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Preventing Sodium Battery Thermal Runaway by Potassium Alloying

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Sodium batteries are promising alternatives to lithium ion batteries for stationary energy storage thanks to sodium's abundance. However, similarly to lithium-based batteries, sodium batteries are prone to dendrite growth, thermal runaway and battery fires. Thermal runaway is typically initiated by internal shorting caused by dendrite growth on the battery anode. Methods to mitigate thermal runaway have been proposed and studied by increasing surface atom mobility of metal anodes: for instance, fully molten sodium anodes and Na-K eutectic alloy liquid anodes are effectively dendrite free [1]. Fully molten metal anodes, however, present assembly and containment difficulties. Recently, we proposed a room-temperature, surface-molten Na-K-S battery in which a Na-K alloy anode is formed in situ during battery assembly and found that the Na-K-S battery exhibits substantially higher current density and more complex electrochemical activity than comparable Na-S batteries [2]. The current work employes quantum chemistry and molecular dynamics simulation to investigate the effect of K addition on local surface melting and electrochemical performance, guiding the design of dendrite-free sodium batteries.

Density functional theory calculations are used to evaluate the electrochemical potentials of discharging reactions and determine Na-K-S battery charge and discharge mechanisms. Calculations are performed using the B3LYP functional and the 6-31+G(2df,p) basis set in a THF implicit solvent: a method that has been shown to reproduce structural and electrochemical properties of Li-S and Na-S batteries [3,4]. Like Li-S and Na-S batteries, Na_xK_y-S battery discharge is governed by successive sulfur chain shortening reactions in the catholyte, which produce Na_2S, K_2S, and NaKS as discharge products. The impact of anode surface structure on electrochemical activity is analyzed. We find that although the range of anode surface sites introduces a ~0.2 V uncertainty on charging and discharging electrochemical potential, anode elemental composition has a small impact on electrochemistry: the K adatom stripping potential is largely independent of where stripping occurs, from a Na or a K surface.

Finally, molecular dynamics simulations are used to explain the enhanced surface mobility of metal atoms on the Na-K anode surface. Surface melting simulations for Na and K demonstrate that surface melting occurs at a temperature lower than the bulk melting point. Introducing a small amount of K on a Na metal surface allows local surface melting at room temperature, facilitating faster mass transport with higher current density. Further work will utilize molecular dynamics to analyze local room-temperature dendrite melting.

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