The Investigation of Bi_2Se_3@SWCNT heterostructure as anode for lithium-ion batteries

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INTRODUCTION

Over the last 20 years, lithium-ion batteries (LIBs) have become the main choice in the development of portable devices and have gained huge attention as efficient energy storage devices. Graphite is the most commonly used anode for LIBs, however, a low theoretical capacity is a main drawback. To achieve a better performance of LIBs, one of the main goals is to replace graphite with the best possible anode candidate.

Bismuth selenide (Bi_2Se_3) is a unique material with a layered structure that has been already studied as an anode for LIBs. However, a large volumetric expansion and significant dissolution of selenium are the main issues that worsen LIBs' performance. To solve this issue, Bi_2Se_3 has been studied by nanostructuring it with carbon nanotubes (CNT) or graphene in the form of a mechanical mixture (slurry).

To achieve even better performance as innovation would be nanostructuring Bi_2Se_3 directly on single-walled carbon nanotubes (SWCNT) which ensures stable electrical and mechanical contact.

The aim of this research was to investigate the electrochemical performance of Bi_2Se_3@SWCNT heterostructure as a possible anode for LIBs.

MATERIALS AND METHODS

Bi_2Se_3@SWCNT heterostructures were synthesized in the two-step synthesis using sputtering and physical vapour deposition methods. Accordingly, to this synthesis method different Bi_2Se_3@SWCNT heterostructures were synthesized with different Bi_2Se_3:SWCNT mass ratios – (1:1), (2:1), and (5:1).

For the electrochemical measurements, CR2032 half-cells were assembled **(Fig.1)**. Lithium foil was used as a cathode, and Bi_2Se_3@SWCNT as an anode. As electrolyte 1 M $LiPF_6$ in EC/DEC = 50/50 (v/v) was used and a separator was the Celgard film.

The electrochemical properties were investigated using different measurement techniques *(cycling voltammetry, galvanostatic charge/discharge electrochemical impedance spectroscopy)*. The surface morphology and chemical compositions were analysed using a scanning electron microscope equipped with energy-dispersive X-ray, and X-ray diffraction analysis.

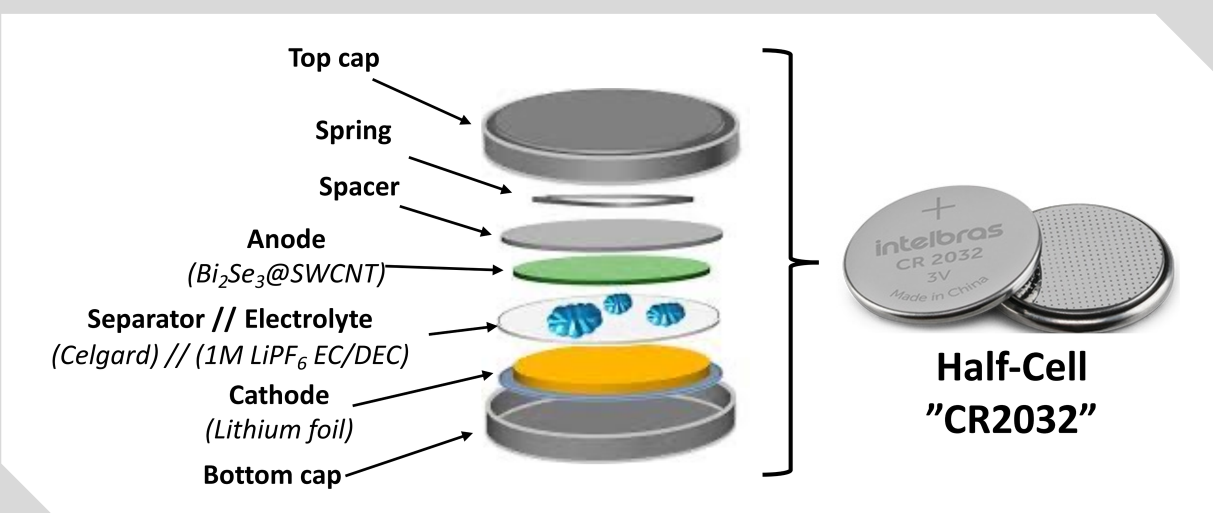

Figure 1. The schematic illustration of half-cell (CR2032)

RESULTS AND DISCUSSION

A synthesized Bi_2Se_3@SWCNT heterostructure consists of both Bi_2Se_3 nanoplates and SWCNTs **(Fig.2)**. The diameter of SWCNT varies from 20 nm to 80 nm. The nanostructured Bi_2Se_3 grows around the SWCNTs in the form of thin films and nanoplates [1]. Bi_2Se_3 nanoplates represent a rhombohedral crystal system with a size from 0.2 µm to 2.0 µm. The presence of copper represents the substrate.

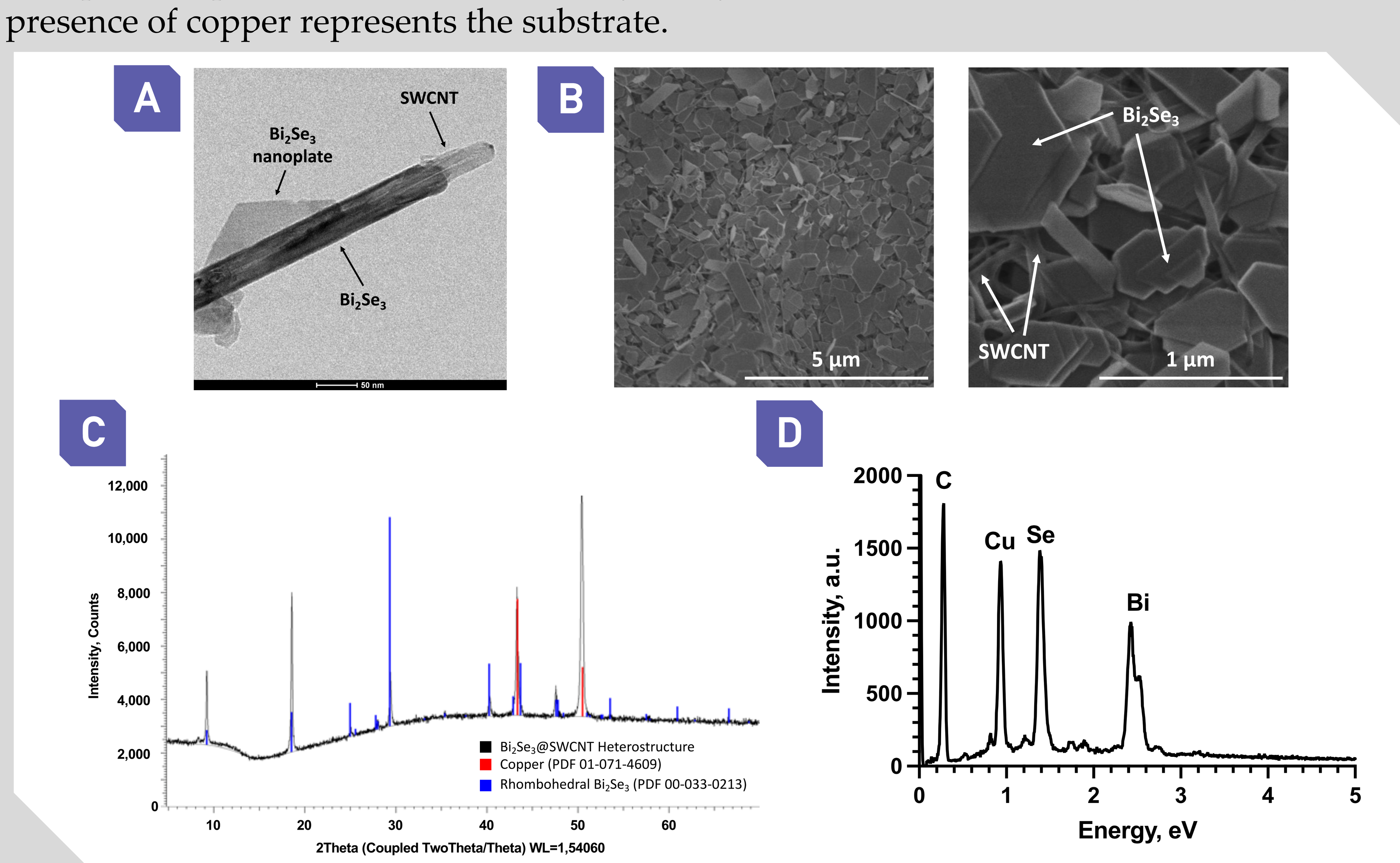

Figure 2. Synthesized Bi_2Se_3@SWCNT heterostructure: **A** – TEM image, **B** – SEM image, **C** – XRD pattern, **D** – EDX spectra

During the galvanostatic charge/discharge measurements, all samples demonstrated a higher initial capacity (1:1 – 879 mAh g^{-1}, 2:1 – 506 mAh g^{-1}, 5:1 – 459 mAh g^{-1}) than a graphite (372 mAh g^{-1}). The sample with a mass ratio (1:1) demonstrated the best performance which might be related to a great cooperative interaction between SWCNT and Bi_2Se_3. Samples (2:1) and (5:1) demonstrate worse performance which might be related to the significant volume expansion and pulverization of Bi_2Se_3 due to an insufficient amount of SWCNTs. The comparison of discharge capacities of Bi_2Se_3@SWCNT (1:1) with previously reported Bi_2Se_3 anodes shows the highest discharge capacity (~523 mAh g^{-1}) by showing its possible perspectives of an anode for LIBs.

RESULTS AND DISCUSSION

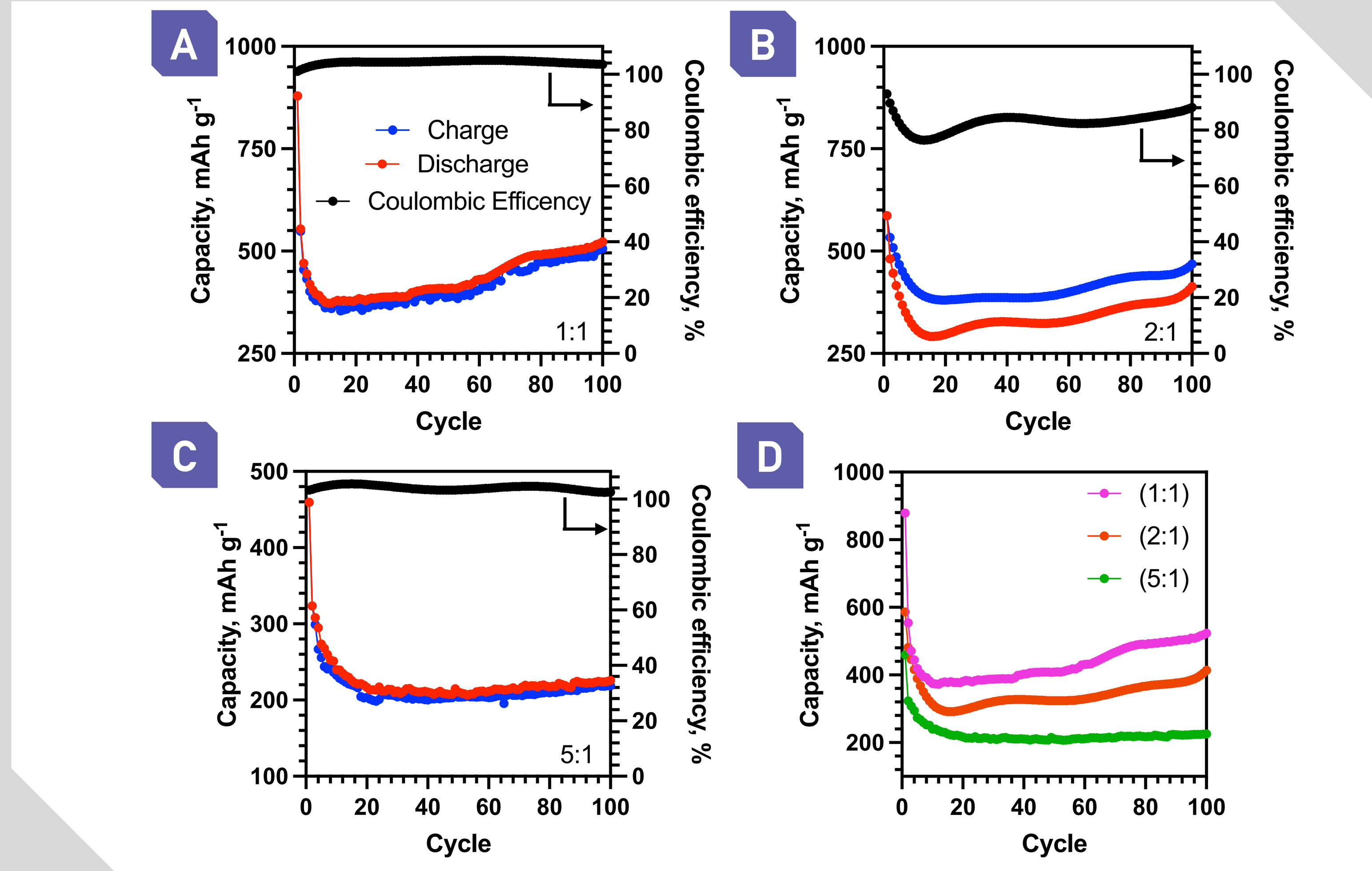

Figure 3. Galvanostatic charge/discharge cycling performance of Bi_2Se_3@SWCNT heterostructures with different Bi_2Se_3:SWCNT mass ratios for 100 cycles at current density of 0.1 A g^{-1}: **A** – (1:1), **B** – (2:1), **C** – (5:1), **D** – discharge capacity comparison between (1:1), (2:1) and (5:1)

The comparison of galvanostatic discharge cycling performances of different Bi_2Se_3 anodes in LIBs

Anode	Current density	Initial specific capacity	Specific capacity after 100 cycles	Coulombic efficiency	Reference
Bi_2Se_3@SWCNT (1:1)	0.1 A g^{-1}	879 mAh g^{-1}	523 mAh g^{-1}	~100 %	This study
Bi_2Se_3/graphene	0.05 A g^{-1}	695 mAh g^{-1}	205 mAh g^{-1}	~100 %	[2]
Bi_2Se_3 microrods	0.05 A g^{-1}	870 mAh g^{-1}	55 mAh g^{-1} *(50 cycles)*	-	[3]
Bi_2Se_3nanosheets/N doped carbon	0.1 A g^{-1}	943 mAh g^{-1}	411 mAh g^{-1} *(50 cycles)*	~100 %	[4]
CNTs@C@Bi_2Se_3	0.1 A g^{-1}	903 mAh g^{-1}	431 mAh g^{-1}	~100 %	[5]

The EIS measurements were carried out for the sample with a mass ratio of (1:1) before and during the cycling **(Fig.4)**. The intercept with the Z′ axis represents the bulk resistance (R_s). A semicircle in the medium-frequency range illustrates the charge-transfer resistance (R_{ct}). The slope illustrates the Warburg open element (W_o) characterizing the ion and/or molecule diffusion. After the 1st cycle, a new semicircle (high-frequency range) appears due to the presence of the SEI layer which is represented as the resistance of (R_{SEI}).

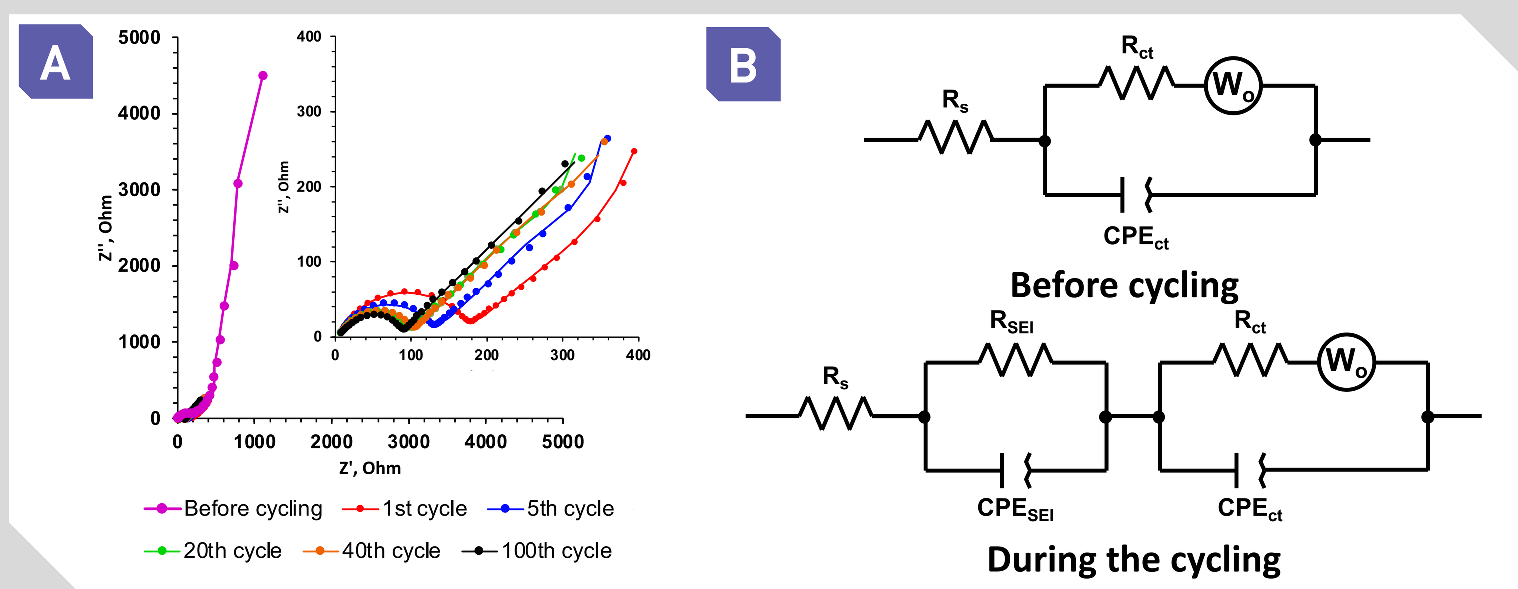

Figure 4. Electrochemical impedance spectroscopy of Bi_2Se_3@SWCNT (1:1): **A** – Nyquist plot, **B** – equivalent circuit scheme before and during the cycling

The cyclic voltammetry measurements **(Fig.5)** of the first 10 cycles of the sample with a mass ratio of (1:1) demonstrated 5 cathodic *(I, II, III, IV, V)* and 4 anodic *(VI, VII, VIII, IX)* peaks.

Intercalation/Deintercalation

$$Bi_2Se_3 + Li^+ + xe^- \leftrightarrow Li_x^+[Bi_2Se_3]^{x-} \quad \textbf{(I/IX)}$$

Substitution reaction

$$Bi_2Se_3 + 6Li^+ + 6e^- \leftrightarrow 3Li_2Se + 2Bi \quad \textbf{(II/VIII)}$$

Alloying reaction

$$Bi + Li^+ + e^- \rightarrow LiBi \;/\; LiBi + 2Li^+ + 2e^- \rightarrow Li_3Bi \quad \textbf{(IV/V)}$$

Dealloying reaction

$$Li_3Bi \rightarrow Bi^+ + 3Li^+ + 3e^- \quad \textbf{(VI)}$$

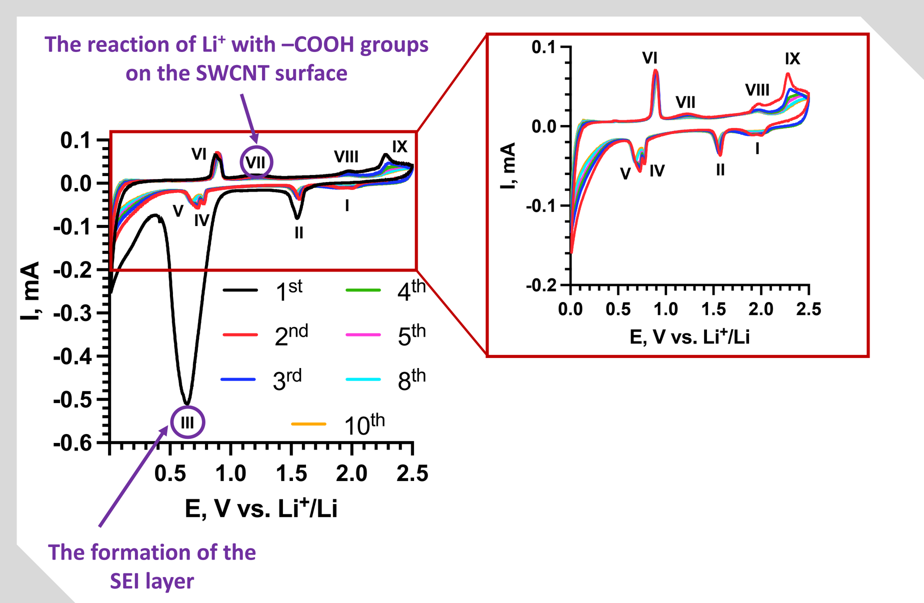

Figure 5. CV curves of the first 10 cycles of Bi_2Se_3@SWCNT (1:1) in the potential range 0.01-2.5 V vs. Li^+/Li at the scan rate 0.1 mV s^{-1}

CONCLUSIONS

The results of this work show a perspective application of Bi_2Se_3@SWCNT heterostructure as an anode for LIBs. The Bi_2Se_3@SWCNT heterostructure with a mass ratio (1:1) demonstrates the highest specific discharge capacity after the 100 cycles (~523 mAh g^{-1}). The great cooperative interaction between Bi_2Se_3 and SWCNT ensures stable electrical and mechanical contact, thus significantly improving the overall performance of LIBs.

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