SnO_2/(OLC) anode for lithium-ion battery applications

Mesfin Kebede
Energy Centre, CSIR
Meiring Naude Road, Pretoria, 0001, South Africa
Email: mkebede@csir.co.za – www.csir.co.za

INTRODUCTION

SnO_2 emerged as a promising anode material due to its low cost, safety, high theoretical capacity (782 mA h g^{-1}). However, it experiences large volume changes (~250% or larger) during charge and discharge cycles that cause rapid capacity fade and poor cyclability, which limits its practical use as an anode material. To solve this challenge, one option is utilising effective nanostructures such as nanorods and nanowires. one-dimensional SnO_2 nanorods (NRs) benefit from their favourable geometry that enables them to have direct channels for efficient electron transport. Unfortunately, the direct exposure of SnO_2 nanorods to the electrolyte still cause capacity fading due to the rapturing and unstable nature of the SEI layer, causing reduced coulombic efficiency, high ionic resistance and low electronic conductivity.

In this work, the electrochemical performance of SnO_2 nanorods anchored on onion like carbon (OLC) structure (OLC-derived from the nano-diamonds with diameter of 5-10 nm) were synthesised via microwave irradiation technique. The effect of SnO_2-OLC composites before and after annealed was studied and proved that our SnO_2 integrated OLC exhibits an excellent stable capacity cycling behaviour compared to various other carbon composites reported to date.

Aim

- To utilize nanostructured approach to enhance lithium kinetics.
- To use carbon composite to stablize SEI layer and columbic efficiency.

Materials & Methods

SnO_2 nanorod and SnO2/OLC nanocomposite synthesis

Tin (II) chloride dihydrate (5.65 gm, $SnCl_2{\cdot}2H_2O$, Sigma Aldrich, purity 99%) and 0.99 gm of NaOH (Sigma Aldrich, purity 99%) were dissolved in 25 ml of deionized water. The solution subjected to a microwave reaction using Anton Paar Multiwave 3000. The microwave set at constant temperature of 200 °C with 400 W for 20 minutes while stirring.

For SnO_2-OLC, the appropriate amounts of OLC (0.1 g) was dispersed in deionized water by using sonication and add the above raw materials into the solution and the rest of the process is same as above. The dried samples were then annealed at 350 °C at the heating rate of 2°/min, for 3 h under Argon. The as prepared samples were named herein as SnO_2, SnO_2-OLC and the annealed samples are SnO_2-350°C, SnO_2-OLC 350°C, respectively.

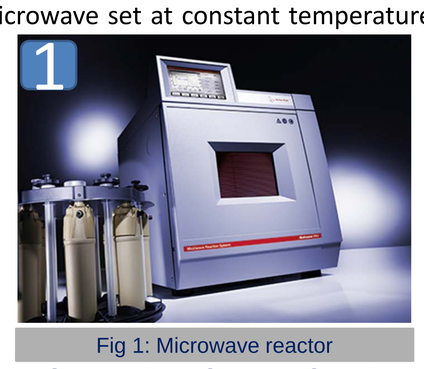


Fig 1: Microwave reactor

Structure, Morphology and electrochemical analysis

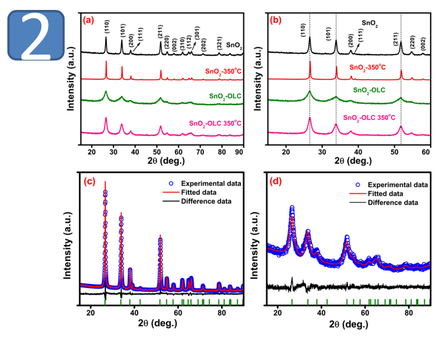
The structure investigated by X-ray diffraction, and lattice parameters derived from the TOPAS-3 software. The SEM images obtained using FE-SEM, JEOL-7600F, and TEM and HR-TEM images obtained from a JEOL-Jem 2100 microscope.

1 M $LiPF_6$, EC: DMC (1:1) used as electrolyte and Li foil as counter/reference electrode. The electrodes prepared using mixture of an active material, Super P carbon and PVDF binder in the weight ratio of 70:15:15. The electrodes were assembled using a CR2032 coin cell and finally crimped to get a two electrode cell. The assembled coin cells were galvanostatically cycled at 25°C between 0.005 and 1.5 V in a Maccor 4000 battery tester.

Cyclic voltammetry and electrochemical impedance spectroscopy (EIS) were carried out using a Bio-logic VMP3 potentiostat/galvanostat controlled by EC-lab v10.40 software. EIS measurements were obtained with the Autolab Frequency Response Analyser (FRA) software at a frequency range between 100 kHz and 10 mHz with a perturbation amplitude (rms value) of the ac signal of 10 mV. The impedance data were analyzed using Z-view software (version 2.2, Scribner Assoc., Inc., USA).

RESULTS AND DISCUSSIONS

- Diffraction peaks of all the samples were matched to SnO_2 rutile structure with respect to the JCPDS pattern (No. 41-1445 and a = 4.738 Å and c = 3.187 Å).

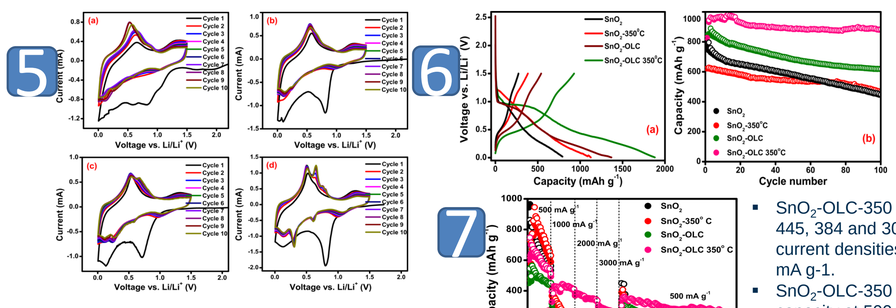


Materials Name	Lattice parameter (Å)		Crystalline size (nm)
	a	c	
SnO_2	4.740	3.188	36
SnO_2 -350 °C	4.741	3.188	45
SnO_2/OLC	4.741	3.193	4
SnO_2/OLC-350 °C	4.738	3.187	17

Fig. 2 (a) XRD pattern for all the samples, (b) Enlarged XRD pattern of all the samples between 20° to 40° and Rietveld analysis of (c) SnO_2 nanorod and (d) SnO_2 nanorod-OLC 350 °C composite.

Fig. 3 (a-d) FE-SEM images of the samples (a) SnO_2, (b) SnO_2-350 °C, (c) SnO_2-OLC, (d) SnO_2-OLC 350 °C.
Fig. 4 TEM and HR-TEM images of the annealed materials; (a, b) SnO_2-350°C, (c, d) SnO_2-OLC 350°C, and inserts SAED patterns.

- HR-TEM in Fig 4d shows the presence of OLC ring type structure which successful anchored on SnO_2. The ring radius for the OLC is of the order of 5 nm.

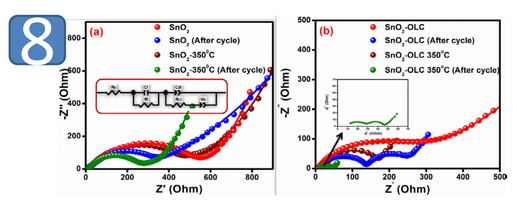


Materials	Capacity at 1st cycle (mAh g^{-1})		1st coulombic efficiency (%)	Capacity at 100th cycle (mAh g^{-1})	Capacity retention (2nd-100th) cycles (%)
	Discharge	Charge			
SnO_2	791	273	34.5	449	56.4
SnO_2-350 °C	1126	384	34	468	74.5
SnO_2-OLC	1368	540	39.5	618	66.4
SnO_2-OLC 350 °C	1881	929	49	884	93.5

- SnO_2-OLC-350 °C exhibited capacity of 748, 445, 384 and 307 mA h g-1, corresponding current densities of 500, 1000, 2000 and 3000 mA g-1.
- SnO_2-OLC-350 °C exhibits the lowest specific capacity at 500 mA g-1, however at high current densities (1000, 2000 and 3 A g-1) it delivers high capacity.
- After deep cycling at high current density (3 A g-1), the specific capacity returns to around 361 mA h g-1 in the initial cycles and the capacity reduced to 238 mA h g-1 at the end of the 100th cycles.

Fig. 5: CV of SnO_2 (a), SnO_2-350 °C (b), SnO_2-OLC (c) and SnO_2-OLC 350 °C (d).;
Fig. 6: First cycle of voltage vs. capacity (a) and cycling performance (b) graphs for all samples, cycled at 100 mA g^{-1}.;
Fig. 7: Rate performance of SnO_2 and SnO_2-OLC and calcined at 350 °C with the potential window of 0.005-1.5 V.

- $SnO_2 + 4Li^+ + 4e^- \rightarrow 2Li_2O + Sn$ (1)
- $Sn + xLi^+ + xe^- \leftrightarrow Li_xSn\ (0 \le x \le 4.4)$ (2)



Materials	R_1		R_2		R_3		R_4		C_{dl}	
	Before	After	Before	After	Before	After	Before	After	Before	After
SnO_2	4	7	82	102	467	226	-	-	23	25
SnO_2-350°C	7	9	57	64	506	210	-	-	27	25
SnO_2-OLC	7	11	49	33	262	117	-	56	22	21
SnO_2-OLC 350°C	13	15	42	21	169	35	-	11	22	23

Fig. 8: Nyquist plots SnO_2, SnO_2 350 °C (a) SnO_2-OLC, SnO_2-OLC 350 °C (b) and Equivalent circuit for all the compounds shown in inset (a) for before and after 100 cycling.

CONCLUSIONS

- Facile and rapid microwave process was implemented to synthesize SnO_2 nanorods anchored on OLC composites as an anode material for LIB applications.
- XRD reveals that, all the composites exhibited tetragonal structure of SnO_2, without any sign of other impurities.
- The OLC coated SnO_2 annealed at 350 °C exhibits highest specific capacity of 884 mA h g^{-1} at the end of the 100th cycles with the capacity retention of ~ 94%, and improved coulombic efficiency as the OLC serves as barrier layer between the SnO_2 structure and electrolyte to stabilize the SEI.
- Also it exhibits excellent specific capacity at high current rates with good cycling stability, which attributed to the high surface area of OLC and could enhance the electron transportation and high lithium ion diffusion during cycling.
- EIS evidenced that the OLC-SnO_2 composite after cycling showed low resistance and the electron transportation are associated with grain and grain boundary of the materials.

REFERENCES

1. G. Du, C. Zhong, P. Zhang, Z. Guo, Z. Chen, H. Liu, Electrochim. Acta. 55 (2010) 2582-2586.
2. Y. Wang, J.Y. Lee, The Journal of Physical Chemistry B. 108 (2004) 17832-17837.