CHAPTER III

EXPERIMENTAL

3.1 Research procedure

The research process involves five steps, starting with base glass preparation, followed by sample preparation, which includes four processes yielding eight samples. The final step focuses on characterizing these samples to evaluate their structural properties. The workflow is shown in Figure 3.1.

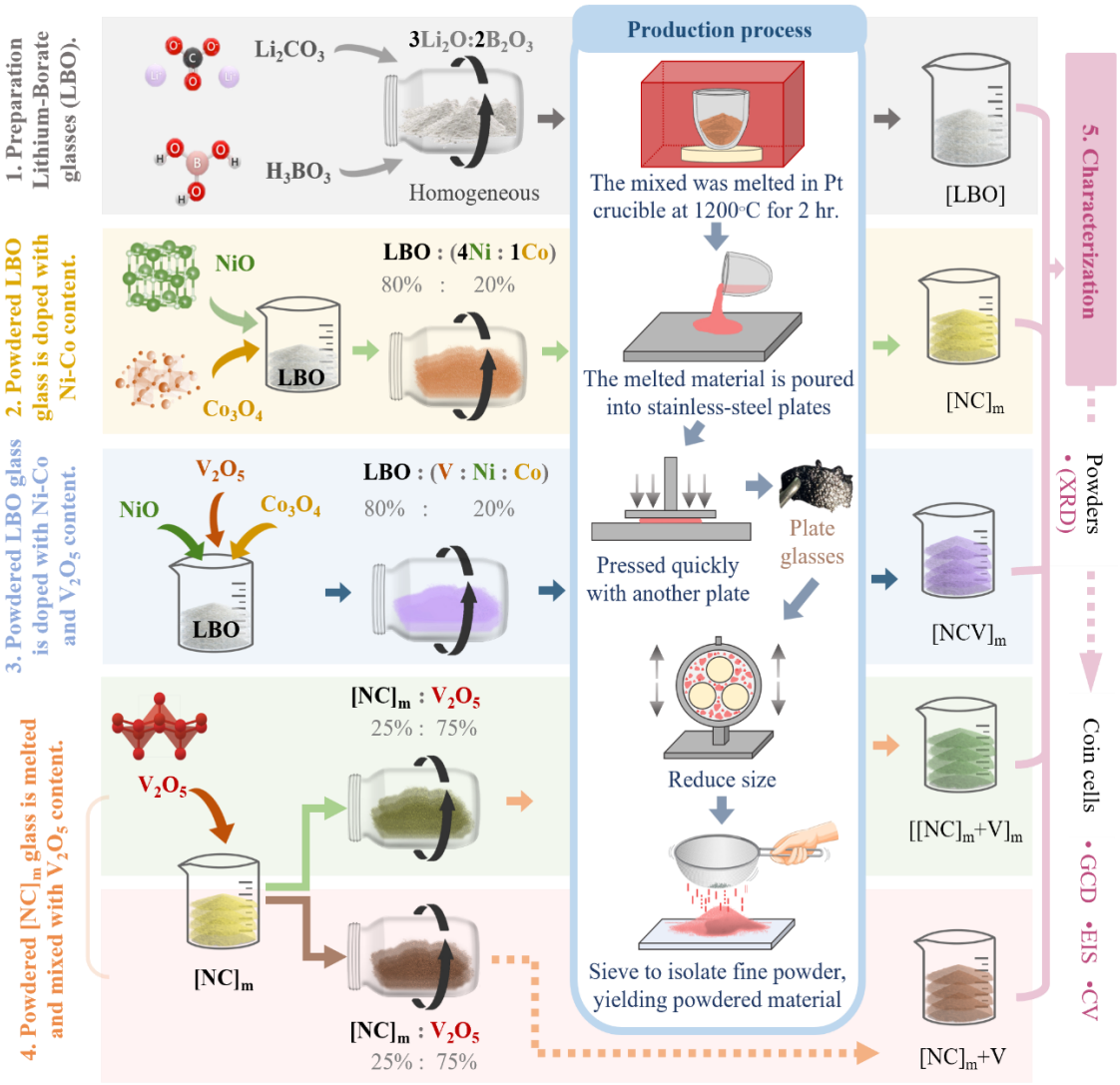

Figure 3.1 Overview of the Research Workflow.

3.2 Sample Preparation

To prepare all the samples, the process is divided into two official steps. The first step involves the preparation of Lithium-Borate glasses (LBO), and the subsequent step entails doping with substances such as Ni, Co, and V_2O_5. In this work, the formula for preparing the glass samples is given as follows:

Chemical system $LiBO_3$: NiO + Co_3O_4 + V_2O_5 with fixed $LiBO_3$ and V_2O_5 content but varied NiO and Co_3O_4 content.

- Sample 1) 0.800LBO: 0.100NiO-0.100Co_3O_4 or $[NC11]_m$
- Sample 2) 0.800LBO: 0.160NiO-0.040Co_3O_4 or $[NC41]_m$
- Sample 3) 0.250$[NC11]_m$-0.750V_2O_5: Mix or $[NC11]_m$ +V
- Sample 4) 0.250$[NC41]_m$ - 0.750V_2O_5: Mix or $[NC41]_m$ +V
- Sample 5) 0.250$[NC11]_m$ - 0.750V_2O_5: Melt or $[[NC11]_m$ +V$]_m$
- Sample 6) 0.250$[NC41]_m$ - 0.750V_2O_5: Melt or $[[NC41]_m$ +V$]_m$
- Sample 7) 0.200LBO- 0.025NiO-0.025Co_3O_4-0.750V_2O_5 or $[NC11+V]_m$
- Sample 8) 0.200LBO- 0.040NiO-0.010Co_3O_4-0.750V_2O_5 or $[NC41+V]_m$

3.2.1 Preparation LBO glasses

Glass-based of $LiBO_3$, generally called LBO is obtained by burning and $2H_3BO_3$ together, leading to the precipitation reaction with the following chemical formulas:

$$Li_2CO_3 \longrightarrow Li_2O + CO_2 \qquad \text{Equation 3.1}$$

$$H_3BO_3 \longrightarrow B_2O_3 + 3H_2O \qquad \text{Equation 3.2}$$

The products of this chemical reaction, when mixed with each other (Equation 3.1 and 3.2), are H_2O and CO_2, which are completely evaporated by heat, leaving only Li_2O and B_2O_3 as precipitation reactions, and the resulting product is $LiBO_3$ (LBO). In this work, the ratio between Li_2O and B_2O_3 of 1:2 was used. Its total molecular mass is 99.464 g/mol. 20 g of LBO was required, so 14.8521 g of Li_2CO_3 and 49.7101 g of H_3BO_3 are needed (Figure 3.2a). The powders of Li_2CO_3 (99.5% purity, Himedia) and H_3BO_3 (99.8% purity, Himedia) were finely powdered and mixed by ball milling for 24 hours (Figure 3.2b). After mixing, it was put in a platinum (Pt) crucible using an electric furnace

at 1100°C for 120 min (Figure 3.2b-c). by heating was fixed at 10°C/min. Each melt was splat-quenched between stainless-steel plates and pressed quickly with another plate at room temperature (RT) (Figure 3.2d-e). This will yield a glass LBO plate as depicted in Figure 3.2f. After that, they were mixed and ground thoroughly using a Mini Mill Pulverisette 23 at a frequency of 30 Hz for 10 min using a Grinding Bowl zirconium oxide and Grinding Balls zirconium oxide 10 mm (3 pcs) (Figure 3.2g). By sieving to filter out only the fine powder, the resulting material is in powdered form (Figure 3.2h-i).

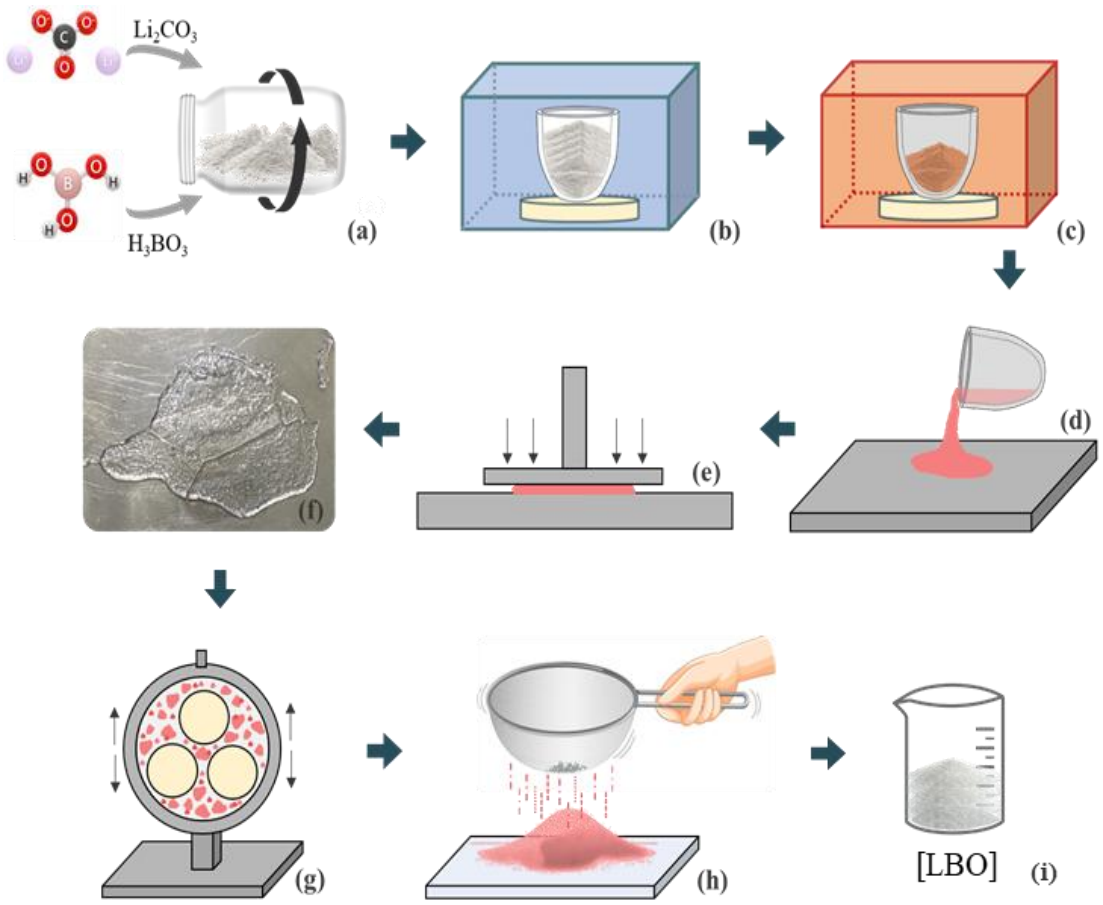

Figure 3.2 Shows the process of preparing LBO glasses.

3.2.2 Preparation of Li-borate base glass mixed with NiO, Co_3O_4, and V_2O_5

Moving on to the next section, we will provide a detailed exposition on the sample preparation process for the eight samples. This comprehensive exploration will delve into the intricacies of each preparation step, offering a more in-depth understanding of the procedures involved.

3.2.2.1 Samples of $[NC11]_m$ and $[NC41]_m$

Preparation Ni, Co and V_2O_5 doped Li-borate base glass electrode. Table 3.1 shows chemical composition ratios in of samples $[NC11]_m$ and $[NC41]_m$, which contain lithium borate glass with nickel (II) oxide and cobalt (III) oxide (LBO: NiO: C_3O_4). The preparation method involves using 80% LBO and the remaining 20% consists of Ni and Co. In the case of $[NC11]_m$, the Ni:Co ratio is 1:1, while for $[NC41]_m$, it is 4:1. Each sample is prepared with a total mass of 10 grams. Subsequently, they are mixed together and subjected to a Melt-quenching and size reduction process, as shown in figure 3.1 (Production process). After completion of the process, glass plates are obtained, as seen in figure 3.1 for samples $[NC11]_m$ and $[NC41]_m$ are (a) and (d), respectively. Finally, the resulting material is sieved to isolate the fine powder.

Table 3.1 Illustrates the ratio conditions of the $[NC11]_m$ and $[NC41]_m$ formulas for a total of 10 g of prepared samples.

Sample	%LBO	%NiO	$\%Co_3O_4$	$MW._{all}$ (g/mol)	Preparation of glass compounds (g)		
					LBO	NiO	Co_3O_4
$[NC11]_m$	80.0	10.0	10.0	101.15	7.1611	0.6721	2.1667
$[NC41]_m$	80.0	16.0	4.0	111.12	7.8666	1.1813	0.9521

3.2.2.2 Samples of $[NC11+V]_m$ and $[NC41+V]_m$

Examples of $[NC11+V]_m$ and $[NC41+V]_m$ involve the co-melting of NiO, Co_3O_4, V_2O_5 and LBO. The chemical composition ratios for these components are

presented in Table 3.2. The preparation method utilizes 80% lithium borate (LBO) with the remaining 20% consisting of Ni, Co, and V_2O_5. However, there is a difference between the two examples in terms of the Ni:Co ratio. For $[NC11+V]_m$, the ratio is 1:1, whereas for $[NC41+V]_m$, it is 4:1. Each sample is prepared with a total mass of 10 grams. After preparing the substances according to their respective weights, they were mixed together for 24 hours. Subsequently, they were introduced into the process outlined in figure 3.1 (Production process). After the glass melting process, it was poured into stainless steel sheets, glass plate is obtained as shown in figure 3.1 c and f for samples $[NC11+V]_m$ and $[NC41+V]_m$, respectively. In the final step, we obtain powdered material.

Table 3.2 Show the ratio conditions for the $[NC11+V]_m$ and $[NC41+V]_m$ formulations.

Sample	**% LBO**	**% NiO**	**% Co_3O_4**	**% V_2O_5**	**Preparation of glass compounds (g)**			
					LBO	NiO	Co_3O_4	V_2O_5
$[NC11+V]_m$	20.0	2.5	2.5	75.0	1.2118	0.1137	0.3667	8.3078
$[NC41+V]_m$	20.0	4.0	1.0	75.0	1.2305	0.1848	0.1489	8.4358

Table 3.3 Illustrates the ratio conditions of the $[NC11]_m$ +V, $[NC41]_m$ +V, $[NC11]_m$ +$V]_m$, and $[NC41]_m$ +$V]_m$ formulas for a total of 10 g of prepared samples.

Sample	% $[NC11]_m$	% $[NC41]_m$	% V_2O_5	**$MW._{all}$ (g/mol)**	**Preparation of glass compounds (g)**		
					$[NC11]_m$	$[NC41]_m$	V_2O_5
$[NC11]_m$ +V $[NC11]_m+V]_m$	25.0	-	75.0	164.15	1.6922	-	8.3078
$[NC41]_m$ +V $[NC41]_m+V]_m$	-	25.0	75.0	161.66	-	1.5642	8.4358

3.2.2.3 Samples of $[NC11]_m$ +V and $[NC41]_m$ +V

For the remaining four samples, their chemical compositions are presented in table 3.3. Notably, the Mix and Melt samples share the same chemical composition, which consists of a mixture of nickel cobalt glass doped with vanadium pentoxide (GNC: V_2O_5) in a 25:75 ratio. The key difference lies in the glass fabrication process. In the case of the 'Mix' samples, it involves blending Glass Nickel Cobalt (GNC) with V_2O_5 for a duration of 24 hours to complete the process. The outcome is a powdered form of the samples denoted as $[NC11]_m$ +V and $[NC41]_m$ +V, as illustrated in figure 3.1.

3.2.2.4 Samples of $[[NC11]_m +V]_m$ and $[[NC41]_m +V]_m$

In the case of the Melt sample, after achieving a homogeneous mixture ($[[NC11]_m+V]_m$ and $[[NC41]_m +V]_m$), it is subjected to the glass melting process (as shown in figure 3.1, Production Process). This process results in glass plates, depicted in figure 3.1 b and e. Once completed, the process results in the production of powders denoted as $[[NC11]_m+V]_m$ and $[[NC41]_m +V]_m$, respectively.

3.3 Manufacturing of Li-ion battery coin cells

The cell was assembled using the coin cell technique figure 3.3 shows an overview of the components of a coin cell construction.

3.3.1 Preparation of Cathode

- In this work, carbon black (CB) was used as a conductive material, and polyvinylidene fluoride (PVDF) was used as a binder to help adhere the material to both the CB and the foil. The ratio used was 8 : 1 : 1 (glass powder: CB: PVDF), which was prepared by mixing 1.2 ml of 2.5% PVDF solution, 0.03 g of CB, and 0.24 g of glass powder, as shown in Figures 3.3a-b. The three components were combined using two 2 mm grinding balls and one 5 mm ball to ensure better homogeneity.
- The mixture was then shaken for 30 minutes (Figure 3.3c). Afterward, the grinding balls were removed, leaving only the well-mixed sample.

- A layer of PVDF was evenly applied to the glass base, followed by placing aluminum foil on top. Another layer of PVDF was used, and the foil was smoothed to ensure full contact. The Doctor Blade Coating Device was adjusted to a thickness of 20 µm, and the device was placed on the aluminum foil. The prepared sample mixture was poured onto the foil and then coated to form a uniform layer, as shown in Figures 3.3d-e.
- The coated sheet was dried in an oven at 80°C for 1 hour to prevent cracking and ensure proper drying. The section of the aluminum foil with the sample was pressed using a force of approximately 1 ton Figure 3.3f.

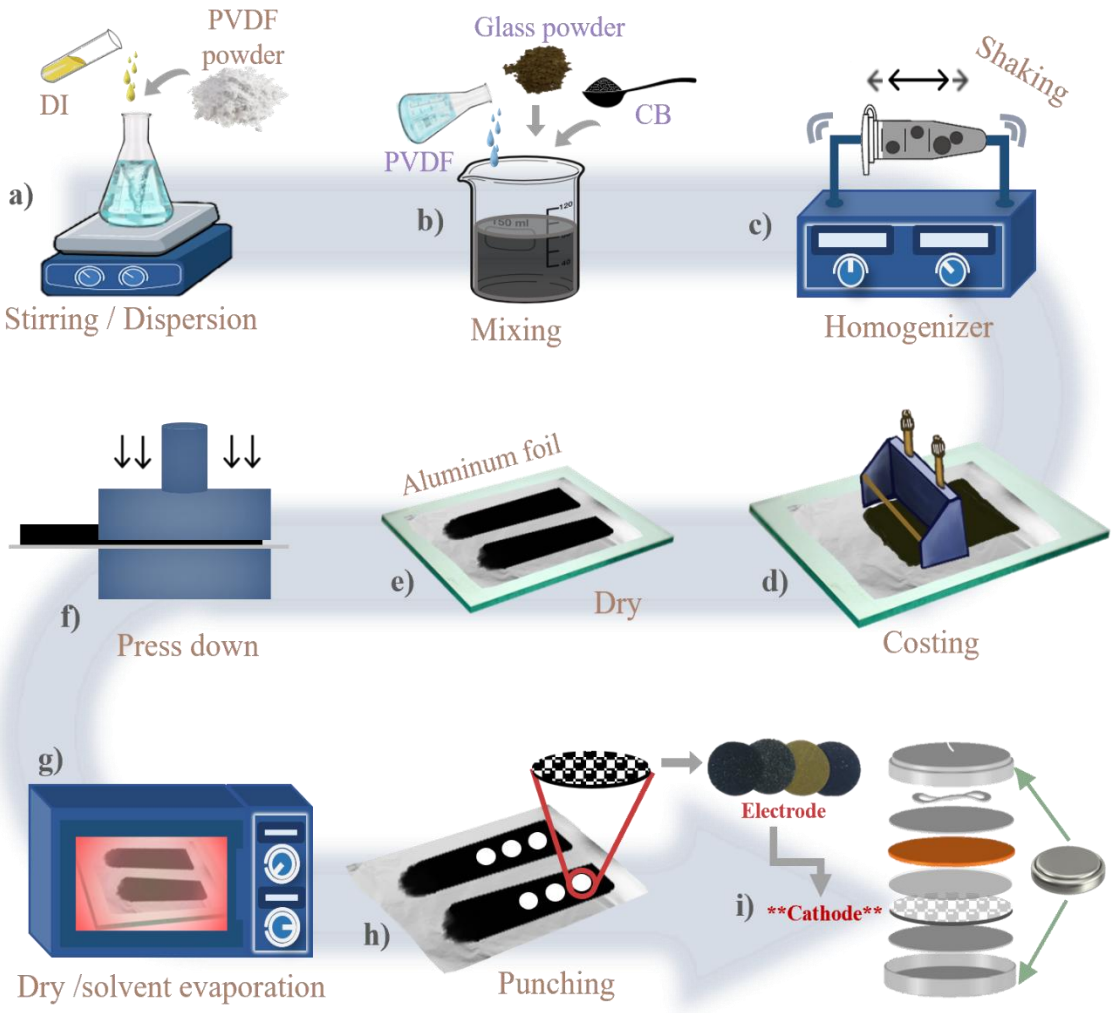

Figure 3.3 Schematic representation of the stages in cathode preparation, from material selection to assembly.

- The pressed sheet was then baked again at 120°C for 1 hour to completely remove any moisture (Figure 3.3g).
- Finally, the sheet was cut into 16 mm diameter circles, as shown in Figure 3.4b.

3.3.2 Coin Cell Assembly

In Figure 3.4, the cathode was constructed using a V_2O_5 mixed Ni/Co glass-based Li-borate film on an Al foil, featuring various compositional conditions, with a PP separator film (Celgard 2400) dividing it (Kayyar, Huang, Samiee, and Luo, 2012), while the anode consisted of Li foil. Afterward, it was infused with 50 microliters of 1 M $LiPF_6$ in an ethylene carbonate (EC): dimethyl carbonate (DMC) (1:1) electrolyte solution. Subsequently, the coin cell was sealed by utilizing an ECCCM-160E-A crimping machine from MTI Corporation with a 1-ton push.

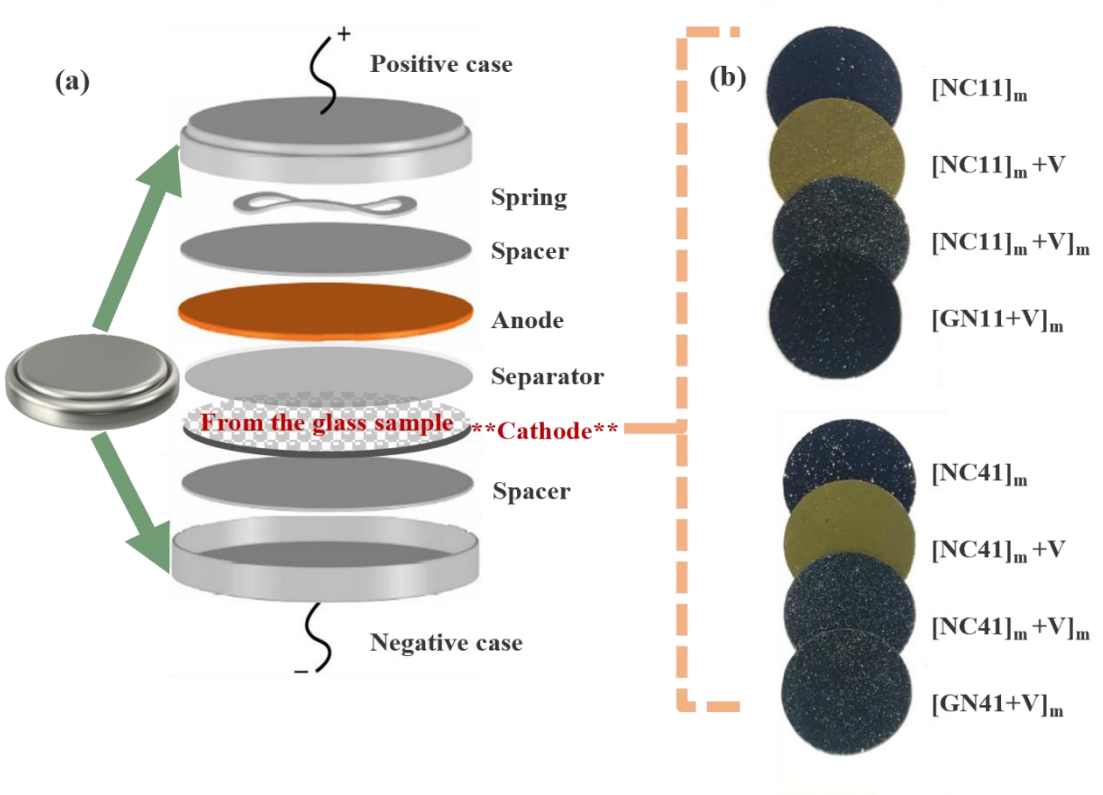

Figure 3.4 This figure show (a) The coin cell assembly components. (b) The photograph of film composition of $[NC11]_m$, $[NC11]_m$ +V, $[NC11]_m$ +V]$_m$, $[NC11+V]_m$, $[NC41]_m$, $[NC41]_m$ +V, $[NC41]_m$ +V]$_m$ and $[NC41+V]_m$.

3.4 Instrumentation

3.4.1 Powder X-ray Diffraction Analysis using Bruker D8 Advance

Figure 3.5 Bruker D8 X-ray diffractometer (XRD) was used for the analysis.

In this work, we utilized the Bruker D8 Advance Powder X-ray Diffractometer (XRD). This system is equipped with a high-performance PhotonMax 9 kW rotating anode X-ray source and a HyPix-3000 multidimensional semiconductor detector with high-energy resolution. The HyPix-3000 detector supports 0D, 1D, and 2D measurement modes, allowing for versatile applications without the need to switch detectors for different tasks. With this detector, 2D powder diffraction patterns can be obtained. Additionally, the system features an in-plane diffraction arm and a high-resolution, closed-loop goniometer drive mechanism. The Cross-Beam Optics (CBO) system, featuring fully automated switchable optics (CBO-Auto), enables both reflection and transmission modes with ease.

3.4.2 Neware Battery Testing Systems

The Neware Battery Testing Systems BTS4000-5V10mA and 5V50mA are essential tools for measuring battery capacity and analyzing electrochemical performance. These systems are designed to evaluate the charge and discharge behavior of batteries, providing crucial insights into their electrochemical properties.

The BTS4000 series supports precision testing at both low and moderate current ranges, with the 5V10mA model suitable for small-scale battery cells and the 5V50mA model ideal for larger cells. These systems allow for accurate tracking of voltage, current, and capacity over time, which is critical for determining battery efficiency, energy density, and stability.

Figure 3.6 Battery Capacity Measurement using Neware BTS4000-5V10mA5V50mA Systems.

Through the charge and discharge curves generated during testing, users can assess the battery's performance under various conditions, including cycle life and capacity retention. The versatility of the Neware BTS4000 systems makes them widely used in research and development of new battery materials, including lithium-ion, solid-state, and other advanced energy storage technologies.

3.4.3 Potentiostat galvanostat analysis using metrohm autolab

The Biologic SP300 Potentiostat/Galvanostat is a versatile and high-performance electrochemical workstation designed for a wide range of electrochemical measurements, including cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and charge-discharge studies. In this research, the Biologic SP300 was used to evaluate the electrochemical properties of battery electrodes.

For EIS measurements, the SP300 was employed to determine the impedance values of the battery electrodes, providing insights into the electrode's charge transfer

resistance and electrolyte resistance. This analysis helps in understanding the behavior of the electrode material and the efficiency of ion transport in the system. Additionally, cyclic voltammetry (CV) was used to measure the specific capacitance of the glass electrodes. By applying a varying voltage and recording the resulting current, the CV data from the SP300 provided information on the charge storage capability and redox activity of the electrode material.

Figure 3.7 Potentiostat Galvanostat Analysis using Metrohm (Biologic) SP300.

The SP300 features a high-frequency response and wide dynamic range, making it ideal for precision electrochemical measurements, ensuring reliable data for the characterization and development of advanced battery materials.

3.4.4 SUT-NANOTEC-SLRI XAS beamline at SLRI

X-ray absorption spectroscopy (XAS) is the only focus of the SUT-NANOTEC-BL5.2 SLRI beamline. Chemical speciation and local structure (number of coordination complexes, inter-atomic distance, etc.) can both be determined with this method. X-ray absorption spectroscopy (XAS) is a non-destructive technique that can be applied to any solid (crystalline or amorphous), liquid, or gas (pressure and temperature control) outside of ambient conditions. Real-world samples from fields as varied as materials science, biology, environmental science, archaeology, and geology can all be studied with this method. To detect and quantify S species in difficult materials such as minerals, coals, sediments, and rubber, X-ray Absorption Near Edge Structure (XANES) spectroscopy is an excellent, non-destructive option. Materials in this category include minerals, coals, sediments, and even rubber. Differences in the S-K apex and XANES bands can oxidize sulfur compounds in either an inorganic or organic form. Like fingerprints, XANES bands can provide insight about a substance's coordination

chemistry. The fundamental idea of both BL5.2 and BL8 is the same. It relies heavily on an in-house-built double-crystal monochromator (DCM) with a fixed outlet. To adjust the level of x-ray radiation, a DCM equipped with a wide range of crystals, from 1240 eV to 12100 eV, is employed. All the way from magnesium to gallium, you can do K-edge absorption tests. The L and M limits are useful for studying heavier atomic species.

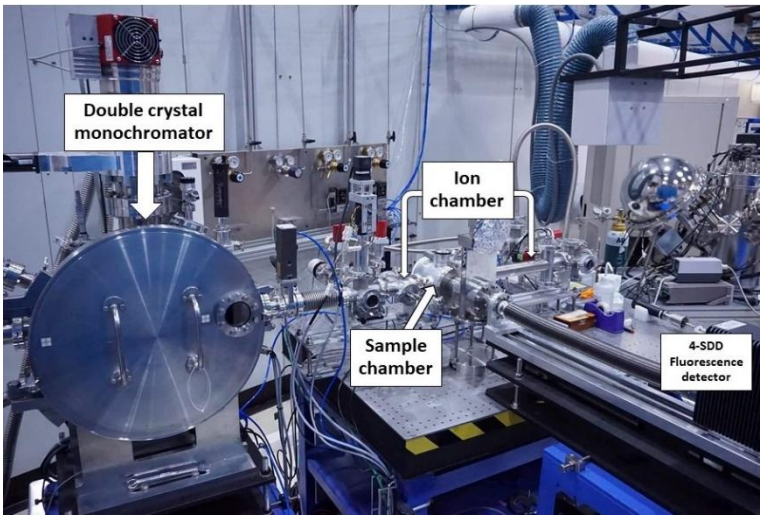

Figure 3.8 BL5.2: SUT-NANOTEC-SLRI XAS Beamline.