

Structural, Electrical, and Electrochemical Properties of a Na₂O-V₂O₅ Ceramic Nanocomposite as an Active Cathode Material for a Na-Ion Battery

Ahmed IBRAHIM¹, Satoshi WATANABE¹, Marta RAZUM², Luka PAVIĆ², Zoltán HOMONNAY³, Ernő KUZMANN³, Mohamed HASSAAN⁴ and Shiro KUBUKI^{1,*}

¹ Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University, Tokyo 192-0397, Japan

² Division of Materials Chemistry, Ruđer Bošković Institute, 10000 Zagreb, Croatia

³ Institute of Chemistry, Eötvös Loránd University, 1117 Budapest, Hungary

⁴ Physics Department, Faculty of Science, Al-Azhar University, Nasr City, Cairo 11884, Egypt

1 Introduction

Rechargeable sodium-ion batteries (SIBs) would significantly ease and grow the present energy storage industry, primarily based on the lithium-ion battery (LIB) technology [1]. SIBs are a more economical way to LIBs regarding material abundance, allowing their use in high-scale energy storage, such as in smart-grid applications [1]. Among the most common rechargeable batteries (LIBs) used in smartphones and laptops are those with a total capacity of 3861 mAh g⁻¹ [1]. Also, due to the increasing use of Li-ion batteries in the automotive market (vast quantities of lithium are required), SIBs may become the preferred battery for plug-in hybrid electric vehicles (PHEVs), powering hybrid electric vehicles (HEVs) and electric vehicles (EVs) [1]. Nonetheless, the rising costs associated with the rapid increase in demand for lithium and the uneven global distribution of lithium have become a severe problem. Therefore, the development of new secondary batteries is desired. Vanadium oxides and vanadate, such as V₂O₅, NaV₃O₈, and Na_{1.1}V₃O_{7.9}, have been extensively investigated as potential electrode materials due to their favorable characteristics, including high capacity, cost-effectiveness, and abundant availability. Recently, there has been a growing interest in β-Na_{0.33}V₂O₅, distinguished by its robust 3D tunneled structure [2]. This 3D tunneled structure exhibits excellent stability compared to layered structures and suggests an efficient pathway for ion diffusion [2]. Vanadium bronze is predicted to be applied as an active cathode material for secondary batteries because it has high electrical conductivity (10⁰–10¹ S cm⁻¹) and high cycle stability.

In the present work, we studied a relationship between the local structure and electrochemical properties of Na₂O-V₂O₅ ceramics by X-ray diffractometry (XRD), X-ray absorption spectroscopy (XAFS), Cyclic Voltammetry (CV), Electrochemical impedance spectroscopy (EIS), and the charge-discharge capacity test of the SIB.

2 Experiment

The starting reagents of the ceramics system with the composition xNa₂O·(100 - x)V₂O₅ (5 ≤ x ≤ 45 mol%, abbreviated as xNV) were mixed and put into a platinum crucible. The mixtures were melted in an electric muffle furnace at 1200 °C and kept there for one hour. Then, the temperature of the electric furnace decreased to room temperature (RT), with a cooling rate of 10 °C min⁻¹. Raw chemical materials for preparing the ceramics system were Na₂CO₃ (Wako, Osaka, Japan, 199-01585) and V₂O₅ (Wako, Osaka, Japan, 226-00125). Depending on the ratio of Na₂O and V₂O₅ starting materials, various types of sodium vanadate phases are expected to form (even unreacted V₂O₅ in case of insufficient amount of Na₂O). The relatively slow cooling results in microcrystalline composite materials.

3 Results and Discussion

A relationship between the local structure and electrochemical properties of xNV with 'x' from 5 to 45 mol% was investigated. From the XRD results, V₂O₅, Na_{0.33}V₂O₅, NaV₃O₈, and NaVO₃ crystalline phases were observed in xNV. XANES study of xNV showed that the absorption edge of 15NV ceramics is shifted towards the lowest energy side. This shift shows the reduction of V⁵⁺ to V⁴⁺ ions; therefore, V⁴⁺ is the most abundant in Na_{0.33}V₂O₅. The Fourier transform of EXAFS curves showed the micro-environment of vanadium; it is close to that in V₂O₅. Furthermore, the V-O bond length in the first coordination sphere and the V-V length in the second coordination sphere increased and decreased, respectively, with x. In the EIS measurement, the charge transfer resistance increased from 50.3 Ω to 196 Ω during the charge-discharge capacity test in 15NV ceramics. The diffusion coefficient of sodium (*D*_{Na⁺}) decreased from 8.28 × 10⁻¹¹ to 1.23 × 10⁻¹² cm² s⁻¹ with increasing 'x' from 5 to 45 mol% Na₂O. The CV measurement observed a reduction peak near 1.30 V, 1.80 V, and 2.70 V, while it did not show any oxidation peaks; therefore, an irreversible reaction occurred. In addition, precipitation of NaV₂O₅ was observed after the charge-discharge test. So it is considered that the irreversible reaction is a transformation from Na_{0.33}V₂O₅ to NaV₂O₅. The highest discharge

capacity of 203 mAh g⁻¹ was recorded for the 15NV ceramics at the current rate of 50 mA g⁻¹. Finally, we can conclude that the precipitation of vanadium bronze is considered promising for achieving higher capacity for Na-ion batteries.

References

- [1] T. Kim *et al.*, *J. Mater. Chem. A* **7**, 2942 (2019).
[2] A. Ibrahim *et al.*, *Crystals* **13**, 1521 (2023).

*kubuki@tmu.ac.jp