SYNTHESIS OF NASICON BASED $(Na_3V_{2-x}Mo_x(PO_4)_3/C)$ AS HIGH CAPACITY AND STABLE CYCLING CATHODE MATERIALS FOR SODIUM-ION BATTERIES

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DOCTOR OF PHILOSOPHY
(PHYSICS)

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ABSTRACT

Sodium-ion batteries are techno-economically viable as a complement to the lithium-ion battery market segment. Among its kind, NASICON-structured $Na_3V_2(PO_4)_3$/C offers improved Na^+ insertion-extraction retention over high capacity, however, suffered from deterioration of cycle life and reduction of capacity retention. Establishment of the novel stoichiometric cathode by rejuvenating the interoperable parameters of calcination temperature and Mo^{6+} substitution on $Na_3V_2(PO_4)_3$/C physicochemical performance is presented. Series of $Na_3V_{2-x}Mo_x(PO_4)_3$/C ($0 \leq x \leq 1$) were synthesized by the self-catalysed sol-gel route have been investigated via experimental work and Density Functional Theory (DFT) simulation, to resolve these issues. Thermal Gravimetric Analyzer (TGA) designed optimum heat treatment procedure while X-ray Diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS), and Fourier Transform Infrared (FTIR) results confirmed the Mo^{6+} partial replacement on the V^{3+} site lattice resulting in significant electrochemical enhancement exhibited by Charge-Discharge (CD), Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) profile. $Na_3V_{1.7}Mo_{0.3}(PO_4)_3$/C demonstrates the highest specific capacity of 122 mAh g^{-1} at 0.2C current rate. Two potential discharged plateaus are observed at 3.4 V and 1.6 V (vs. Na^+/Na), corresponding to the V^{3+}/V^{4+} and V^{2+}/V^{3+} redox couple's activities respectively. Varied Mo^{6+} substitutions in $Na_3V_2(PO_4)_3$/C crystalline structure indicate variations in d-spacing and lattice parameter values. Interestingly, $Na_3V_1Mo_1(PO_4)_3$/C corresponds to the highest Mo^{6+} concentration exhibits an extended voltage plateau in the low voltage region at 1.6 V which is promising as an anodic electrode for Na-ion batteries.

ABSTRAK

Bateri ion-sodium secara tekno-ekonomi berdaya maju sebagai pelengkap segmen pasaran bateri ion-litium. Dikalangan jenisnya, $Na_3V_2(PO_4)_3/C$ berstruktur NASICON menawarkan daya kekal penyisipan-pengekstrakan Na^+ yang lebih baik terhadap kapasiti tinggi, namun mengalami kemerosotan hayat kitaran dan pengurangan kapasiti kekal. Pembangunan stoikiometrik katod baru dengan menjajarkan semula parameter saling operasi suhu kalsinasi dan substitusi Mo^{6+} terhadap prestasi fizikokimia $Na_3V_2(PO_4)_3/C$ telah dibentangkan. Siri $Na_3V_{2-x}Mo_x(PO_4)_3/C$ ($0 \leq x \leq 1$) disintesis melalui proses sol-gel katalis spontan dikaji melalui eksperimental dan simulasi Teori Fungsi Kepadatan (DFT) untuk menguraikan permasalahan ini. Analisa Gravimatrik Terma (TGA) merekabentuk prosedur rawatan haba optimum sementara Pembelau X-ray (XRD), Spektroskopi Fotoelektron X-ray (XPS), dan Inframerah Transformasi Fourier (FTIR) mengesahkan substitusi Mo^{6+} terjadi pada kekisi V^{3+} menghasilkan peningkatan elektrokimia signifikan berdasarkan profil Cas-Nyahcas (CD), Voltammetri Kitaran (CV) dan Spektroskopi Impeden Elektrokimia (EIS). $Na_3V_{1.7}Mo_{0.3}(PO_4)_3/C$ menunjukkan kapasiti spesifik tertinggi iaitu 122 mAh g^{-1} pada beban arus 0.2 C. Dua dataran voltan nyahcas diperhatikan pada 3.4 V dan 1.6 V (terhadap Na^+/Na), menepati aktiviti pasangan redoks V^{3+}/V^{4+} dan V^{2+}/V^{3+}. Substitusi Mo^{6+} yang berbeza dalam struktur kristal $Na_3V_2(PO_4)_3/C$ menunjukkan variasi pada nilai parameter jarak-d dan parameter kekisi. Menariknya, $Na_3V_1Mo_1(PO_4)_3/C$ yang berpadanan dengan kepekatan Mo^{6+} tertinggi memperlihatkan lanjutan dataran voltan di kawasan voltan rendah pada 1.6 V yang menjanjikan potensi sebagai elektrod anodik untuk bateri ion-sodium.

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APPROVAL

The Examination Committee has met on **16 November 2021** to conduct the final examination of **Mohamad Firdaus bin Rosle** on his degree thesis entitled **'Synthesis of NASICON Based ($Na_3V_{2-x}Mo_x(PO_4)_3$/C) as High Capacity and Stable Cycling Cathode Materials for Sodium-ion Batteries.**

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LIST OF ABBREVIATIONS

LIBs	-	Lithium-Ion Batteries
SIBs	-	Sodium-Ion Batteries
NASICON	-	Sodium Super Ionic Conductor
DFT	-	Density Functional Theory
CASTEP	-	Cambridge Serial Total Energy Package
BESS	-	Battery Energy Storage System
TGA	-	Thermo-Gravimetric Analysis
XRD	-	X-Ray Diffraction
BET	-	Brunauer-Emmet-Teller
FTIR	-	Fourier Transform Infrared
XPS	-	X-ray Photoelectron Spectroscopy
SEM	-	Scanning electron microscope
BJH	-	Barret-Joyner-Halenda
EDX	-	Energy-Dispersive X-ray
CD	-	Charge-Discharge
CV	-	Cyclic Voltammetry
DOS	-	Density of State
EIS	-	Electrochemical Impedance Spectroscopy
EEC	-	Equivalent Electrical Circuit
IUPAC	-	International Union of Pure and Applied Chemistry

LIST OF SYMBOLS

I	-	Current
V	-	Voltage
R_{el}	-	Electrolyte resistance
R_{ct}	-	Charge transfer resistance
R_{sl}	-	Surface layer resistance
CPE	-	Capacitive constant phase element
W	-	Warburg diffusion
Q	-	Charge
P	-	Pressure
C	-	Current rate
r	-	Radius
X_m	-	Electronegativity value
θ	-	Incident angle
d	-	Inter-planar spacing
λ	-	Wavelength of X-ray
E_{be}	-	Binding energy
hv	-	Shift in photon energy
σ	-	Warburg coefficient
Z’	-	Real Impedance

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CHAPTER 1

INTRODUCTION

1.1 Background

The growing demand for high-capacity energy and power storage, fuelled by the urgent needs of contemporary electronic gadgets and the electric vehicle industry, has resulted in a recent surge in sales of rechargeable lithium-ion batteries. Since its commercial establishment in the early 1990s pioneering by Sony, rechargeable lithium-ion batteries have dominated the energy storage market under which had seized out the lead-acid, nickel-cadmium, and nickel-metal-hydrate as the previous nomination technology of choice. Lithium-ion batteries are notable for their large electrochemical potential, high gravimetric and volumetric energy density, low self-discharging rate, and excellent storage characteristic. Despite those significant key features, massive production of lithium-ion batteries had increased the global market anxiety towards the imminent exhaustion of lithium resources consequently to the arising of lithium precursor global price.

The new pace of change in large-scale smart grid technology developments remarkably required a large-scale energy storage system. Therefore, economic cost reduction and renewable resources are twofold concerns required to manage optimum