Fabrication of 3D electrodes for all-solid state lithium thin film batteries

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Micro-power sources are increasingly required with the development of microelectromechanical systems (MEMS). The advantages of all-solid-state thin film lithium ion battery (TFLB) high power densities, low self-discharge rate and long cycle life and easy to be fabricated in specific shape and size, make them be one of the most promising micro-power sources. But it is hardly to provide higher current density and capacity because there is limit area for embedded microbattery on most MEMS components.

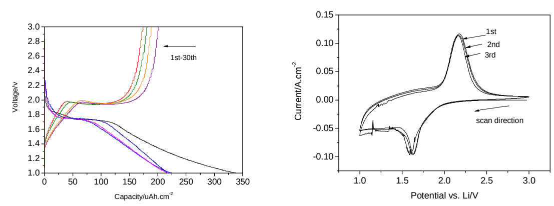
We designed 3 kinds of substrates to build 3D structured thin film electrodes with higher current density and capacity. 1) 3D Si rod arrays patterned by UV-Lithography with the h/w ratio about 5 and the rod diameter is 5um; 2) Porous silicon (PS) substrate electrochemically etched in 5% HF/ethanol solution(the average pore size is 0.2um,etching depth is 2um); 3)Nitrogen-doped carbon nano tubes(N-CNT) arrays grown on SiO2/Si substrates with Fe thin film as the catalyst layer.

The Ti/Pt thin films were sputtered on the non-conducting Si rod arrays and the porous silicon except the conductive N-CNT arrays as the adhesion layer and current collector layer. Then the TiO_2 thin films were deposited on different substrates by ALD deposition at 250℃. The synthesis of ALD-TiO2 on CNTs used the TTIP and water as precursors.

The experiment results showed that the 3D thin film electrodes on N-CNT array substrate have the largest capacity and best capability compared to the other two kinds of substrate. Its first discharging capacity is 350 uAh/cm^2 and the stable capacity could reach $230uAh/cm^2$ with $50uA/cm^2$ discharging current density (Fig.1a). The capacity retention is nearly 63% after first discharge. It is much higher than that of TiO_2 thin film on Si rods arrays, its first discharge capacity for the latter is just 100 uAh/cm^2 and decrease to 25 uAh/cm^2 after first cycle even with the much lower discharging current of $2uA/cm^2$.Its cyclic voltammograms showed the good reversibility, the 1.52v/2.5v redox peaks fits the TiO_2 electrochemical characteristics very well. The PS substrates provide bigger surface than 3D Si rod arrays but because there's no effective barrier layer between Si substrate and the active material, it showed the polycrystalline silicon characteristics(the silicon substrate became polycrystalline after the electrochemical etching). But it is still a choice for 3D structure substrate after more modification, such as pore size control, TiN barrier layer coating before current collector layer deposition[1].

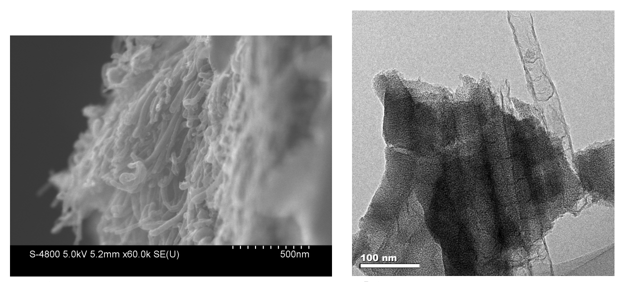
SEM photograph showed the CNT length is about 10um and the diameter is about 50nm(Fig.2a). Further TEM test showed the TiO_2 thin films were coated uniformly on the N-CNT arrays as Fig.2b shows.

In 3D-structured electrodes, the electrode is specifically designed such that diffusion paths in the materials are short and that the transport of electrons and Li ions is improved[2]. Our work shows the N-CNT arrays serve as the best current collector and the 3d substrate compared with the PS and 3D Si structure substrates coated by Pt. Because the N-CNT arrays allow for easy transport of electrons to the active material TiO_2 deposited on the nano bube and provide the largest surface to load more active material. It shows that the N-CNT arrays grownon Si substrate should be a potential candidate as 3D substrates for all solid thin film batteries.



a) b)

Fig.1 Performance of TiO_2 thin film on 3D N-CNT arrays anchored on Si/SiO_2 substrate .a) Discharging curve b)Cyclic voltammograms ($1mol \cdot L^{-1}$ $LiPF_6$ in a nonaqueous solution of ethylene carbonate and dimethyl carbonate (DMC), lithium reference electrode, scan rate is 0.5mv/s)



a) b)

Fig.2 a)The SEM photograph of N-CNT array; b) HRTEM image of TiO_2 thin film on N-CNT arrays

References:

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