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# $ZnV_2O_4$: A potential anode material for sodium-ion batteries

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ABSTRACT

A template-free solvothermal method was employed to successfully obtain $ZnV_2O_4$ spinel oxide and its electrochemical properties as anode materials for sodium ion battery system were investigated for the first time. The structural, morphological, elemental composition, electrochemical properties and theoretical calculations of the as-prepared $ZnV_2O_4$ were carried out. XRD revealed the presence of ZnO and $VO_2$ impurities when synthesized for 1 day, while complete formation of $ZnV_2O_4$ was attained when the synthesis procedure was increased to 3 days. When cycled at 50 mA/g, it delivered an initial capacity of as high as 537 mAh/g at a potential window of 0.01–3.0 V. Meanwhile, a reversible capacity of ~ 113 mAh/g was obtained when cycled at 100 mA/g for 30 cycles. These results indicate the potential applications of $ZnV_2O_4$ as anode materials for sodium ion battery systems.



## 1. Introduction

Lithium ion batteries (LIBs) have become the front runner for secondary batteries since its commercialization in 1991 due to their high gravimetric and volumetric energy density, long cycle life and no memory effect lithium ion batteries (LIBs) have become the front runner for secondary batteries since its commercialization in 1991 due to their high gravimetric and volumetric energy density, long cycle life and no memory effect [1–9]. LIBs have been extensively developed to power the next generation of electric vehicles (hybrid and plug-in hybrid electric vehicles) and harvesting renewable energy storage sources [8,10–13]. Taking into account the cost and geographical constraints of lithium resources, however, it would be impossible for LIB to meet the growing demands for rechargeable batteries [12,14–17]. Due to these limitations, new rechargeable battery systems using abundant materials [18] such as sodium metal, magnesium, metal air, and metal-sulfur batteries [14] are being considered as alternatives for LIBs. Among these new systems, sodium ion batteries (SIBs) have the highest consideration to replace LIBs owing to its low cost, abundance (being the 4th most abundant element in the Earth's crust) and better safety compared to LIBs [12,14,17,19–21]. However, the ionic radius of Na ion is 55% larger than that of Li ion, which makes it difficult for Na ion to obtain efficient reversible insertion and extraction from the host materials [12]. Therefore, it is very essential to develop new electrode materials that can meet the requirements of Na-ions. Countless studies on SIBs have focused on the advancements of cathode materials while most of the progress on the anode material is limited to non-graphitic carbonaceous compounds (or also known as hard carbon) since their commercialization for LIBs [22]. Hard carbon is given the highest considerations due to their large interlayer distance disorder structure [10,17]. Pyrolized glucose derived hard carbon prepared by Stevens and Dahn delivered a reversible sodium capacity of 300 mAh/g [10,23]. However, non-graphitic carbonaceous compounds suffer from high irreversible capacity loss and low capacity retention [10]. Na-alloying type anodes, such as Sn, Sb, P, Ge and In have also been reported to deliver high reversible capacities [10,24,25]. Howbeit, these materials suffer from large volume change during electrochemical tests which results in electrode pulverization, loss of contact with the current collector, and subsequent capacity fading [24,26].

Transition metal oxides (TMOs) are also popular anode materials for LIBs due to their low cost, natural abundance, hypotoxicity, high theoretical specific capacities (>600 mAh/g), [7,27] and diverse phases which could provide a large variety of possible candidates for SIBs. In intercalating and alloying reactions, metal atoms are reversibly shuttled in and out of a host lattice. On the other hand, conversion reactions (redox of metal species upon

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charge/discharge process) involve the chemical transformation of one or more of the metal species into a host lattice to form a new compound [28,29]. Alcántara et al. initially proposed the application of spinel compound $NiCo_2O_4$ as anode material for SiBs [10,30]. They evaluated full cell SiB using: $Na_xCoO_2$ (cathode), $NiCo_2O_4$ anode and $NaClO_4$ in EC: DMC (electrolyte). When the battery is discharged from 4.1–0 V, it delivered an initial capacity of *ca*. 350 mAh/g and decreased to ~250 mAh/g at 0.2 V after four cycles. These values are generally lower than its Li counterpart, however, it still provided a higher capacity compared to hard and soft carbon-based SIBs. $Fe_3O_4$ nanoparticles developed by Kumar et al. delivered reversible capacity of 248 mAh/g after 50 cycles at 83 mA/g [31]. Jiang et al. developed a series of TMOs including $Fe_2O_3$, NiO, $Co_3O_4$ and $Mn_3O_4$ thin films as anodes for SIBs which were all evaluated at 100 mA/g and delivered reversible capacities of ~385, 100, 350, and 200 mAh/g, respectively for 100 cycles [10].

Vanadium metal typically takes multiform valence states can provide series of metal vanadium based compounds ($A_xV_yB_z$) (A = Co, Cr, Fe, Zn, Mn, Mg, Bi, *etc*., B = O, S or Se) [32]. For instance, in LIB systems, numerous vanadium containing compounds have been studied such as, $CoV_2O_6$ [33], $CuV_2O_6$ [34], $Cu_{2.33}V_4O_{11}$ [35], $FeVO_4$ [32,36] and so forth. Recent studies of the applications of vanadates for SIBs showed favorable results. Krengel et al. recently studied the electrochemical properties of $CuV_2S_4$ and the results revealed a high reversible capacity of 350 mAh/g at 0.7 A/g after 300 cycles with a Coulombic efficiency of ~99% [37]. Furthermore, they also developed $FeV_2S_4$ and applied it for both LIB and SIB systems. Initial discharge capacities for Li and Na—systems are 890 and 723 mAh/g, respectively [38].

The electrochemical performance of $ZnV_2O_4$ has been investigated for supercapacitor, hydrogen storage and anode for LIBs [2,16,39–43]. However, no studies on the applications on SIBs have been published. Apprised by the potential applications of vanadates, the researchers developed and applied $ZnV_2O_4$ as an anode material for SIB system. The crystal structure, morphologies and electrochemical tests were carried out and analyzed in this research. Moreover, ex-situ XRD was carried out on the electrode to further the understanding on the conversions of metals during charge and discharge.

## 2. Experimental

### 2.1. Synthesis and methods

The synthesis of $ZnV_2O_4$ was similar to the procedure performed by Zheng et al. [16], wherein 0.0593 g of zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, 96% Junsei Chemical Co. Ltd.), 0.068 g of ammonium vanadate, ($NH_4VO_3$, 99%, Junsei Chemical Co. Ltd.), 0.03 g of dodecyltrimethylammonium bromide (DTAB, 98%, Tokyo Chemical Co. Ltd.) were mixed in 10 mL ethanol (99%, Wako) under vigorous stirring for 2 h at 50 °C. The mixture was then transferred to a 20 mL Teflon-lined stainless-steel autoclave and kept in a muffle furnace at 200 °C for 1–3 days. The obtained powder was then purified by further dispersion in 40 mL ethanol and water alternately, as it was centrifuged, for 3 times, using 15,000 rpm for 15 min. The obtained product was dried using a vacuum oven at room temperature for 1 h.

### 2.2. Structural and physical characterization

The crystallinity and phase structure of the produced product was characterized using X-ray diffraction (XRD, Rigaku Miniflex II desktop X-ray Diffractometer, Cu K$\alpha$, 1.5418 Å, radiation), while the elemental composition was characterized using X-ray photoelectron spectroscopy (XPS, JEOL Photoelectron Spectrometer (ESCA), JPS-9200, monochromatic Al-K$\alpha$), Zn and V K-edge X-ray absorption near edge spectra (XANES at BL01C1 beam, NSRRC) and Energy Dispersive X-ray Spectroscopy (EDS) equipped with scanning transmission electron microscope (FEI-Titan3 G2-60-300 (300 kV)). The morphology of the produced product, the corresponding elemental mapping, and crystal structure were examined using both scanning electron microscope (SEM, JEOL JSM-6510LA) and Cs-corrected scanning transmission electron microscope (FEI-Titan3 G2-60-300 (300 kV)). For ex-situ XRD characterizations, the batteries were opened after designated charge and discharge voltages inside an Ar-gas filled glove box with $H_2O$ and $O_2$ content < 0.5 ppm. The anode electrodes were carefully collected, washed with dimethyl carbonate (DMC) to remove the electrolyte and were vacuumed overnight to remove excess solvents. The XRD measurements were also collected using X-ray Diffraction (XRD, Rigaku Miniflex II desktop X-ray Diffractometer, Cu K$\alpha$, 1.5418 Å, radiation).

### 2.3. Theoretical calculations

Band structure and density of states for the $ZnV_2O_4$ system were obtained by spin-polarized DFT + U calculations using the CASTEP software [44] at the GGA-PBE level of theory [45] and ultrasoft pseudopotentials. Cell parameters and atomic positions were determined experimentally by Reuter et al. [46], corresponding to *Fd-3m* space group. Experimental lattice parameters of 8.409 Å were maintained while atomic positions were relaxed as the structure was optimized utilizing plane wave basis sets with a cut off energy of 660 eV and $3 \times 3 \times 3$ k-point sampling. The same settings were used for electronic structure calculations with a Hubbard U value of 3.40 eV applied on the 3d orbitals of V atoms, giving band gap values close to that reported experimentally [47]. Convergence tolerances for energy, maximum force, maximum stress, and maximum displacement were $5 \times 10^{-6}$ eV/atom, 0.01 eV/Å, 0.02 GPa, and $5 \times 10^{-4}$ Å, respectively.

### 2.4. Electrochemical tests

The electrochemical performances of the batteries were measured by assembling CR2032 coin cells. A slurry composed of 70 wt.% active material, 15 wt.% Super P (Carbon black, 40 nm), 15 wt.% polyvinylidene fluoride (PVdF, $MW = 1 \times 10^6$ Da) were coated onto 10 µm copper foil which was used as the working electrode of the half-cell battery. The samples were punched (14 mm) and dried at 120 °C for 8 h in vacuum system to remove the residual water. The batteries were assembled in an Ar-gas filled glove box with $H_2O$ and $O_2$ content < 0.5 ppm using sodium disks as the counter electrode, $NaClO_4$ in ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 in volume ratio) and glass fiber filter disks as separators. The discharge/charge tests were analyzed using AcuTech System in the voltage range of 0.01 V and 3.0 V at room temperature and constant voltage charge process. The mass loading of these samples is in the range of $2.50 \pm 0.50$ mg/cm$^2$. The cyclic voltammograms (CV) were measured by CH instruments analyzer CHI 6273E at a scan rate of 0.1 mV/s between 0.01 V and 3.0 V. Meanwhile, the electrochemical impedance of the samples was tested in the frequency range from 0.01 to 100,000 Hz. For ex-situ evaluations, KS6 was introduced into the slurry solution in order to clearly identify the diffraction peaks at different depths of charge/discharge. The electrodes were opened inside an Ar-filled glove box with $H_2O$ and $O_2$ content < 0.5 ppm and were washed thoroughly with dimethyl carbonate (DMC) to remove excess electrolytes and were dried inside the vacuum chamber overnight to prevent oxidation. The electrodes were mailed to Japan and the XRD ex-situ analysis was carried out in there. The prolonged exposure in air caused the Cu foil to be oxidized which was evident in the ex-situ XRD.

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