CHAPTER V
CONCLUSIONS

This thesis demonstrates that the electrochemical properties of lithium borate glass can be enhanced through the incorporation of transition metals. The amounts and ratios of these transition metals, along with different melting processes, have varying effects on the properties of the glass. In this research, the influence of transition metal ratios and melting procedures has been investigated using a diverse array of methodologies.

The production of transition metal-doped lithium borate glass samples was successfully achieved using a melt-quenching approach. Initially, the samples exhibited a shiny and brittle appearance, characterized by a distinct black hue, indicative of transition metals, specifically nickel and cobalt oxides. The fundamental objective of this investigation was to assess the properties of the lithium borate glass, which was accomplished through X-ray diffraction (XRD) analysis. The XRD results demonstrated that both the pure LBO glass base and the NiO/Co_2O_3-doped glass base maintained an amorphous structure ($[NC11]_m$ and $[NC41]_m$). However, the addition of V_2O_5 resulted in it resulted in a higher capacitance value due to the formation of a glass-ceramic structure of $Li_6B_4O_9$. In this system, the incorporation of V_2O_5 facilitates the reaction between boron and vanadium, leading to their fusion into a glass matrix, while the amount of Li_2O remains constant. In contrast, B_2O_3 content decreases as it reacts with vanadium, affecting the ratio of Li_2O to B_2O_3. Moreover, the substantial addition of vanadium (75%) slows down the cooling process, resulting in the formation of $Li_6B_4O_9$ with a hexaborate structure in samples such as $[NC11]_m$+V]$_m$, $[NC41]_m$+V]$_m$, [NC11+V]$_m$, and [NC41+V]$_m$. The study of the $Li_6B_4O_9$ peak revealed that the [[NC]$_m$+V]$_m$ sample exhibited a higher peak intensity compared to the $[NCV]_m$ sample, indicating that the latter possesses a more amorphous nature. The improved crystallinity observed in the

$[[NC]_m + V]_m$ sample can be attributed to the three melting cycles it underwent, which facilitated more thorough crystallization compared to samples subjected to only two cycles. Consequently, the crystalline structure in the $[[NC]_m + V]_m$ sample became more defined and complete following the additional melting process.

Performance tests on batteries prepared via the melt quenching process reveal that the $[NC41+V]_m$ sample displays excellent energy storage capabilities, with an average capacity of 111.42 mAh/g and an energy density of 306.26 mWh/g—values significantly higher than other samples. Notably, the capacity retention of $[NC41+V]_m$ reaches an impressive 80.69% after 100 cycles, highlighting its stability and resistance to degradation. Additionally, samples $[NC11]_m+V$ and $[NC41]_m+V$, incorporating 75% V_2O_5, achieve high capacity and energy density values, with $[NC41]_m+V$ recording a peak capacity of 140.13 mAh/g and an energy density of 410.93 mWh/g. This indicates exceptional energy storage and release efficiency; however, V_2O_5-based batteries often experience capacity retention declines due to structural vulnerability and potential degradation during prolonged usage. Still, combining V_2O_5 with GNC significantly enhances the battery's capacity.

This study also investigates the chemical properties of the samples, beginning with EIS measurements, followed by three CV cycles, and concluding with a final EIS measurement. Analyses from Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) reveal that incorporating LBO in the sample materials greatly reduces internal resistance, indicating improved charge transfer and structural reinforcement. Specifically, $[NC11]_m+V$ and $[NC41]_m+V$ initially exhibit high internal resistance that decreases markedly after three CV cycles, signifying improved ionic conductivity. For materials such as $[NC11]_m+V]_m$, $[NC41]_m+V]_m$, $[NC11+V]_m$, and $[NC41+V]_m$, internal resistance remains largely unchanged throughout EIS testing. CV measurements further highlight V_2O_5 crystal phase transitions during the redox process, signifying efficient Li^+ acceptance and transfer. $[NC11]_m+V$ and $[NC41]_m+V$ samples demonstrate distinct redox peaks consistent with V_2O_5 phase changes. However, melting V_2O_5 into the glass matrix lowers current density, effectively prolonging battery life. CV graphs from cycles 1 to 3 for $[NC11]_m+V]_m$, $[NC41]_m+V]_m$, $[NC11+V]_m$, and

$[NC41+V]_m$ maintain steady resistance, indicating material durability, electrode stability, and consistent reversibility, aligning with long-term capacity retention.

Electron transfer in the context of oxidation-reduction (redox) reactions is a fundamental component of electrochemical phenomena. Understanding the charge transfer effects associated with incorporating transition metals into glass requires detailed knowledge of their oxidation states. To investigate these oxidation states, X-ray Absorption Near Edge Structure (XANES) analysis was employed. Nickel within the glass exhibits both Ni^{2+} and Ni^{3+} oxidation states, with a higher concentration of Ni^{2+}. For cobalt, oxidation states Co^{2+} and $Co^{2+,3+}$ are present, with Co^{3+} being more dominant. Vanadium exists in both V^{4+} and V^{5+} states, with a higher presence of V^{5+}. Adjustments in the Ni and Co ratios lead to slight shifts in the oxidation states of these transition metals within the glass samples, potentially impacting their electrochemical properties.

The interplay of Li^+ and Ni^{2+} is notable, as higher Ni^{2+} levels can limit the specific capacity in nickel-rich NC materials. For instance, if Ni^{2+} substitutes Li^+ ions, lower-valence nickel ions can migrate from the transition metal layer into the lithium layer, filling lithium vacancies and impeding Li^+ diffusion, which constrains battery charging capacity. However, restricting Ni^{2+} transport into the Li layer, even with minimal cobalt (Co^{3+}), helps maintain structural integrity. Additionally, the presence of Co enhances conductivity and enables the material to perform effectively work at high rates.

The study of X-ray absorption spectra in the EXAFS region of glass samples doped with NiO, Co_3O_4, and V_2O_5 aimed to observe local atomic changes of these elements. Glass samples analyzed using Athena and Artemis software effectively identified the scattering paths of atoms surrounding the absorber atom, allowing efficient fitting with experimental data. Key parameters such as R (interatomic distance), $\boldsymbol{\sigma}^2$ (Debye-Waller factor), $\boldsymbol{s_0^2}$ (scattering amplitude), ΔE_0 (edge energy shift), and R-factor (model-experiment fit difference) for NiO- and Co_3O_4-doped glass samples were within acceptable ranges across all cases. However, in V_2O_5-doped glass samples, while some parameters fell without acceptable limits, the fit with both the V_2O_5 model and alternative models did not align closely with the best-fit line. This suggests that

vanadium in the glass samples may exhibit a complex structure or unique bonding with other components not accurately represented by the existing models.

This study employed XANES to analyze the changes in oxidation states and the local structure of vanadium atoms in V_2O_5 during the intercalation and deintercalation of lithium ions during discharge and charge cycles. During the first discharge at 0.1 C, the intensity of the pre-edge peak decreased and shifted to lower energy, indicating a reduction in distortion within the VO_5 square pyramid structure. The K-edge shift to lower energy is aligned with reducing the vanadium oxidation state. During the charging process, the energy and intensity of the pre-edge peak increased, signaling greater distortion and an increase in the oxidation state. Following the first cycle, the VO_5 structure showed slightly reduced distortion and increased oxygen symmetry around vanadium compared to its initial state. XANES results revealed structural reversibility during Li^+ intercalation and deintercalation. However, the observed irreversible capacity loss was attributed to forming the of solid electrolyte interphase (SEI) film.

In this study, XANES analysis was conducted on V_2O_5 to observe changes in the oxidation state of vanadium atoms during Li^+ insertion and extraction, with particular attention to the $[NC41]_m$+V sample, which exhibited significant phase changes in V_2O_5. The first discharge cycle revealed alterations in the XANES spectrum, including a decrease in the pre-edge peak intensity and energy, indicating an increase in local symmetry around vanadium atoms as Li^+ infiltrated V_2O_5. Additionally, a shift of the K-edge to lower energy suggested the reduction of vanadium from V^{5+} to V^{4+}. Conversely, during the initial charge cycle, the spectrum reversed, reflecting an increase in oxidation state as Li^+ ions were removed, thus restoring local structural symmetry. In the second discharge, the XANES data showed similar trends but with reduced distortion in the VO_5 square pyramid and greater symmetry in the local vanadium environment compared to the first cycle. This indicates partial irreversibility due to incomplete SEI layer formation, as residual Li^+ affects later performance. Calculated oxidation states further support these findings, showing a 10.49% reduction during the first discharge and partial re-oxidation during charging. EXAFS analysis of the disordered glass materials underscores the importance of appropriate sample preparation and

analysis techniques to accurately understand the structural and electronic properties of these materials.

The conclusions from the establishment of two research objectives are as follows:

5.1 The ratio of Ni:Co (4:1) resulted in better specific capacity and improved stability.

5.2 Samples with $Li_6B_4O_9$ crystals showed high stability after multiple cycles. Particularly, $[NCV41]_m$ demonstrated outstanding performance with an average capacity of 111.42 mAh/g, energy density of 306.26 mWh/g, and 80.69% capacity retention after 100 cycles, indicating excellent battery durability.