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Evaluation

of the doctoral thesis entitled „Strategies for designing high performance sodium-ion capacitors" presented by Mr. Xuexue Pan.

Mr. Pan has investigated in his doctoral thesis novel approaches for the fabrication of energy storage devices based on sodium-ion capacitors. The main focus was the understanding of the critical chemical features to enhance the electrochemical performance in these energy storage devices. One important aspect was the investigation of the surface chemistry for the binary tin phosphide system during electrochemical sodiation and subsequent cycling.

The first chapter reviews the progress in the literature on electrical double-layer capacitors, sodium-ion batteries, and sodium-ion capacitors with an emphasis on pre-sodiation of electrode materials.

The experimental part begins in the second chapter with hybrid sodium-ion capacitors that contain tin phosphide, i.e. Sn_4P_3, as negative electrode and carbon as positive electrode. Mr. Pan could show that such capacitor achieves in the voltage range from 2.2 to 3.8 V a capacitance retention of 94% after 6500 cycles at 0.2 A g^{-1}. In relation to the introduction in chapter 1, Mr. Pan writes that the first sodiation process of Sn_4P_3 leads to Na_3P (page 40, formula 14). However, during electrochemical cycling many binary phases could be potentially formed as intermediate products, such as the Na_3P_7. How can one interpret the electronic structure of the latter? Another question arises in the characterization of the Sn_4P_3 electrode based on the EDX analysis on page 202 of *Energy Storage Materials* 22 (2019) 200–206: What is the accuracy of the method/instrument in the determination of the particle composition?

The third chapter discloses a method to use Na_2S as sacrificial material for high performance sodium-ion capacitors based on negative Sn_4P_3 electrodes. Upon pre-sodiation of Sn_4P_3, the activated carbon being a part of the positive electrode stores charges in the electrical double-layer. This results in stable cycling between 2.0 V and 3.8 V with high specific energy of 48 Wh kg^{-1}. In the fourth chapter, Mr. Pan demonstrated a pre-sodiation strategy by using $Na_2C_4O_4$ as precursor, which is irreversibly oxidized in the cell, to address the metal deficiency issue of anode materials for sodium-ion capacitors. Mr. Pan could show that upon oxidation a passivating Na_2CO_3 layer is formed on the $Na_xSn_4P_3$ surface. The prepared capacitor achieved a specific energy of 44 Wh kg^{-1} at 1 kW kg^{-1} with a retention of 94% over 11 000 cycles. Here I would have another question on the decomposition of $Na_2C_4O_4$ into the mentioned carbon and CO_2: does the formation of carbon occur as a contact reaction between the active electrode material? Is the formed carbon therefore a complete coating?

In the fifth chapter, Mr. Pan elucidates the role hard carbon particles as buffer for the volumetric changes of Sn_4P_3 particles and highlights the importance of the capacity ratio Q_-/Q_+.

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Mr. Pan has combined in his doctoral thesis solid-state-chemical approaches to synthesize nanostructured composite materials and to study subsequently the physicochemical properties. The synthetic methodology covers besides wet-chemical approaches also mechanochemical (ball-milling) methods to obtain electrochemically-active materials. The complementary used analytic methods encompass cyclic voltammetry, open-circuit potential measurements, electrochemical determination of capacitance, galvanostatic charging/discharging, determination of specific surface area using nitrogen sorption/desorption, Raman spectroscopy, and infrared spectroscopy.

The quality of Mr. Pan´s research is reflected in the publication of five (5) peer-reviewed articles in international scientific journals (2x *Electrochimica Acta*, 2x *Energy Storage Materials*, 1x *Energy & Environmental Science*). Given both the high quality of the publications and the high impact of the corresponding scientific journals, I consider this to be an excellent result for PhD studies performed in four (4) years. In two (2) of these articles, Mr. Pan is the first author (*Electrochimica Acta* and *Energy Storage Materials*), which proves the scientific independence that he accomplished during his PhD studies. The scope of these published articles is the basis for the here presented doctoral dissertation. I would like to point out that the authors number on the published articles does not exceed in each case more than four (4) authors. This proves that the candidate has performed diverse experiments, covering both synthesis and characterization, in these published articles.

The doctoral thesis can be clearly understood and does not require further grammatical corrections. In summary, I recommend to award Mr. Xuexue Pan the PhD degree with distinction in the field of natural sciences (discipline - chemical sciences).

Stockholm, 24th August 2021

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