Abstract

Sodium-ion batteries (SIBs) are considered as one of the most promising alternatives to lithium-ion batteries (LIBs) for large-scale energy storage applications, electric vehicles, and smart grids. Several factors that make SIBs dominant over LIBs are low cost, the abundance of Na compared with Li in the World, and environment-friendliness. However, one of the biggest bottlenecks in the design of SIBs is getting an appropriate anode material with high electrochemical performance and low cost. Thus, the present work envisage the electrochemical properties of tin oxide (SnO2) thin films as anode for SIBs. To evaluate the intrinsic electrochemical properties of SnO2 as an anode unmixed from additives and binders, we prepared thin films by the pulsed laser deposition (PLD) technique for substrate temperatures (Td) ranging from 300-500 ºC. Among all the samples, SnO2 thin film deposited at Td = 300 ºC exhibits superior electrochemical performance with a specific capacity of 488 mAh g-1 (at 20 mA g-1) after 50 cycles. Moreover, it maintains Coulombic efficiency of 96% after 200 cycles at 130 mA g-1 in the voltage window between 0.01 - 2.0 V. The effect of thin-film thickness on electrochemical properties have also been analyzed in the study. Subsequently, a restricted upper cut-off voltage window (0.005-1 V) has been imposed to improve cyclability. Among all the three varied thicknesses of ~483 nm (T1), ~200 nm (T2), and ~90 nm (T3), the T3 sample registers a maximum specific discharge capacity of 626 mAh g-1 (13 th cycle, at 60 mA g-1). Followed by this, it retains 167 mAh g-1 after the 150th cycle with a Coulombic efficiency of ~95% for the electrolyte combination 1M NaClO4 salt in EC-PC. Although sample T3 records a reasonable discharge capacity, the capacity fades rapidly after few cycles. However, this problem of capacity fade for T3 can be controlled with an electrolyte combination of 1M NaClO4 salt in ECDEC. Thus, a maximum discharge capacity of 400 mAh g-1 after 32 cycles is achieved retaining 245 mAh g-1 after 150 cycles with a Coulombic efficiency of ~93%. Furthermore, it is observed that FEC (5 wt. %) as an additive in the electrolyte solution of 1M NaClO4, EC-PC increases the discharge capacity with cycling. The discharge capacity increases from 205 mAh g -1 (2nd cycle) to 461 mAh g-1 (140th cycle). In addition to the experimental methods, other computational methods such as density functional theory (DFT) and continuum approach are also used in this study to understand and enhance the performance of SnO2 thin films as an anode. DFT-based studies are augmented to calculate the discharge curve and volume expansion for sodium insertion in SnO2. The different aspects of the first discharge curve of SnO2 obtained through the computational methodology are discussed and attempted to validate them with experimentally obtained values. Taken together the diffusion coefficient obtained through the Galvanostatic Intermittent Titration Technique (GITT) and volume change from DFT calculation, the evolution of Na+ ion concentration and estimation of von Mises stress in the thin films of 100 - 500 nm thicknesses at various state-ofcharge (SOC) such as 20%, 50%, 80%, and 100% are simulated through continuum modelling.

Keywords: Sodium-ion batteries, Lithium-ion batteries, Tin oxide, Pulsed laser deposition, DFT, von Mises stress.