Titanium and Vanadium based Bimetallic Prussian Blue Analogue as a Cathode Material for Sodium Ion Batteries

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MASTER OF SCIENCE

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SUPERVISOR’s DECLARATION

I hereby declare that I have checked this thesis and, in my opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Master of Science.

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STUDENT’S DECLARATION

I hereby declare that the work in this thesis is based on my original work except for quotations and citations, which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at Universiti Malaysia Pahang Al-Sultan Abdullah or any other institutions.

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ABSTRAK

Peningkatan terhadap pengunaan sumber tenaga boleh diperbaharui gantian menyebabkan permintaan meningkat terhadap sistem penyimpanan tenaga yang stabil dan mudah didapati. Terkini, tahap prestasi bateri ion natrium (SIB) telah mengatasi prestasi bateri ion litium (LIB). Namun, SIB masih menghadapi beberapa cabaran besar yang berkait dengan bahan katod, seperti ketumpatan tenaga terhad, kegagalan struktur dan kestabilan kitaran. Disebabkan cabaran itu, proses penskalaan dan pengkomersialan SIB menghadapi kesukaran. Reka bentuk bahan katod adalah pendekatan yang mudah untuk meningkatkan kecekapan SIB secara keseluruhannya. Objektif utama penyelidikan ini adalah untuk menyiasat bagaimana perbezaan kepekatan dopan dalam sampel bahan katod memberi kesan kepada prestasi elektrokimianya; khususnya dari segi kapasiti dan kestabilan semasa kitaran cas-nyahcas. Untuk mencapai tujuan ini, penyediaan pelbagai sampel natrium titanium vanadium hexacyanoferrate dengan nisbah titanium dan vanadium yang berbeza-beza Ti: V iaitu 1:1, 3:7, 4:6, 6:4 dan 7:3 telah dihasilkan. Pencirian struktur and komposisi bahan katod dicirikan oleh XRD, FESEM-EDX, BET dan FT-IR. Pencirian XRD menunjukkan puncak mewakili PBA dan natrium yang jelas pada 17° dan 31°. Fungsi bahan juga telah disahkan dengan pencirian FT-IR yang menunjukkan ikatan regangan C=C pada 1634 cm-1 yang kuat dan ikatan pada 961 cm-1 mewakili ikatan lentur C+C yang kuat. Puncak luas pada 3500cm-1 mewakili kehadiran ikatan O-H yang kuat. Purata saiz liang dalam julat 40-70 nm telah dicapai pada ujian BET. Perbandingan secara keseluruhan semua bahana, menunjukkan bahawa sampel dengan nish=bah 1:1 menunjukkan morfologi, difraksi dan saiz liang yang lebih baik. Prestasi elektrokimia dianalisis dengan ujian kitaran voltammetri (CV) dan ujian nyahcas galvanostatic (GCD). Cv menunjukkan puncak redoks yang jelas pada 3.25 V, mewakili sifat redoks sampel semasa kitaran cas-nyahcas dalam SIB. Plot analisis GCD juga telah dilakukan, menunjukkan lengkung cas-nyahcas dicapai dalam tetingkap potensi 1.5 V – 4.5 V untuk semua sampel. Nilai kapasiti khusus juga dikira untuk semua analisis. Untuk menilai kestabilan kitaran bahan katod, kitaran cas-nyahcas jangka panjang dijalankna untuk jangka masa 50 kitaran. Daripada semua analisis yang dilakukan, dapat disimpulkan bahawa sampel dengan nisbah 1:1 memberikan prestasi keseluruhan yang terbaik berbanding yang lain.

ABSTRACT

The growing need for alternative and renewable energy sources has led to a higher need for robust and readily available energy storage solutions. So far, the sodium ion battery (SIB) has demonstrated superior performance compared to lithium-ion batteries. However, it still faces challenges related to the cathode materials, such as limited energy density, structural integrity issues, and cycle stability concerns. As a result of these challenges, the process of scaling up and commercialization of sodium ion batteries is currently facing difficulties. The designing of cathode material is a straightforward approach to enhance the overall efficiency of the sodium ion battery. The main objective of this research is to investigate how varying concentrations of dopants in the cathode sample impact its electrochemical performance, specifically in terms of its specific capacity and stability during the charge-discharge cycle. For this purpose, this study aimed to prepare various samples of sodium titanium vanadium hexacyanoferrate with varying ratios of titanium and vanadium with ratios of 1:1, 3:7, 4:6, 6:4, and 7:3 were produced. These samples were first characterized by XRD, FESEM-EDX, BET, and FTIR to analyse the structural and compositional details of all the prepared cathode materials. The FESEM-EDX showed cubic shaped consistent all the samples which matches best with its XRD as well in which clear peaks of PBA and sodium were observed at 17^{o} and 31^{o} respectively. The functionality of the materials was confirmed by the identification bands in FTIR at 1634 cm^{-1} represents the strong C=C stretching bond and the bond at 961 cm^{-1} represents the strong C=C bending bond. The broad peak at 3500 cm^{-1} represents the presence of strong O-H bond. Average pore size in the range of 40-70 nm was achieved on BET testing. An overall comparison of all the materials shows that Ti:V 1:1 showed better morphology and diffraction pattern with good pore size. The electrochemical performance was analysed by cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) testing. The CV showed clear and promising redox peaks at 3.25 V which supports the redox behaviour of the prepared samples during charge-discharge cycles in SIB set-up. The same was further confirmed by GCD plots where charging and discharging curves are achieved in relevant potential window of 1.5-4.5 V for all the prepared and tested samples. The specific capacity was also calculated for all the scan rates. To evaluate the cyclic stability of the cathode material, the long-term charge discharge cycles were run for a span of 50 cycles. From all the analyses done, it can be concluded that the sample with ratio 1:1 giving the best overall performance compared to the others.

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