2S sacrificial cathodic material for high performance sodium-ion capacitors* is devoted to utilization sodium sulphide as a sacrificial cathodic material to simplify and improve construction of NICs. The usage of sacrificial material is to avoid sodium ion loss from active electrode material during solid electrolyte interphase (SEI) formation in the first cycle. Usually, the capacity loss is over 10% of initial capacity, and that is a lot for a storage energy systems for practical application. Based on the set of experimental data, very well analysed, the obtained results show that implementation of Na_2S as a sacrifice material is the way to improve electrochemical performance of NICs. However, it is evidenced that the type of carbon matrix plays a crucial role in the coulombic efficiency of the whole system. The disadvantage of utilization of AC-Na_2S//Sn_4P_3 electrode material is its complexity during preparation that might be not attractive for industry.

The third paper (Chapter IV) *Advantageous carbon deposition during the irreversible electrochemical oxidation of $Na_2C_4O_4$ used as a presodiation source for the anode of sodium-ion systems* is a continuation studies on presodiation process presented in Chapter III. Utilization of $Na_2C_4O_4$ was, on the one hand, to avoid complex and sensitive to moisture synthesis of Na_2S, and, on the other hand, to remove residual and parasitic reactions originating from the presence of sulfur after presodiation. Very detailed analysis evidenced that $Na_2C_4O_4$ undergoes decomposition with carbon dioxide (CO_2) and carbon monoxide (CO) evolution as well as with elemental carbon (C) formation. It is noteworthy, that it is for the first time when the presence of carbon, as a product of $C_2O_4^{2-}$ oxidation, was confirmed. Additionally, after oxidation of $Na_2C_4O_4$, the carbon deposit enhances electrical conductivity of the sacrificial material. The studied electrode (YP80F//$Na_xSn_4P_3$) material exhibits a capacitance of 94% after 11000 cycles that is better than for AC-Na_2S//Sn_4P_3 (Chapter III) and it is almost 1.7 times higher in comparison with pure Sn_4P_3 (Chapter II). Such improved electrochemical performance is due to formation of Na_2CO_3 layer on the surface of YP80F//$Na_xSn_4P_3$ film allowing sodium ions to penetrate it, but it blocks electrons to pass through it. The synthesized $Na_2C_4O_4$ is an easy in handle and zero dead mass sacrificial material that might be successfully utilized in NICs improving their electrochemical performance.

The Chapter V *A strategy for designing more durable sodium-ion capacitors with optimized output energy* is devoted to avoid issues related to pulverization of Sn_4P_3 during sodium ion insertion/extraction. It is in a form of a manuscript submitted to the journal belonged

Noh

to The Royal Society of Chemistry family. Although in the Chapters II-IV it is shown that Sn_4P_3 exhibits promising electrochemical performance for NICs it still suffers from huge volume changes during sodiation. To overcome this issue Sn_4P_3 is mixed with hydrothermally carbonized glucose (HCG). The HCG serves as a source of carbon. Carbon phase is know to acts as a stress accommodating phase which preserves volume changes as well as allows electric contact between tin particles. Additionally, to improve electrochemical performance of NICs (specific energy, life span) the capacity ratio between both electrodes (Q_-/Q_+) was controlled by changing the low presodiation potential (E_{p-}) of Sn_4P_3 and/or the mass of activated carbon (AC). The obtained results shows the problem is very complex. The E_{p-} affects the cell cycle life as it directly influences on the capacity of negative electrode (Q_-) and so on the Q_-/Q_+ ratio also in NICs. The capacitance of NICs depends directly on the positive electrode (Q_+). Hence, changing Q_-/Q_+ simultaneously with the change of mass and/or E_{p-} affects cyclability and output energy in an opposite way. The type and mass of activated carbon play also very important role showing that there is no simple solution to improve metal-ion based system. Nevertheless, the results suggest that the proper selection of AC may lead to improvement electrochemical properties of NICs. It is especially important if NICs are expected to replace LIBs in energy storage application.

In the summary of the review, I conclude that the dissertation is very important contribution to the study of energy storage systems based on sodium-ion capacitor. The presented work is not limited to synthesis negative electrode material for NICs itself but it goes beyond that including improving electrochemical properties by utilization of sacrificial cathodic material as well as optimizing the performance of the obtained anode.

During the implementation of the planned research Mr. Xuexue Pan achieved his goals. Moreover, he demonstrated his ability to conduct experimental work, select appropriate research techniques, the ability to discuss the results obtained against the background of the subject literature and draw conclusions based on the obtained results. The manner of conducting the discussion in the chapters II-V proves the PhD student's research maturity.

Last but not least, Mr. Xuexue Pan is a co-author of 4 publications, in 2 of them as the first author, of the total impact factor IF=54,086. That is very impressive. The excellent publications made based in this work, are obviously one of the most important consequences for the validity and importance for the research field, adding suitable new and valuable approaches, that the scientific and technological community has recognized the value.

Noh

Notwithstanding the insightful results presented in the chapters II-V of the articles, I have the following comments to consider:

- The reversible capacities of Sn_4P_3 are 447 mAh g^{-1} (Chapter II, page 63), 524 mAh g^{-1} (Chapter III, page 77) and 514 mAh g^{-1} (Chapter V, page 121) in the potential range from 0,1 V od 2,0 V vs. Na/Na^+. Could you comment what is the reason of those differences?
- The shape of the curve given in Fig. S1b (pristine BP2000) (page 82) is similar to the shape of the curves shown in Fig. S5a (Na_2S-Maxsorb fresh and after extraction) (page 85) at the range of relative pressure P/P_0 from 0,9 to 1,0. Do you have any idea why pristine BP2000 exhibits such behaviour? In other words is BP2000 really pristine?
- Characterization of BP2000, fresh Na_2S-BP2000 and Na_2S-BP2000 after extraction is missing in Table S1 (page 85). It would be more clear to give such data in supplementary information to compare both porous carbons.
- EDX is not the best technique to characterise the composition of the sample in a quantitative way as it gives only local area. It is written "*…the latte value is at the level of the oxygen amount in the pristine YP80F…*" (page 95). However, there is no EDX analysis data in the text. I would suggest to use other analytical techniques to analyse the element content in the sample i.e. atomic absorption spectrometry (AAS) or inductively coupled plasma with mass spectrometry (ICP-MS) if available.
- Fig. 1d shows the pressure change in the system during galvanostatic oxidation (page 95). It is evidenced that the pressure evolution increases over time. Did you perform such experiment during galvanostatic reduction to see if the pressure (amount) of CO_2 and CO diminishes and reaction given in a form of equation 3 is proper?
- The capacity retention after 11000 cycles is 94% while after 11600 cycles it reaches 80%. This phenomenon is attributed to volume changes and pulverization of the tin alloy (page 99). Did you measure the thickness of the cell at the end of the measurements or performed some XRD measurements? There is no such information in the cited reference 3 (publication presented as Chapter II)
- What was the final thickness of all 9 NICs presented in the chapter V after reaching end-of-life?
- Do you think you could obtain better results if the Q_-/Q_+ was in the range between 6 and 7,5, and the low presodiation potential (E_{p-}) within the range from 0,22 and 0,28 V?

Nah

In summary, although mentioned above comments, the doctoral dissertation submitted by Mr. Xuexue Pan represents very high scientific work. The PhD thesis is well written with negligible errors, and in my opinion it meets all requirements set up in Article 13 para. 1 of the Act of March 14, 2003 on academic degrees and academic title as well as academic degrees and title in the field of art (Journal of Laws 2003 No. 65, item 595, as amended), and I recommend to the Council of the Faculty of Chemical Technology, Poznan University of Technology for the admission of Mr. Xuexue Pan to the next stages of the doctoral dissertation. I would also propose to award Mr Xuexue Pan the PhD degree after successful defense.

Sincerely,

Dr hab. inż. Andrzej Nowak, Profesor PG