The Investigation of Nanostructured Bi_2Se_3 Thin Films as Anodes for Aqueous Rechargeable Lithium-Ion Batteries

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INTRODUCTION

In the last few decades, lithium-ion batteries (LIBs) have become the primary choice in the development of various portable devices (smartphones, tablets, etc.) due to their remarkable advantages (high energy density, long cycling life, .etc). However, the main disadvantage of LIBs is the flammability of non-aqueous electrolytes. The rapid growth of the technology industry has created a huge demand for LIBs which paid attention to more alternative types of batteries. Aqueous rechargeable lithium-ion batteries (ARLIBs) have attracted attention as cheaper and more environmentally friendly battery systems. The application of lithium-aqueous electrolytes (LiCl, $LiNO_3$, etc.) reduces the risk of battery explosiveness and flammability. The development of anode materials still is the main drawback for ARLIBs due to significant capacity fading during charge/discharge processes. Bi_2Se_3 is a unique material with a layered structure that already has shown its perspective use as an anode for LIBs and probably can be a promising candidate for ARLIBs.

The aim of this research was to investigate the electrochemical performance of nanostructured Bi_2Se_3 thin films with formed **solid electrolyte interphase (SEI)** and **Bi_2O_3 layers** in the 5 M $LiNO_3$ electrolyte.

MATERIALS AND METHODS

Bi_2Se_3 thin films were synthesized on the microscopic glass slides using the physical vapour deposition method. Synthesized Bi_2Se_3 thin films represent rhombohedral nanoplates that are partly disordered and grow at different angles **(Fig.1)**. The size of nanoplates varied between 1.0 and 8.0 um and the thickness of thin films varied from 350 nm to 500 nm. In addition, this type of Bi_2Se_3 morphology has no dead volume or gap spacing shrinkage which could lead to the decrease of the anode active sites, thus making it a promising candidate as anode material for ARLIBs. The XRD results also illustrate the cubic form of γ-Bi_2O_3, which could appear by the oxidation of Bi_2Se_3 powder due to increased surface area after scratching and is more prone to oxidation in an ambient environment.

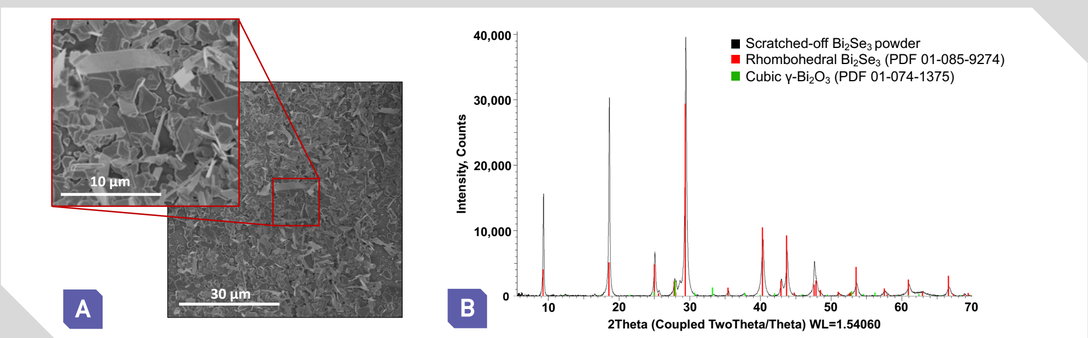

Figure 1. Synthesized Bi_2Se_3 thin film on the glass substrate: **A** – SEM image, **B** – XRD pattern of Bi_2Se_3 powder obtained by scratching the as-grown thin film off the substrate

The electrochemical measurements were performed at room temperature using a 3-electrode cell with 3 M Ag/AgCl as a reference electrode (RE), Pt wire as a counter electrode (CE), and Bi_2Se_3 thin film on a glass substrate as a working electrode (WE). 5 M $LiNO_3$ was used as an electrolyte. To ensure appropriate electrical contact, copper wire was fixed to the surface of the working electrode with silver conductive paint. The electrochemical measurements were carried out by using cycling voltammetry, galvanostatic charge/discharge, and electrochemical impedance spectroscopy techniques.

RESULTS AND DISCUSSION

Cyclic voltammetry of Bi_2Se_3 thin film was obtained in the two potential ranges which represent the formation of **SEI** (-1.0 ÷ 1.3 V) **(Fig.2a)** and **Bi_2O_3 layer** (-1.0 ÷ 0.5 V) **(Fig.2b)**. For the sample with **SEI layer** was observed 2 cathodic (I, II) and 4 anodic (III, IV, V, VI) peaks. However, for the **Bi_2O_3 layer** sample, 2 cathodic (I, II) peaks and 3 anodic (III, IV, VII) peaks were observed.

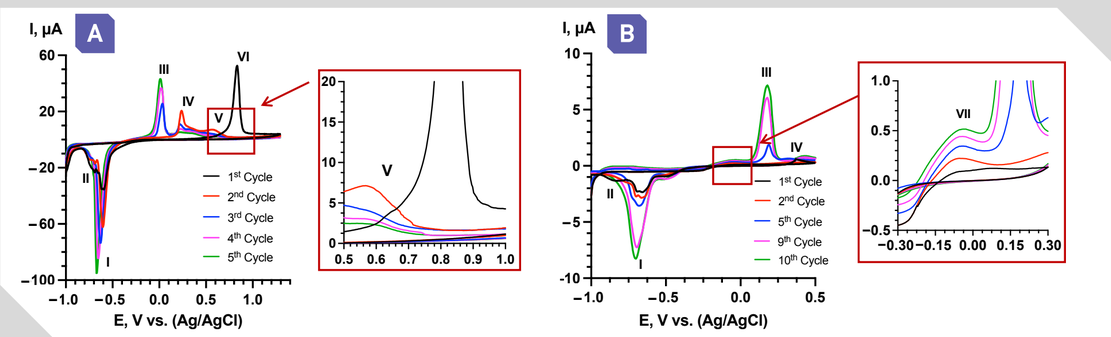

Figure 2. Cyclic voltammograms of Bi_2Se_3 thin films in 5 M $LiNO_3$ at the scan rates 0.25 mV s^{-1}: **A** – sample with **SEI layer** (-1.0 V ÷ 1.3 V), **B** – sample with **Bi_2O_3 layer** (-1.0 V ÷ 0.5 V)

Intercalation/Deintercalation	$Bi_2Se_3 + Li^+ + xe^- \leftrightarrow Li_x^+[Bi_2Se_3]^{x-}$	(I/III)
Substitution reaction	$Bi_2Se_3 + 6Li^+ + 6e^- \leftrightarrow 3Li_2Se + 2Bi$	(II/IV)
Formation of nitrite ions	$NO_3^- + 2H^+ + 2e^- \rightarrow NO_2^- + H_2O$	(V)
SEI layer formation	$O_2 + 4Li^+ + 4e^- \rightarrow 2Li_2O$ $2Li^+ + 1/2O_2 + 2e^- \rightarrow Li_2CO_3$	(VI)
Bi_2O_3 layer formation	$4Bi^{3+} + 3O_2 + 6e^- \rightarrow 2Bi_2O_3$	(VII)

The results of SEM, XRD, and XPS demonstrate the structural differences of the Bi_2Se_3 thin film surface before and after cycling voltammetry measurements for the samples with **SEI** and **Bi_2O_3 layers** **(Fig.3,4)**.

The SEM results for the sample with the **SEI layer** demonstrate that after 5 cycles, the surface of the Bi_2Se_3 thin film was covered with an amorphous layer which represents the **SEI layer** **(Fig.4b)**. The XPS results confirm this fact with a noticeable Li 1s peak, which may indicate the presence of Li_2O and Li_2CO_3 **(Fig.3a,b)**.

In turn, the SEM images of the sample with the **Bi_2O_3 layer** demonstrate that after 10 cycles, the surface was smoother than before cycling (Fig.4a,c). This fact could mean that the Bi_2Se_3 thin film was covered with the thin and dense **Bi_2O_3 layer**. This assumption is also supported by XRD data where cubic **γ-Bi_2O_3** peaks were detected **(Fig.3c)**.

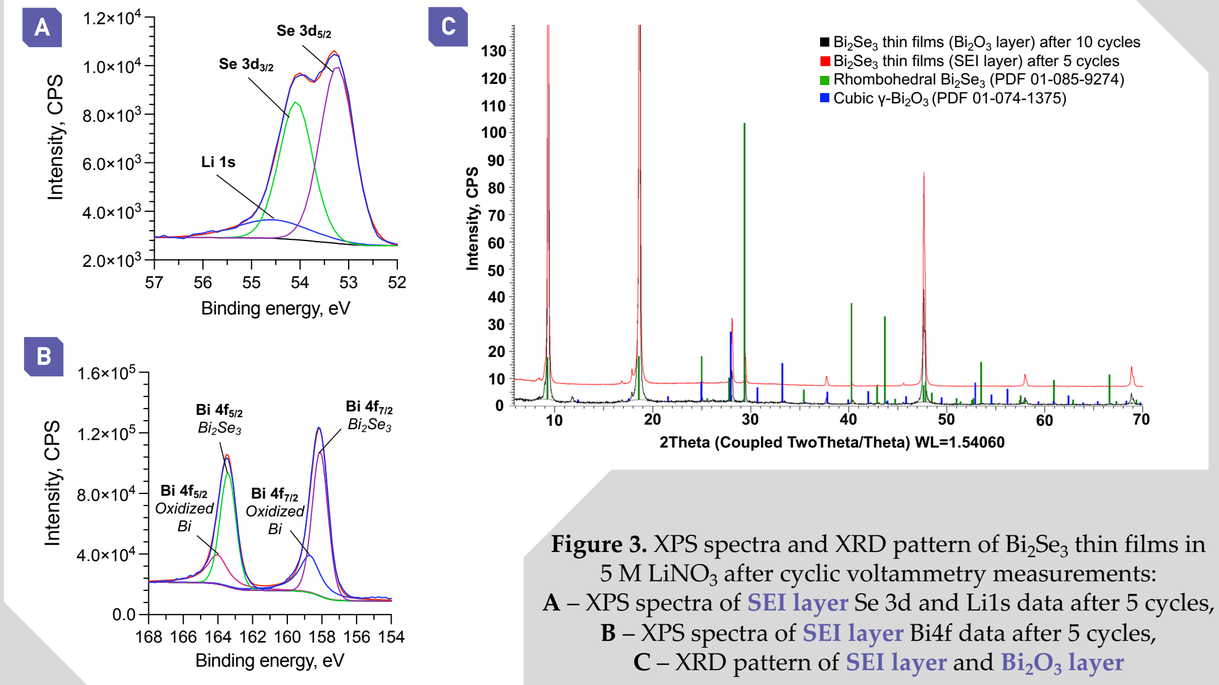

Figure 3. XPS spectra and XRD pattern of Bi_2Se_3 thin films in 5 M $LiNO_3$ after cyclic voltammetry measurements: **A** – XPS spectra of **SEI layer** Se 3d and Li1s data after 5 cycles, **B** – XPS spectra of **SEI layer** Bi4f data after 5 cycles, **C** – XRD pattern of **SEI layer** and **Bi_2O_3 layer**

RESULTS AND DISCUSSION

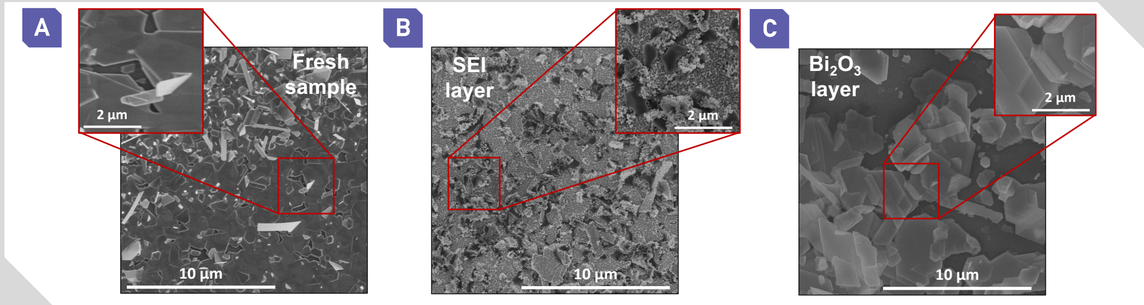

Figure 4. Scanning electron microscope images of Bi_2Se_3 thin films before and after cyclic voltammetry measurements: **A** – fresh sample, **B** – **SEI layer** sample, **C** – **Bi_2O_3 layer** sample

Electrochemical impedance measurements were carried out during the charge/discharge measurements over 100 cycles **(Fig.5)**. Before cycling, both samples with **SEI** and **Bi_2O_3 layer** represent the electrochemical properties at the electrolyte/electrode interface **(Fig.5c)** – electrolyte resistance (R_{el}), charge-transfer resistance (R_{ct}), constant phase element (CPE_1) and Warburg element (W). During the cycling, equivalent the circuit scheme was modified with (R_{layer}) which represents the resistance of **SEI** and **Bi_2O_3 layer** with parallel-connected (CPE_2) representing the inhomogeneity of layer **(Fig.5d)**.

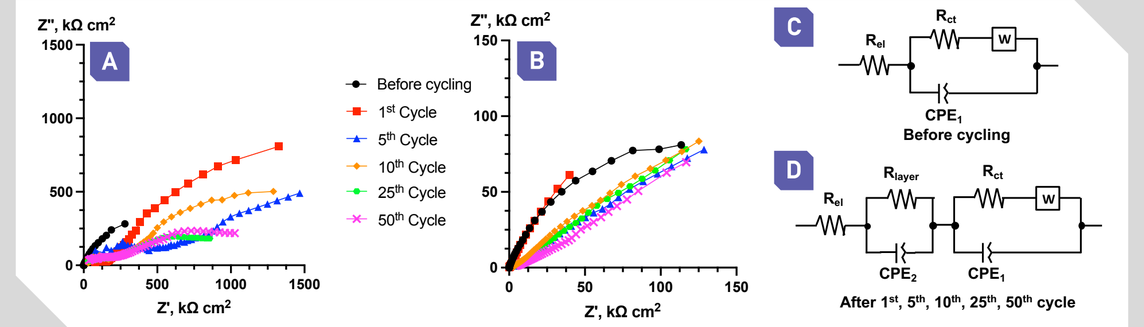

Figure 5. Electrochemical impedance spectroscopy of Bi_2Se_3 thin film: **A** – Nyquist plot for the **SEI layer**, **B** – Nyquist plot for the **Bi_2O_3 layer**, **C** – equivalent circuit scheme before cycling, **D** – equivalent circuit scheme during the cycling

Cycle-depended fitted resistance values (kΩ cm²) of Bi_2Se_3 thin films with SEI and with Bi_2O_3 layer

Layer	Resistance	Before cycling	1st	5th	10th	25th	50th	100th
SEI	R_{el}	0.5	0.9	2.3	2.8	2.9	3.0	3.1
	R_{layer}	-	2162	1515	772	252	208	225
	R_{ct}	584	154	379	275	1246	1965	490
Bi_2O_3	R_{el}	0.1	0.4	0.8	1.3	1.4	1.7	2.0
	R_{layer}	-	112	130	170	196	39	26
	R_{ct}	111	13	10	17	25	17	20

Galvanostatic charge/discharge measurements were carried out at 1 C over 100 cycles **(Fig.6)**. During the first 30 cycles, the capacities of the **SEI layer** sample decreased which might be associated with the gradual degradation of the **SEI layer** **(Fig.6a)**. Sample with **Bi_2O_3 layer** demonstrates capacity increment and decrement till the 10th to 30th cycle indicating the gradual formation and degradation of the **Bi_2O_3 layer** **(Fig.6b)**. The initial Coulombic efficiency for the samples with the **SEI layer** was 41 %. However, after cycling up to the 30th cycle it increased up to 73 %. For the samples with the **Bi_2O_3 layer**, the Coulombic efficiency was almost constant (~40 %). Comparison of discharge capacities of the Bi_2Se_3 thin films with different anodes in the lithium aqueous electrolytes demonstrates that Bi_2Se_3 has the highest specific capacity at the fastest charge/discharge rate (1 C), indicating their perspective application as anode electrodes in ARLIBs.

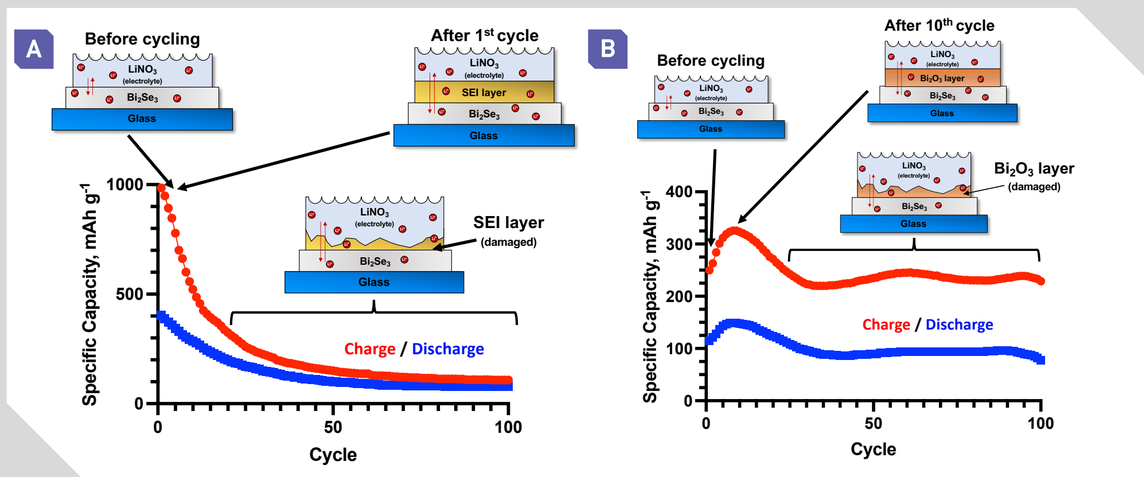

Figure 6. Galvanostatic charge/discharge cycling performances of Bi_2Se_3 thin film: **A** – **SEI layer**, **B** – **Bi_2O_3 layer**

Comparison of galvanostatic discharge cycling performances of different anodes in lithium aqueous electrolyte

Electrode	Electrolyte	C-rate	Initial capacity, mAh g^{-1}	Cycles	Capacity, mAh g^{-1}	Coulombic efficiency	Ref.
Bi_2Se_3 (SEI layer)	5 M $LiNO_3$	1 C	404	30	151	70 %	-
Bi_2Se_3 (Bi_2O_3 layer)	5 M $LiNO_3$	1 C	115	30	96	43 %	-
TiO_2	21 M LiTFSI	0.2 C	115	40	8	70 %	[1]
TiP_2O_7	5 M $LiNO_3$	0.1 C	42	25	15	-	[2]
$Li_{0.3}V_2O_5$	5 M $LiNO_3$	1 C	75	50	38	99 %	[3]

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CONCLUSIONS

For the first time, the results of this work show possible perspectives of Bi_2Se_3 thin films as anode for ARLIBs system and the comparison of electrochemical properties between formed **SEI** and **Bi_2O_3 layer**. With the formed **SEI layer**, Bi_2Se_3 thin films demonstrated rapid pre-treatment, high reversibility, and high transportation of Li^+ during the intercalation/deintercalation processes. The EIS investigation showed significantly lower resistance values (R_{ct} and R_{layer}) for the **Bi_2O_3 layer** which might be related to the different structures and electron affinities of the **SEI** and the **Bi_2O_3 layers**. The galvanostatic charge/discharge demonstrated that the formation of the **SEI layer** in the first cycle plays a crucial role in electrode stabilization, which ensures high Coulombic efficiency (73 %), high charge/discharge capacity, and protection from the mechanical and electrochemical degradation up to 100 cycles.

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