Synchrotron chemical and structural analysis of Na-preconditioned silicon anodes for Li-ion batteries

Erick Espinosa-Villatoro[1], Jesse S. Ko[2], Johanna Nelson Weker[2], Alina Santillán-Guzmán[3], Enrique Quiroga-González*[1]

[1]Institute of Physics, Benemérita Universidad Autónoma de Puebla (BUAP), 72570 Puebla, Mexico.
[2]SLAC National Accelerator Laboratory, 2575 Sand Hill Road, Menlo Park, 94025 California, United States.
[3]Universidad Popular Autónoma del Estado de Puebla, 72410 Puebla, Mexico.
* equiroga@ieee.org

Introduction

The current social challenges in energy storage have led to an increase in research to find new materials for a new generation with improved characteristics of Li-ion batteries (LIBs). Therefore, there is an extreme need to improve the performance, capacity, durability, and safety of LIBs to enable the development of new applications.[1,2] Silicon (Si) has been found to be one of the best candidates because of its high theoretical gravimetric capacity of 4200 $mAhg^{-1}$ about ten times higher than that of graphite (372 $mAhg^{-1}$). In addition, it is also the second most abundant material in the earth's crust, is environmentally friendly and has a low electrochemical potential (~0.37 V vs. Li/Li^+).[3] In this work an electrochemical preconditioning process of Si anodes with Na, for their use in LIBs, is proposed. In order to overcome some drawbacks of Si as an anode. Considerable interest exists in the structural and chemical changes of Si. In this sense, through synchrotron radiation we analyze several samples with X ray diffraction (operando and ex situ), to observe the crystalline phase changes in Si during and after the preconditioning processes with Na. In addition, NEXAFS characterization was performed to provide an insight of the evolution of the SEI layer, and through ptychography allows to observe the morphology of Si particles after the preconditioning processes. Additionally, impedance spectroscopy cyclic voltammetry were performed to observe the electrochemical performance of Na-conditioned Li-ion cells.

1. M. R. Lukatskaya, et al., *Nature Commun.* 7 (2016) 1–13.; 2. S. Nohren, et al., ECS Trans., 64 (23) (2018) 1–10.
3. C. Cao, et al., Acc. Chem. Res., 52 (2019) 2673–2683.

Experimental Aim

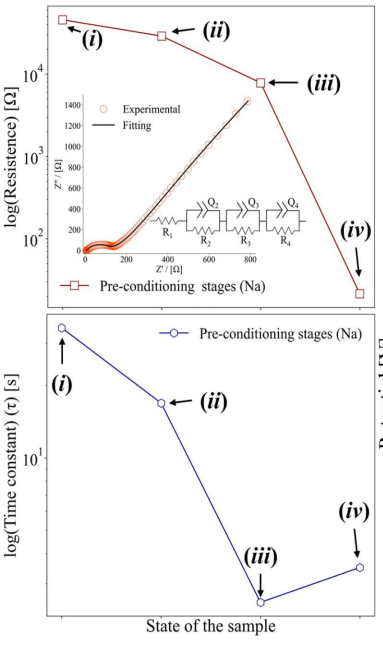
To elucidate the chemical and structural changes in Si anodes during and after the Na preconditioning process using synchrotron radiation. Also, to observe the electrochemical performance of Na preconditioned Si anode in a LIB.

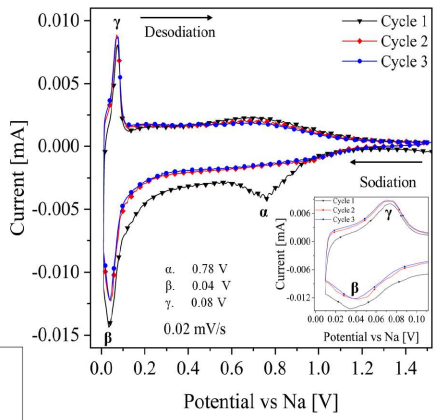
Experimental Methods

Cyclic voltammetry (CV)

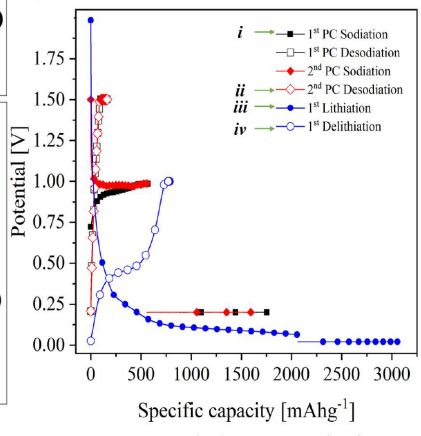
- In the figure on the right the peak α (0.78 V) corresponds to the formation of the SEI layer, Peak β is related to the sodiation (0.04 V) and peak γ to the desodiation process at 0.08 V.[4]

Electrochemical pre-conditioning process & Impedance Spectroscopy (IS)





- By fitting the Nyquist diagrams, it is possible to know the evolution in the diffusion of Na/Li ions in Si at different stages of preconditioning
- The specific capacity *vs.* potential curves (see figure below) show the electrochemical preconditioning processes.

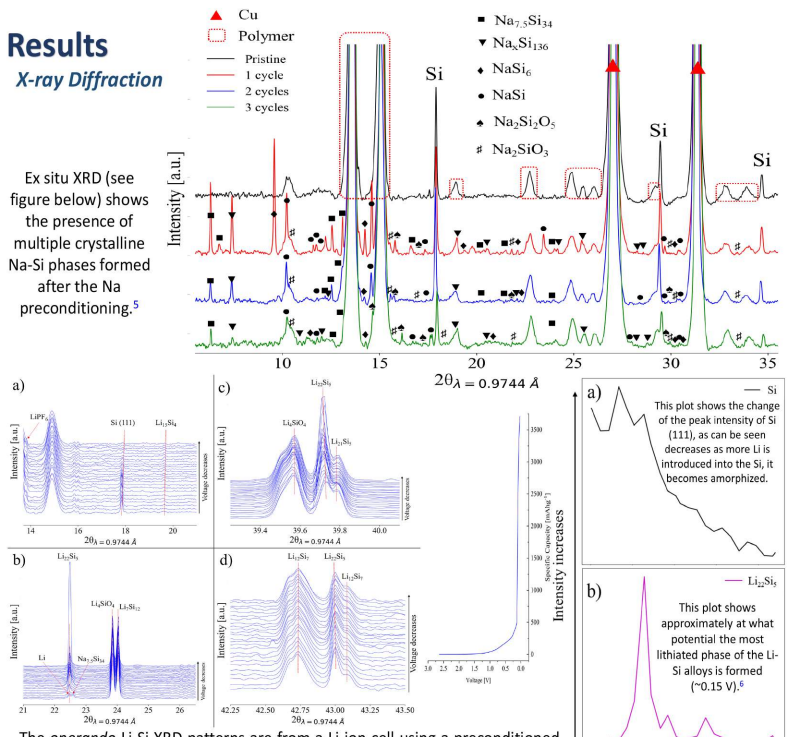


4. Y. Xu, et al., *Adv. Energy Mater.* 6 (2016) 1501436.

Results

X-ray Diffraction

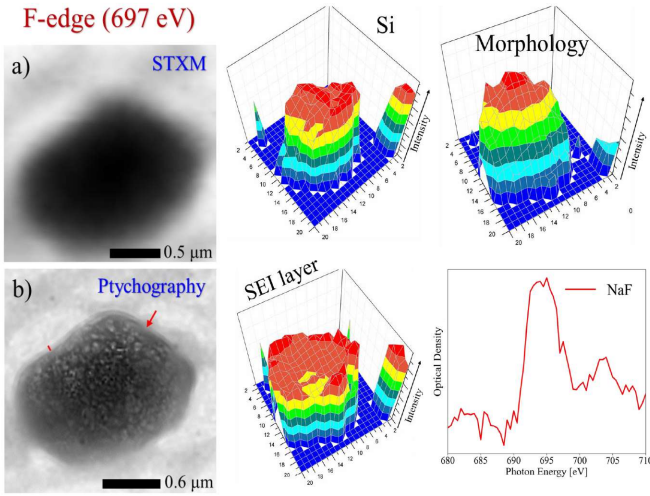
Ex situ XRD (see figure below) shows the presence of multiple crystalline Na-Si phases formed after the Na preconditioning.[5]



The *operando* Li-Si XRD patterns are from a Li-ion cell using a preconditioned Si anode taken during lithiation process. [4]

Ptychography and XANES

F-edge (697 eV)



By NEXAFS it was possible to know the chemical composition (SEI, Si) and a 3D map composition of the Na preconditioned Si particle. [7,8]

Ptychography allows to observe the SEI layer around the Si particle after the Na preconditioning process.

5. A. Brennhagen, et al., Batter. Supercaps, 4 (2021) 1-26. 6. O. Pérez-Díaz, *et al.*, *Mater. Technol.*, (2019) 1–7.
7. S.J. Rezvani, et al., J. Phys. Chem. C 121 (2017) 26379-26388. 8. E. Hudson, et al., Condensed Matter, 49 (6) (1994) 3701–3708.

Conclusions

- By means of CV, it was possible to determine where the sodiation, desodiation and SEI layer formation on Si take place. The curves of Na preconditioning show that Na is inserted into Si. In addition, by IS the enhancement of Na and Li diffusion in Si was demonstrated through the calculation of τ.
- Ex situ XRD confirmed the insertion of Na into the micrometric Si, as different Na-Si crystalline phases could be identified. On the other hand, *operando* XRD shows the amorphization of Si from a sample preconditioned with Na, as well as the voltage at which the most lithiated Li-Si phase ($Li_{4.4}Si$ at ~0.15 V) is formed.
- Ptychography shows the SEI layer formed around the preconditioned Si particle, which is confirmed by NEXAFS analysis.

Acknowledgments

Use of the Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Contract No. DE-AC02-76SF00515. This research used resources of the Advanced Light Source, which is a DOE Office of Science User Facility under contract no. DE-AC02-05CH11231.
The author E. Espinosa-Villatoro acknowledges the financial support CONACyT through scholarship number 582796.