Can Na⁺ Transport Faster Than Li⁺ inside Zn-Sb Intermetallic Nanomaterials?

Anmin Nie^{1, 3}, Yingchun Cheng⁴, Robert F. Klie³, Sreeram Vaddiraju² and Reza Shahbazian -Yassar¹

¹ Department of Mechanical Engineering-Engineering Mechanics, Michigan Technological

University, 1400 Townsend Dive, Houghton, Michigan 49931, United States

² Artie McFerrin Department of Chemical Engineering, Texas A&M University,

3122 TAMU, College Station, TX 77843, United States

^{3.} Department of Physics, University of Illinois at Chicago, Chicago, Illinois 60607, United States

⁴ Mechanical and Industrial Engineering Department, University of Illinois at Chicago, Chicago,

Illinois 60607, United States

Triggered by the recent exploration of alternative technologies to Li-ion batteries, sodium has strongly broken into energy storage research field thanks to the natural abundance and environmental benignity of sodium resources^{1, 2, 3}. These advantages make Na-ion battery an attractive and potential alternative to the well established Li-ion battery. However, the development of Na-ion battery is currently a challenge because of potential disadvantages, including larger size of Na⁺ and higher redox potential of Na/Na⁺ compared to Li analogues.

Here, an in-depth comparative study between the electrochemical de/lithiation⁴ and de/sodiation of Zn_4Sb_3 nanowires has been conducted by using *in situ* transmission electron microscopy. Surprisingly, we found that sodium ions transport can be 10~100 times faster than lithium ion inside individual Zn_4Sb_3 nanowires. In addition, the cracks were often observed in the first few cycles during de/lithiation of the Zn_4Sb_3 nanowire. However, there was no crack formed even after dozens of cycles during their de/sodiation. Our *in situ* study indicates that the Zn_4Sb_3 nanowires exhibit much better rate capability and cyclability in Na-ion battery compared to Li-ion systems. The underlying reason has also been addressed from the thermodynamic and kinetic aspects of ions transport in Zn-Sb intermetallics.

Reference:

[1] Slater, M. D. et al, Adv. Funct. Mater. 23, (2013), 947

[2] Pan, H. et al, Energy Environ. Sci. 6, (2013), 2338.

[3] Palomares, V. et al, Energy Environ. Sci. 5, (2012), 5884.

[4] Nie, A. et al, Nano lett. 14, (2014), 5301.

[5] The authors acknowledge the funding from the National Science Foundation (Award No. CMMI-1200383) and the American Chemical Society-Petroleum Research Fund (Award No. 51458-ND10). The acquisition of the UIC JEOL JEM-ARM200CF is supported by an MRI-R² grant from the National Science Foundation (Award No. DMR-0959470). Support from the UIC Research Resources Center is also acknowledged.

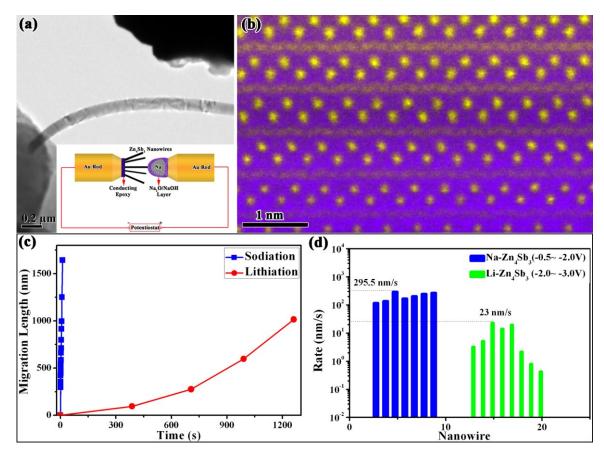


Figure 1. (a) Low-magnification TEM image of the *in situ* electrochemical testing setup and a schematic depiction of the nano-battery. (b) Atomic scale HAADF image of Zn_4Sb_3 nanowire taken with the [1-10] zone axis. (c) Typical reaction front travel distance *vs* time curves for sodiation and lithiation, respectively. (d) Comparison of sodiation and lithiation rates of Zn_4Sb_3 nanowires. Sodiation rates of Zn_4Sb_3 are about 10~100 times faster than their lithiation rates.