Nanoporous Niobium Oxide as an Anode for Na-ion Batteries

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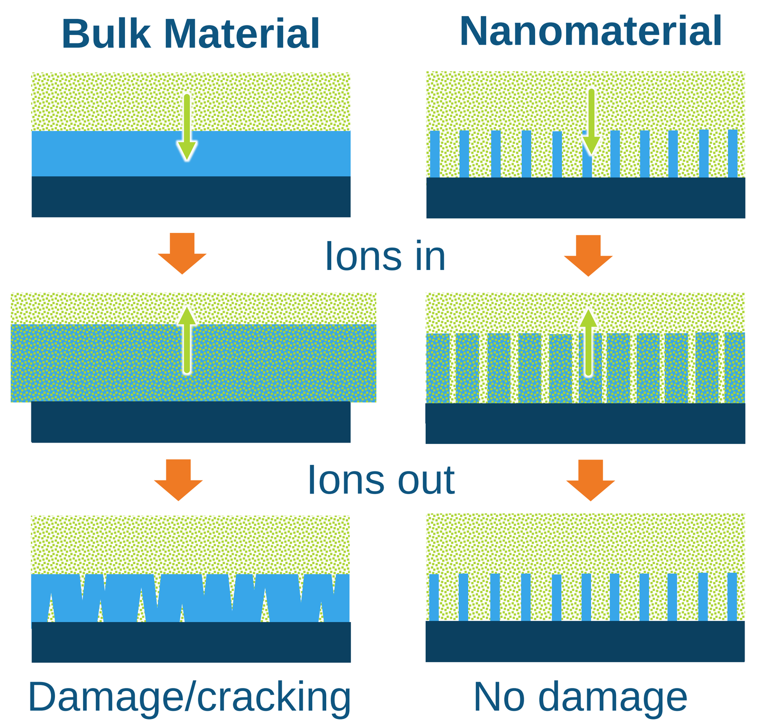
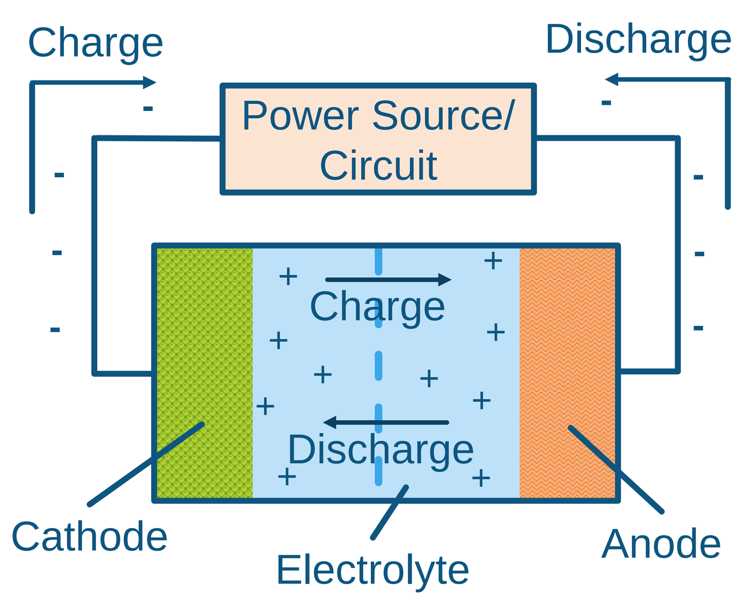
Abstract

Solar, wind, and other renewable energy sources tend to be intermittent, and thus large-scale energy storage is needed to fully utilize them. While sodium-ion batteries currently fall short of the energy density of the leading lithium-ion technologies, they are a potentially cost-effective alternative, since sodium is more abundant but is chemically similar to lithium. Additionally, for stationary applications cost is a much larger driving factor than for mobile applications. However, improvements are needed to increase the stability and reliability of sodium-ion batteries before they become a legitimate option. Nanostructured metal oxides such as nanotube arrays are promising for use in anodes due to their high surface area and ability to withstand the volume changes that accompany repeated Na^+ insertion/extraction during battery cycling. Niobium oxide is one such material, but research into its use in sodium-ion batteries is limited. In this work, nanoporous niobium oxide films were synthesized via anodization of niobium foil, where the morphology was modified by changing the anodization voltage and the crystallinity was modified using heat treatments. The films were characterized with scanning electron microscopy (SEM) and x-ray diffraction (XRD), then cycled in half-cells with sodium foil counter electrodes to assess their electrochemical behavior.

Background

- Lithium- and sodium-ion batteries work by shuffling ions back and forth between an anode and cathode
- The electrons and ions split up at one of the electrodes and meet at the other side, either storing energy or supplying it[1]

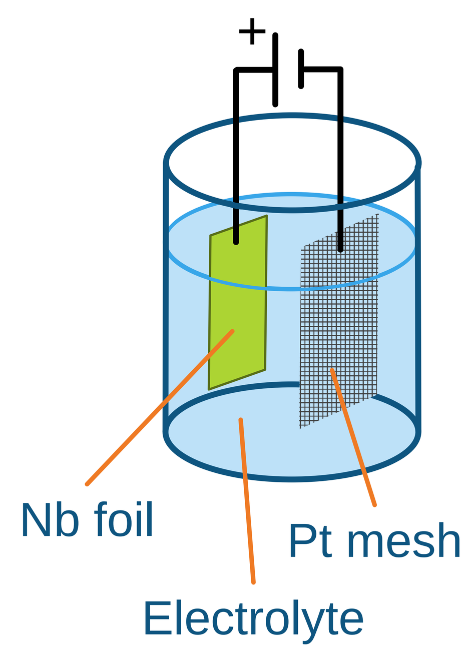




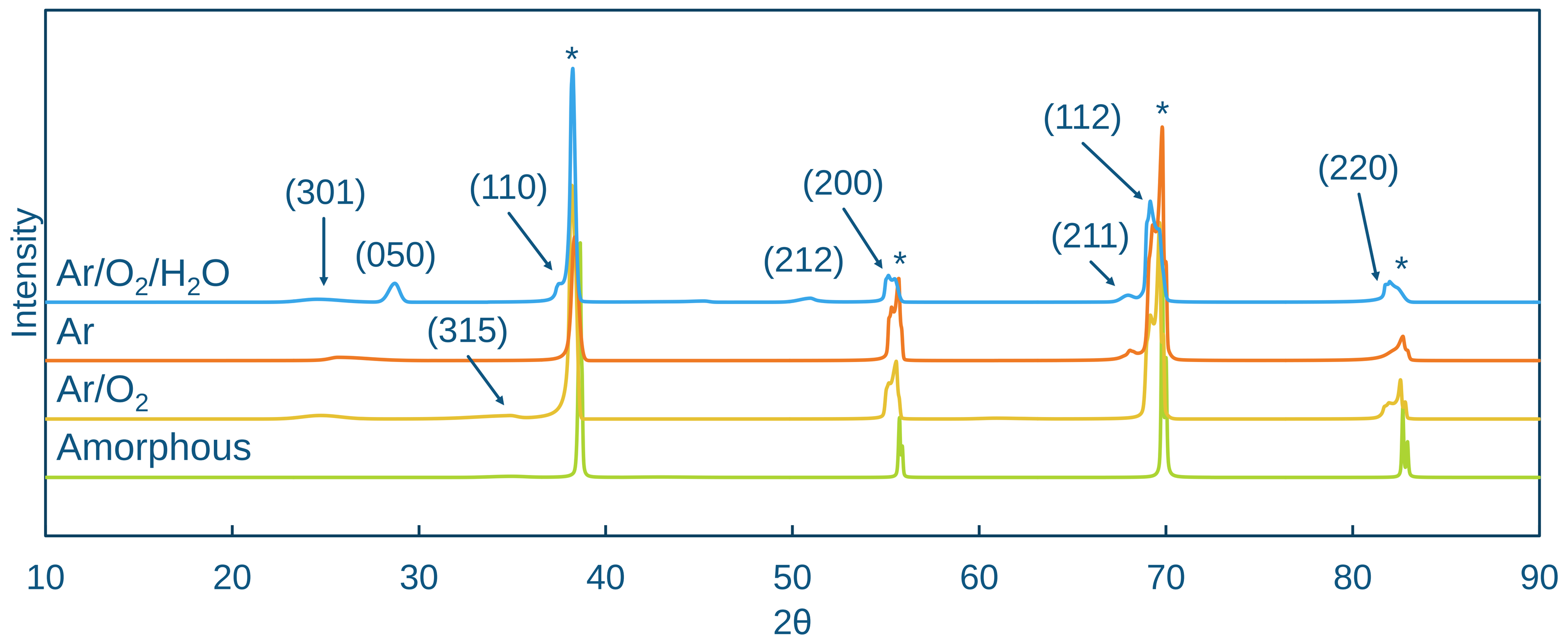
- During intercalation, the ions diffuse into the electrode material, sometimes producing a volume expansion[2]
- Some nanomaterials can survive this kind of repeated volume change due to their small size
- Nanomaterials also create shorter lengths for ions to diffuse, so charge/discharge times can be shorter[2]

Experimental

- When conditions in such as electrolyte, temperature, and voltage are right, the surface of valve metals can polish, or structured oxides like microcones or nanopores can grow[3,4,5]
- Three different atmospheres during heat treatment were used to produce four different crystalline structures:[6]
    - No heat treatment; amorphous
    - Oxygen-containing; crystalline stoichiometric control
    - Oxygen-free; crystalline with oxygen vacancies
    - Water- and oxygen-containing; crystalline with niobium vacancies
- Scanning Electron Microscopy (SEM) was used to look at the nanoarchitecture of the samples and the crystal structure of the samples was confirmed with X-Ray Diffraction (XRD)



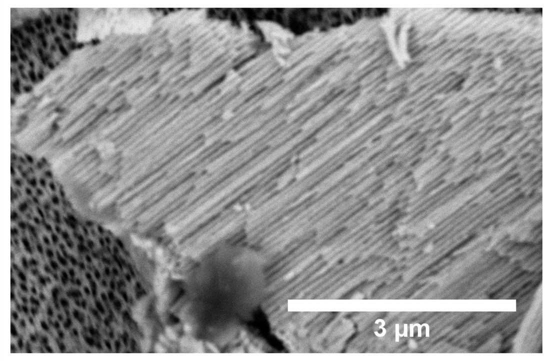
Crystallinity Characterization



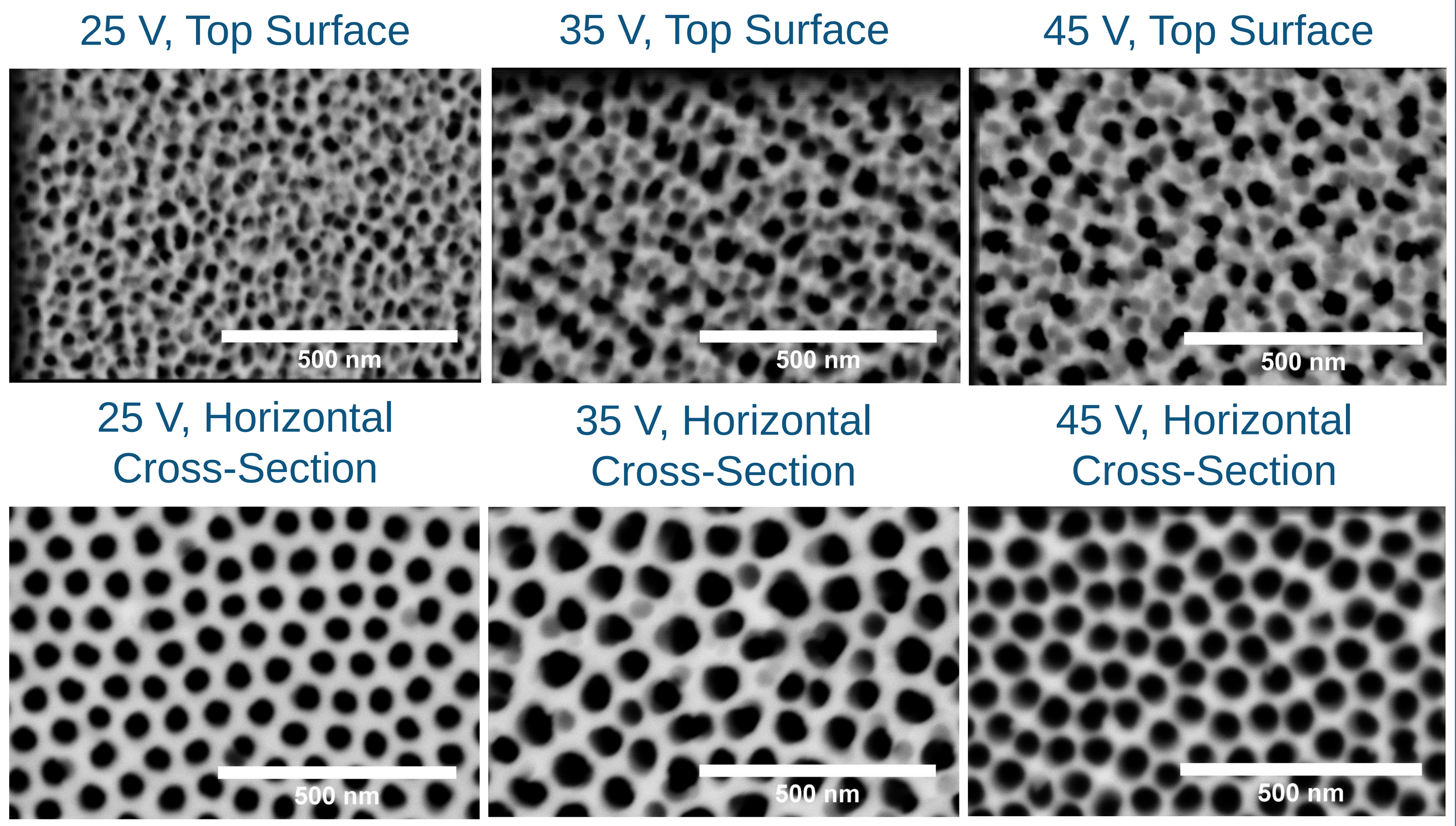
- XRD can be used to tell what phases are present in a sample by recording how x-rays diffract at different angles; peaks in intensity correspond to specific crystal planes
- Starred peaks originate from the niobium substrate, the others are associated with the orthorhombic crystal structure (space group: Pbam)

Nanoarchitecture Characterization

25 V, Side Profile

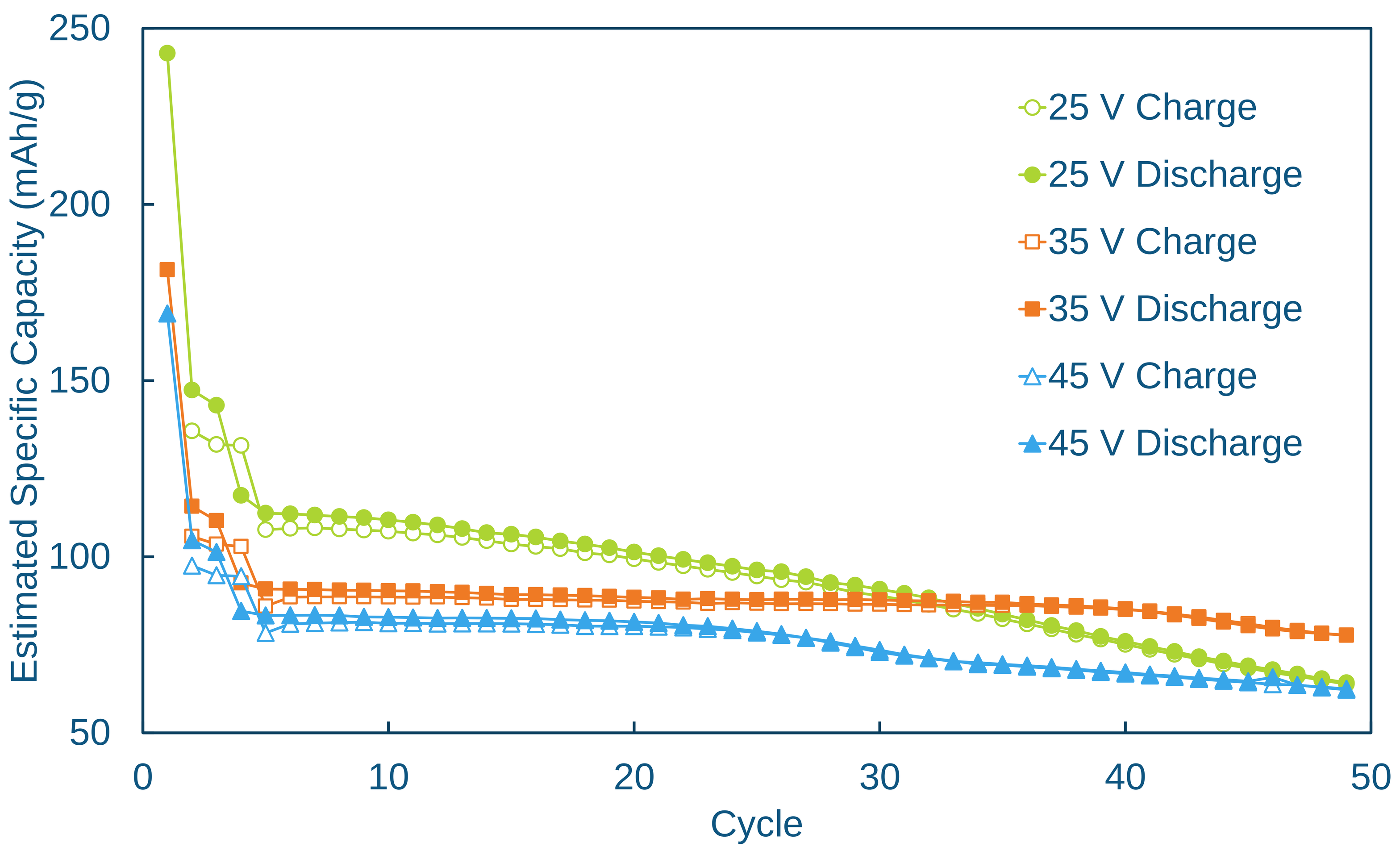


- SEM images of nanoporous niobium oxide films show consistent differences in nanoarchitecture, though there was little to no linear dependence of the surface pore size on anodization voltage
- Two aspects of oxide nanoarchitecture were tested: wall thickness and average pore diameter
- Varying the wall thickness was intended to separate the effects of bulk behavior (intercalation) and surface behavior (pseudocapacitance)



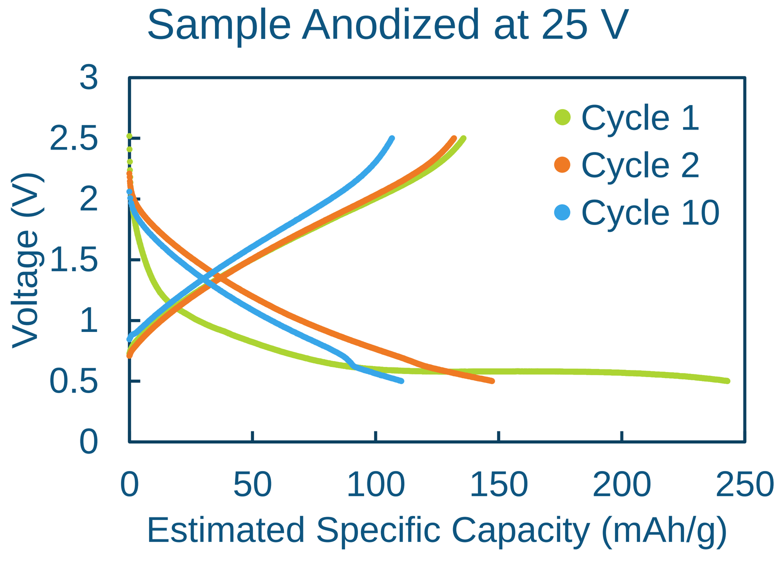
Cycle Life Study

- Capacity can yield information about how much energy the battery is storing, and how capacity changes over time shows how the battery degrades
- The sharp drop in discharge capacity from Cycle 1 to Cycle 2 is typical, since the first discharge involves some irreversible intercalation and the formation of a solid electrolyte interface (SEI) layer, and the drops between Cycles 3 and 4 were due to programmed rate increases
- Though the sample anodized at 25 V initially has the highest specific capacity, the sample anodized at 35 V loses the least capacity after 49 cycles



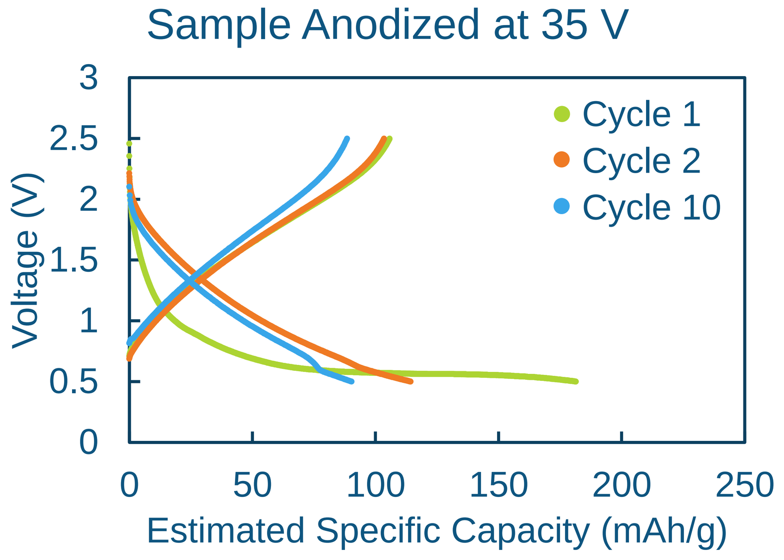
Voltage Profiles

Sample Anodized at 25 V

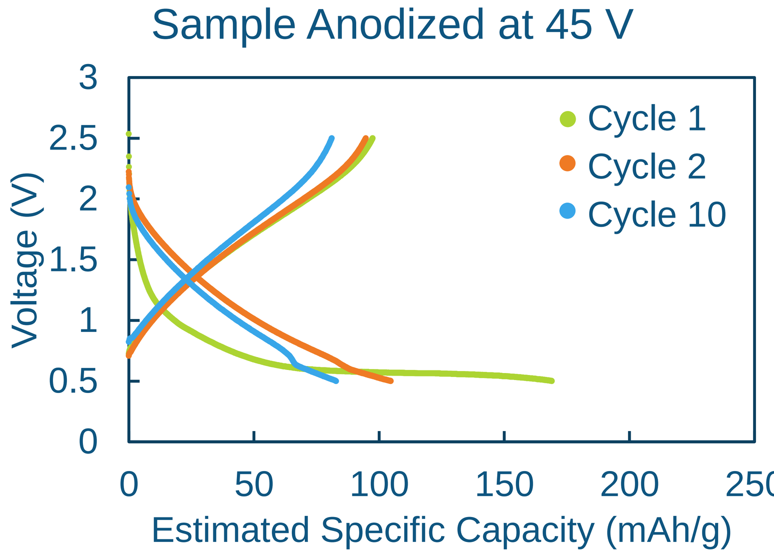


- The shape of the discharge curve for the first cycle is distinct from all following cycles, another result of irreversible intercalation and SEI layer formation
- The lack of humps or plateaus in the first cycles indicates no phase change occurred[7]
- The origin of the bump in the discharge curve for the tenth cycles is unknown, but it has appeared in early cycles for all nanoporous niobium oxide electrodes

Sample Anodized at 35 V

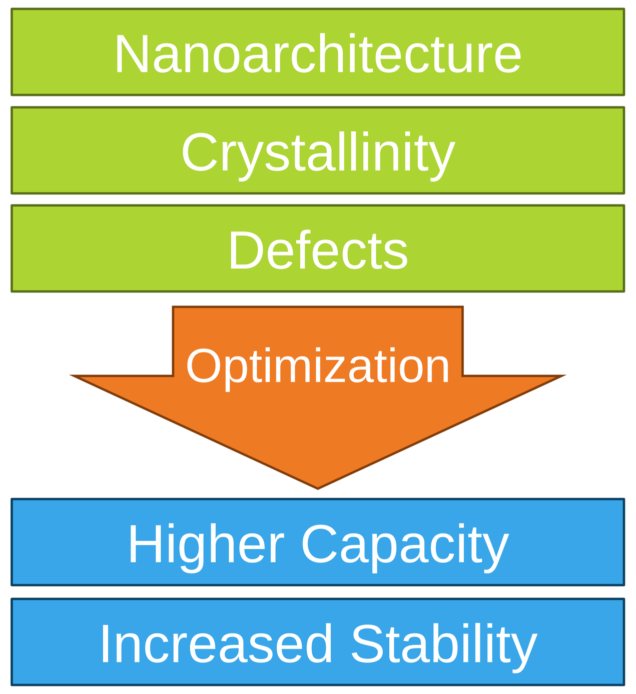


Sample Anodized at 45 V



Conclusions and Future Work

- Differences in nanoarchitecture caused by anodization voltage influence the long-term capacity of electrodes in sodium-ion batteries
- Additional anodizations and SEM is needed to see if nanoarchitecture differences in the interior of the films exist in films anodized at other voltages
- Investigation into methods to remove the messy top layer of nanoporous niobium oxide films to see if this layer inhibits ion diffusion in the electrolyte
- Heat treatments as low as 350°C can crystallize nanoporous niobium oxide films, but the effects of crystallinity and Nb/O vacancies on electrochemical behavior have yet to be tested



- More in-depth characterization is needed to determine the exact crystal structure and whether the intended defects were actually present in heat-treated samples

References and Acknowledgements

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