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Structural Evolution and Electrochemical Performance of Vanadate-Based Glass and Glass-Ceramics for Sodium- and Lithium-Ion Batteries

Shiro KUBUKI* and Abdallah ELSHOUORBAGY
Graduate School of Science, Tokyo Metropolitan University,
1-1 Minami-Osawa, Hachioji, Tokyo 192-0397, Japan

1 Introduction

The ongoing transition to sustainable energy systems requires the development of advanced energy storage technologies. Lithium-ion batteries (LIBs) have been widely used; however, concerns about lithium scarcity and cost have spurred interest in alternative systems, such as sodium-ion batteries (SIBs). Sodium's high natural abundance and similar electrochemical behavior make SIBs promising candidates for next-generation storage devices.

Vanadate-based glass and glass-ceramic materials have attracted attention as electrode materials because of their disordered structure, high free volume, and the presence of multivalent vanadium ions, allowing efficient electron hopping and redox reactions. In this report, recent results on yttrium-doped sodium phosphovanadate glass-ceramics and tin oxide-dispersed phosphovanadate glasses are summarized based on synchrotron X-ray absorption fine structure (XAFS) studies performed at the Photon Factory.

2 Experiment

Glass samples with compositions of $15Na_2O–xY_2O_3–(17-x)P_2O_5–59.5V_2O_5–8.5Fe_2O_3$ (x = 1, 3, 5 mol%) and $xP_2O_5–(90-x)V_2O_5–10SnO_2$ (x = 10–60 mol%) were prepared by the melt-quenching method. After preparation, heat treatment was conducted at 500 °C to obtain glass-ceramic samples. Structural characterization was carried out using differential thermal analysis (DTA), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Mössbauer spectroscopy, and electrical impedance measurements. XAFS measurements at the Fe and V K-edges were performed at the Photon Factory to investigate local structure and oxidation states.
Electrochemical performance was evaluated using coin-type cells under various current densities in the voltage range of 0.8–4.0 V.

3 Results and Discussion

3.1 Structural Features

Y_2O_3 doping resulted in a significant structural modification of sodium phosphovanadate glasses. With increasing Y_2O_3 content, the glass transition temperature decreased, indicating reduced thermal stability due to depolymerization of the glass network. FTIR analysis revealed an increase in non-bridging oxygen (NBO), confirming that Y^{3+} acts as a network modifier by breaking P–O–P and V–O–V linkages.

After heat treatment, crystalline phases such as YPO_4, $NaVP_2O_7$, and $Na_{0.282}V_2O_5$ were observed. In particular, $Na_{0.282}V_2O_5$ is known to provide tunnel-like pathways for Na^+ transport, thereby improving electrochemical performance.

In contrast, xPVS glass systems exhibited composition-dependent phase evolution. At low P_2O_5 compositions, SnO_2 nanoparticles were dispersed in the glass matrix, while at higher P_2O_5 concentrations, SnP_2O_7 crystalline phases were formed. This structural transition significantly affected both electrical and electrochemical properties.

3.2 Electronic Structure and Conductivity

XANES and Mössbauer analyses showed that iron exists predominantly in the Fe^{3+} oxidation state with a mixture of tetrahedral and octahedral coordination environments, while vanadium is mainly in the V^{5+} state.
Electrical conductivity measurements indicated that conductivity increases with Y_2O_3 addition and heat treatment. This behavior is attributed to enhanced polaron hopping, driven by increased structural disorder and shorter distances between vanadium sites.

In the xPVS system, the conductivity decreased with increasing P_2O_5 content, as the substitution of V_2O_5 reduced the number of electron carriers available for conduction. The activation energy increased accordingly, reflecting suppressed electron transport.

3.3 Electrochemical Properties

For Y-doped glass-ceramics, the best performance was obtained for AHT-1YPVFN, which exhibited an initial discharge capacity of approximately 210 mAh g^{-1} at low current density. This enhancement is attributed to the increased NBO concentration and the formation of electrochemically active crystalline phases.
However, excessive Y_2O_3 content led to the formation of inactive YPO_4 phases, which reduced electrochemical performance.

In the xPVS system, the 10PVS composition showed the highest performance. As a cathode, it exhibited a large discharge capacity in both LIB and SIB configurations. Additionally, it also showed promising performance as an anode material.

The superior electrochemical performance is attributed to:

- Multi-valence redox reactions of vanadium
- Contribution of Sn-based phases
- Mixed conduction pathways

With increasing P_2O_5 concentration, the capacity decreased due to reduced conductivity and increased structural rigidity.

3.4 Discussion

Both systems demonstrate that structural control of glass and glass-ceramic materials is crucial for improving battery performance. The introduction of dopants such as Y and Sn enables tuning of the glass network, which directly influences ionic transport, electronic conduction, and redox activity.

These results are consistent with previous studies showing that glass-ceramic materials with nanostructured phases and multivalent transition metals are effective electrode materials for post-lithium energy storage systems.

4 Summary

Vanadate-based glass and glass-ceramic materials exhibit excellent potential as electrode materials for sodium- and lithium-ion batteries. Y_2O_3 doping enhances Na^+ transport and conductivity through structural depolymerization, while SnO_2 dispersion enables multifunctional electrochemical behavior. These findings highlight the importance of compositional and structural design of glass systems for developing high-performance energy storage materials.

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References

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* kubuki@tmu.ac.jp