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Electrochemical Behavior of Li+, Na+ and K+ Ion Electrolyte in Na0.33V2O5 Symmetric Pseudocapacitor with High-Performance and Extremely High Cyclic Stability

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Publication Details

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Abstract
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Electrochemical Behavior of Li\(^+\), Na\(^+\) and K\(^+\) Ion Electrolyte in Na\(_{0.33}\)V\(_2\)O\(_5\) Symmetric Pseudocapacitor with High-Performance and Extremely High Cyclic Stability

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ABSTRACT

A high performance symmetric supercapacitor was fabricated using Na$_{0.33}$V$_2$O$_5$ nanocomposite synthesized via a simple co-precipitation technique. The structural and morphological investigation showed that the synthesized Na$_{0.33}$V$_2$O$_5$ nanocomposite exhibited a monoclinic structure with nanorod like morphology. The electrochemical properties of the Na$_{0.33}$V$_2$O$_5$ symmetric supercapacitor was studied utilizing three different aqueous electrolytes such as 1M of LiCl, NaCl and KCl respectively. Interestingly, the fabricated Na$_{0.33}$V$_2$O$_5$ symmetric supercapacitors exhibited excellent electrochemical capacitance behavior in all the electrolytes with a maximum specific capacitance value of 168 F g$^{-1}$ in 1M LiCl, 146 F g$^{-1}$ in 1M NaCl and 132 F g$^{-1}$ in 1M KCl electrolytes at 0.5 A g$^{-1}$ discharge current density. In addition, Na$_{0.33}$V$_2$O$_5$ symmetric supercapacitors demonstrated an excellent cyclic stability especially in 1M NaCl electrolyte with high capacitance retention of ~81% after 50,000 charge/discharge cycles.

KEYWORDS: Co-precipitation; Na$_{0.33}$V$_2$O$_5$; symmetric supercapacitor; pseudocapacitor; nanorod.
1. INTRODUCTION

Supercapacitors (SCs) or electrochemical capacitors (ECs) exhibits high power density, long cyclic stability and easily charge/dischargeable when compared with other energy storage devices such as secondary cells, fuel cells, lithium-ion batteries etc.\[^1\] Based on the energy storage mechanism, SCs are classified into two types namely electric double-layered capacitor (EDLC) and pseudocapacitors \[^2\]. Whereas, the electric double layer capacitors exhibit low energy density compared to the pseudocapacitors. \[^3\] Since in pseudocapacitors, the capacitance mainly originates from the strong reversible redox (faradaic) reactions take place at electrode/electrolyte interfaces.\[^4\] Hence, there is a considerable interest in development of pseudocapacitor materials specially to enhance the specific capacitance and energy density of supercapacitors. The transition-metal oxides and conducting polymers are normally used as pseudocapacitor electrode materials. \[^5\] Among these, the transition-metal oxides such as RuO\(_2\) \[^6\], MnO\(_2\) \[^7\], Co\(_2\)O\(_4\) \[^8-9\], NiO \[^10-11\], IrO\(_2\) \[^12\] and V\(_2\)O\(_5\) \[^13\] have higher capacity than the carbon based EDLCs or even conducting polymer pseudocapacitors due to the existence of their unique redox mechanism. Thus, series of transition metal oxides have been potentially studied as the electrode materials for pseudocapacitors.\[^14\] Among them, RuO\(_2\) exhibits high specific capacitance, reversible charge/discharge features and good electrical conductivity.\[^15\] However, its lesser abundance, expense, and toxic nature limited its commercial use, so there is a demand in exploring novel metal oxide nanomaterials for supercapacitor electrodes. Recently, various alternative metal oxides have been explored with an efficient strategy by combining one or two metal ions to form multi-metal oxide complexes,\[^16\] such as Zn\(_3\)V\(_2\)O\(_8\),\[^17\] CuV\(_2\)O\(_6\),\[^18\] MnV\(_2\)O\(_6\),\[^19\] Ni\(_3\)(VO\(_4\))\(_2\),\[^20\] Co\(_3\)V\(_2\)O\(_8\),\[^21\]
ZnV$_2$O$_4$,$^{[22]}$ AlV$_3$O$_9$,$^{[23]}$ NiCo$_2$O$_4$,$^{[24]}$ ZnCo$_2$O$_4$,$^{[25]}$ CoMoO$_4$,$^{[26]}$ NiMoO$_4$,$^{[27]}$ and Na$_{0.33}$V$_2$O$_5$,$^{[28]}$ etc. The binary metal oxide Na$_{0.33}$V$_2$O$_5$ is an interesting cost effective system$^{[29]}$ and can be easily synthesized via simple and inexpensive chemical techniques. Moreover, it acquires promising properties than its parent vanadium oxide (V$_2$O$_5$), which is one among the pseudocapacitive metal oxide benefits in aqueous supercapacitors due to its excellent structural aspects that appropriate for the different cationic (Li$^+$, Na$^+$, K$^+$) intercalation/deintercalation reactions. In addition, Na$_{0.33}$V$_2$O$_5$ has several advantages like good conductivity, low cost, natural abundance, good structure stability, high electrochemical performances and existence of multiple oxidation states (V$^{2+}$, V$^{3+}$, V$^{4+}$ and V$^{5+}$) makes feasible to use as the electrodes for supercapacitor.$^{[30]}$

Based on the cell configuration and design, the supercapacitor is further classified into asymmetric and symmetric supercapacitors. Asymmetric supercapacitors are fabricated with the combination of two non-identical or dissimilar electrode materials as cathode and anode. As the name denotes, the symmetric supercapacitors are fabricated with cathode and anode of identical or similar electrode material.$^{[31]}$ Among these, the symmetric supercapacitors possess more advantage than asymmetric device in terms of safety, longer stability, and capacity of charging in both directions.$^{[32]}$ Generally, the carbon base symmetric supercapacitors have been well established and commercially available for various energy storage applications.$^{[33-34]}$ So, the research direction has been focus on the development of metal oxide based symmetric supercapacitors owing to its high energy density and better specific capacitance nature. However, it is a challenge to fabricate a metal oxide based symmetric supercapacitor with comparable specific capacitances and stability than that of EDLCs.
Apart from the device configuration and electrode material, the electrolyte is one of the crucial component for driving supercapacitors. Generally, the electrolytes are classified into aqueous and non-aqueous systems. The advantage of non-aqueous system is, it can operate in a wide range of potential window than that of the aqueous electrolytes. However, they suffer from drawbacks like high viscosity, poor electrical conductivity, high equivalent series resistance (ESR), volatile and toxic nature. These drawbacks can effectively limits the electrochemical performance of the metal oxide based SCs.\cite{30} In other hand, the aqueous electrolytes are inexpensive and can be easily handled in the laboratory without any special precaution; therefore it greatly simplifies the fabrication and processing of devices. Normally, the aqueous electrolyte is mainly an acid or alkaline or a neutral solution such as H$_2$SO$_4$, KOH and LiCl (or KCl or NaCl) etc. In recent past, various neutral electrolytes with different cationic species such as Li$^+$, Na$^+$ and K$^+$ were explored for the development of supercapacitors. \cite{35} Since, the size of the cation, the mobility of the cation and the adsorption/desorption rate of electrolytes can also possesses serious role in the charge storage process across the electrolyte/electrode interfaces.\cite{36-37}

In this work, for the first time we report the fabrication of Na$_{0.33}$V$_2$O$_5$ // Na$_{0.33}$V$_2$O$_5$ symmetric supercapacitor device and the performances were tested in various aqueous electrolytes. The Na$_{0.33}$V$_2$O$_5$ // Na$_{0.33}$V$_2$O$_5$ device exhibited a comparable or even high specific capacitance with excellent capacity retention and good reversibility in all tested electrolytes (Li$^+$, Na$^+$ and K$^+$ respectively). Moreover, the device displayed high specific capacitance values of 168 F g$^{-1}$ in 1M LiCl, 146 F g$^{-1}$ in 1M NaCl and 132 F g$^{-1}$ in 1M KCl electrolytes respectively, which are comparatively higher values than the most recently report metal oxide//metal oxide based symmetric supercapacitors. Further, the work was elaborated utilizing electrochemical
impedance spectroscopy to investigate the electrochemical performance of the device in various electrolytes.

2. Results and Discussion

2.1 Structural analysis

2.1.1 X-ray diffraction and Raman spectrum
**Figure 1.** (a) XRD pattern and, (b) Raman spectrum of Na$_{0.33}$V$_2$O$_5$ sample

The XRD pattern of the as-prepared Na$_{0.33}$V$_2$O$_5$ sample is shown in Figure 1(a). The characteristic peaks at 9.31°, 24.58°, 32.88°, 41.5° and 50.67° are assigned to the (100), (004), (21-3), (106) and (31-7) planes of monoclinic Na$_{0.33}$V$_2$O$_5$ crystal structure (space group: A2/m (12), a=10.08 Å, b=3.60 Å, c=15.36 Å and β=109.411°; JCPDS card no. 48-0382). The resultant diffraction pattern displays a pure phase of Na$_{0.33}$V$_2$O$_5$ crystal structure without any involvement of detectable impurities or secondary phases, representing the phase purity of the synthesized sample.$^{[28-38]}$

2.1.2 Raman spectroscopy

Raman spectrum was recorded in the wavelength range between 100 to 1000 cm$^{-1}$ in order to study the vibrational aspects of V$_2$O$_5$ groups present in the nanostructure. Figure 1(b) shows the obtained Raman spectrum of the Na$_{0.33}$V$_2$O$_5$ sample. The spectrum possesses five characteristic peaks of V$_2$O$_5$ vibrations at 143, 189, 278 and 521 cm$^{-1}$ respectively. The low-wavenumber peaks at 143 and 189 cm$^{-1}$ corresponds the external [VO$_5$]-[VO$_5$] modes.$^{[39]}$ The bending vibration of the V=O bonds arise at 278 cm$^{-1}$. The mode observed at 530 cm$^{-1}$ represents the stretching vibration of triply coordinated oxygen bonds (V$_3$-O).$^{[41]}$

2.2 Surface and morphological analysis

2.2.1 TEM analysis
**Figure 2.** TEM images (a) low, (b) higher magnifications; (c) and (d) HRTEM images of the Na$_{0.33}$V$_2$O$_5$ sample.

**Figure 2** (a), (b), (c) and (d) show the transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images of Na$_{0.33}$V$_2$O$_5$ sample. TEM images of the sample (Fig 2(a) and (b)) clearly depict that the agglomerated nanoparticle comprises of irregular nanorods with length ranges from ~ 50-200 nm and ~ 10-25 nm in width. Further magnified view of the nanorods revealed a self-assembly of some primary nanorods attached along with others to form almost a closed network. The
HRTEM images clearly show the lattice fringes of the crystalline sample (Figure 2c and d) and the highlighted prominent fringe width of ~0.95 nm corresponds to the (100) crystal plane of the monoclinic Na$_{0.33}$V$_2$O$_5$ phase (JCPDS card no. 48-0382), which is in good agreement with the previous report.$^{[28]}$

2.2.2 X-ray photoelectron spectroscopy (XPS)

![XPS spectra](image)

**Figure 3.** (a) XPS survey spectrum, (b), (c) and (d) high-resolution XPS spectrum of the V 2p, Na 1s and O 1s region of the Na$_{0.33}$V$_2$O$_5$ nanorods.

The X-ray photoelectron spectroscopy (XPS) measurement was carried out to investigate the purity, binding energy and the valence state of synthesized Na$_{0.33}$V$_2$O$_5$ sample. **Figure**
3(a) shows the broad scan survey spectrum of Na$_{0.33}$V$_2$O$_5$ nanorods, which displays the presence of V 2s, V 2p, O 1s and Na 1s states. The deconvolution of V 2p XPS peak was carried out to clearly detect the oxidation states of vanadium atom as shown in Figure 3(b). The spectrum of Na$_{0.33}$V$_2$O$_5$ displays that the V 2p$_{3/2}$ contains of two overlapping peaks, i.e. the peak binding energy (BE) at 516.4 eV is due to V$^{5+}$ ions, and other position 515.6 eV corresponds to the V$^{4+}$ ions$^{[42]}$ and these deconvoluted components, V 2p$_{3/2}$ (IV) and V 2p$_{3/2}$ (V) confirming the mixed valences state of vanadium oxide.$^{[43]}$ Similarly, the split spin-orbit component V2p$_{1/2}$ was fitted into two peaks at 524.6 and 522.5 eV, corresponding to the contribution of V$^{5+}$ 2p$_{1/2}$ and V$^{4+}$ 2p$_{1/2}$, respectively. The fitted curve of V$^{4+}$2p$_{3/2}$ and V$^{4+}$ 2p$_{1/2}$ (515.6 and 522.5 eV) show low intensity peaks reveal that the samples possesses a certain amount of V$^{4+}$ ions along with V$^{5+}$ ions.$^{[44]}$ The atomic ratio of V$^{4+}$/V$^{5+}$ was calculated from the peak area is close to 1:5, which is well matches with the formula of Na$_{0.33}$V$_2$O$_5$.$^{[42]}$ Figure 3(c) shows the magnified portion of the peak located at 1071.05 eV is assigned to Na 1s state, confirming that the Na atoms occupying the lattice positions along the b axis of Na$_{0.33}$V$_2$O$_5$.$^{[45]}$ Furthermore, the O1s XPS peak (~530 eV) was fitted with two components (Figure 3(d)). The first intense peak at 529.9 eV corresponds to O 1s state, which is associated to the metal-oxide (V-O) bonding and the second peak at 531.4 eV which corresponds to OH group (V-OH) present in the Na$_{0.33}$V$_2$O$_5$ phase.$^{[46]}$

Furthermore, the energy dispersive X-ray spectroscopy (EDX) was recorded to approximately quantify the composition of the sample. The resultant EDX spectrum of the Na$_{0.33}$V$_2$O$_5$ nanostructure is shown in Figure S2. The spectrum confirms the presence of vanadium, sodium
and oxygen atoms in the synthesized Na$_{0.33}$V$_2$O$_5$ nanomaterial with 4.52% of Na, 52% of V and 41.16% of O atoms respectively.

2.3 Electrochemical studies

2.3.1 Cyclic voltammetry measurements

Figure 4. (a) CV curves of Na$_{0.33}$V$_2$O$_5$ symmetric supercapacitors measured at 25 mV s$^{-1}$, and (b) variation of specific capacitance values of Na$_{0.33}$V$_2$O$_5$ symmetric supercapacitors with different scan rates (5 to 100 mV s$^{-1}$) in 1M LiCl, 1M NaCl and 1M KCl electrolytes, (c) Peak current versus square root of scan rate plot for LiCl, NaCl and KCl electrolytes.

Figure 4(a) shows the cyclic voltammetry (CV) curves of Na$_{0.33}$V$_2$O$_5$ symmetric supercapacitor in LiCl, NaCl and KCl electrolytes at 25 mV s$^{-1}$ scan rates. The CV plots of LiCl, NaCl and KCl
electrolytes were quite similar with nearly a pronounced rectangular shape, with slightly broad redox peaks in the applied range of potential, representing good pseudocapacitive nature of the electrodes in all four electrolytes. The possible redox reaction takes place in the electrode surface is shown in Equation (1).

\[
\text{Na}_{0.33}\text{V}_2\text{O}_5 + x\text{M}^+ + xe^- \Leftrightarrow \text{M}_x\text{Na}_{0.33}\text{V}_2\text{O}_5
\]

(1)

where, (\(\text{M}^+ = \text{Li}^+, \text{Na}^+ \text{ (or) K}^+\))

From the CV curves, the supercapacitors in LiCl electrolyte showed slightly higher background current than that of NaCl and KCl electrolytes representing a pronounced capacitive behavior of the materials in LiCl electrolyte. Figure 4(b) shows the variation of specific capacitance of the devices with various scan rates, obviously the device with LiCl electrolyte shows slightly higher specific capacitance values of 171, 145, 106, 68 and 49 F g\(^{-1}\) for all low scan rates. At the same time, NaCl shows 148, 123, 95, 76 and 65 and KCl electrolyte displays 124, 110, 84, 66 and 56 at 5, 10, 25, 50 and 100 mV s\(^{-1}\) scan rates. These clearly displays that the process of intercalation/deintercalation reaction during CV cycles mainly depends upon the basic parameters such as charge, ion size and charge density of the cations present in the electrolyte. From the above electrolytes, the estimated bare cationic size of electrolytes in the order of Li\(^+\) (0.60 Å) < Na\(^+\) (0.95 Å) < K\(^+\) (1.33 Å). Even though the symmetric supercapacitors show comparable capacitance behavior in all electrolytes, but the considerable enhancement of specific capacitance in LiCl can be mainly attributed to the size of cation. Since, the intercalation/deintercalation reactions of smaller Li\(^+\) ion in the Na\(_{0.33}\)V\(_2\)O\(_5\) electrode surface slightly easier than that of bigger Na\(^+\) and K\(^+\) ions\([36]\). Thus, the obtained specific capacitance values decrease in the order of Li\(^+\) > Na\(^+\) > K\(^+\) for Na\(_{0.33}\)V\(_2\)O\(_5\) based symmetric supercapacitors. The CV curves of Na\(_{0.33}\)V\(_2\)O\(_5\) symmetric devices measured for various scan rates (5, 10, 25, 50
and 100 mV s$^{-1}$) in different electrolytes (LiCl, NaCl and KCl) are shown in **Figure S3** (a, b and c). The area of CV curves raise with respect to increase in scan rates, which attributes the higher charge storage capability of the electrode material.$^{[48]}$ However, the specific capacitance decreases with increase in scan rate, since at higher scan rate, only outer surface of electro active material involves in the intercalation/deintercalation reactions. But at lower scan rates, the rate of cation (Li$^+$ or Na$^+$ or K$^+$) intercalation is possible even into bulk of the electrode material$^{[49]}$ and shows an increase in specific capacitance of the device. **Figure 5**(c), shows the variation of the peak current vs square root of scan rate for Na$_{0.33}$V$_2$O$_5$ symmetric device in different electrolytes. The resultant plots show a linear dependency of peak current with respect to the root of scan rates with R value $\sim$0.99 representing the diffusion controlled characteristics of the redox reaction.$^{[50]}$ The peak current follows the Randles–Sevcik equation$^{[50a,51]}$

$$I_p = (2.687 \times 10^5)n^{3/2}ACD^{1/2}v^{1/2}$$  \hspace{1cm} (2)

where $n$ is the number of electrons transferred in the redox reaction, $A$ is the effective electrode area in cm$^2$, $C$ is concentration in mol cm$^{-3}$, $D$ is the diffusion coefficient in cm$^2$ s$^{-1}$ and $v$ is the scan rate. Using the above equation, diffusion coefficient was calculated for the electrolytes in Na$_{0.33}$V$_2$O$_5$ symmetric device are $6.54 \times 10^{-7}$ cm$^2$ s$^{-1}$, $5.889 \times 10^{-7}$ cm$^2$ s$^{-1}$ and $2.4121 \times 10^{-7}$ cm$^2$ s$^{-1}$ decreases in the order LiCl $>$ NaCl $>$ KCl. The above result confirms that the Li$^+$ ion have slightly favorable diffusion property in the Na$_{0.33}$V$_2$O$_5$ electrode than Na$^+$ and K$^+$ ions.
2.3.2 Galvanostatic charge/discharge test

![Galvanostatic charge/discharge curves](image)

**Figure 5.** (a) Galvanostatic charge/discharge (GCD) curves for Na$_{0.33}$V$_2$O$_5$ symmetric supercapacitor at 0.5 A g$^{-1}$, (b) Relationship between the specific capacitances and discharge current densities of Na$_{0.33}$V$_2$O$_5$ symmetric supercapacitor (c) Ragone plots related to energy and power densities of Na$_{0.33}$V$_2$O$_5$ symmetric supercapacitor in LiCl, NaCl and KCl electrolytes.

The galvanostatic charge/discharge (GCD) measurement is a consistent method to evaluate the electrochemical specific capacitance values of electrode materials under controlled current densities.$^{[52]}$ **Figure 5(a)** shows the resultant GCD curves of Na$_{0.33}$V$_2$O$_5$ symmetric supercapacitor in LiCl, NaCl and KCl electrolytes at 0.5 A g$^{-1}$. The
The shape of the charge/discharge curves show nearly symmetric nature, which indicates the excellent electrochemical reversibility and capacitive performance of Na$_{0.33}$V$_2$O$_5$ electrodes.\cite{53} The slope variation of GCD curves with respect to the time dependence of potential indicates the pseudo-capacitive charge storage nature of the electrode due to the electrochemical charge intercalation/deintercalation process occurs at the electrode/electrolyte interfaces.\cite{54-55} Figure 5(b) shows the variation of specific capacitance values with different current densities (0.5, 1, 2.5, 5, 7.5, 10, 12.5, 15 and 20 A g$^{-1}$) in LiCl, NaCl and KCl electrolytes. The symmetric cells show maximum specific capacitance of 168, 146 and 132 F g$^{-1}$ at 0.5 A g$^{-1}$ in LiCl, NaCl and KCl electrolytes respectively. The above trends and performance in various electrolytes are consistent with those observed in the CV analysis. Thus, the charging/discharging rate of the Na$_{0.33}$V$_2$O$_5$ symmetric supercapacitor is affected by the cation species such as ion size, mobility, cation concentration and the adsorption/desorption rates.\cite{37} Figure S4. (a, b and c), displays the GCD curves of Na$_{0.33}$V$_2$O$_5$ symmetric device in LiCl, NaCl and KCl electrolytes tested at various current densities from 0.5 - 20 A g$^{-1}$. From these graphs, it is clear that while increasing current density the discharge time of the device gradually decreases. This is a significance of the fact that at high currents, the electrolyte ions suffer from low diffusion and get contact only on surface of the active material, which consequences in an incomplete intercalation reaction and shows low specific capacitance.\cite{56}

Energy density (Wh kg$^{-1}$) and power density (kW kg$^{-1}$) are the essential parameters to determine the electrochemical performance of the device. The Ragone plot of Na$_{0.33}$V$_2$O$_5$ symmetric supercapacitor in LiCl, NaCl and KCl electrolytes are shown in Figure 5(c). The device with
LiCl electrolyte shows a highest energy density of 3.74 Wh kg\(^{-1}\) and maximum power density of 4.0 kW kg\(^{-1}\). Similarly, NaCl electrolyte exhibits a maximum energy density of 3.25 Wh kg\(^{-1}\) and power density of 5.0 kW kg\(^{-1}\). And the KCl electrolyte based device with a maximum energy density of 2.94 Wh kg\(^{-1}\) and power density of 4.97 kW kg\(^{-1}\).

Further verifying the performance of the Na\(_{0.33}\)V\(_2\)O\(_5\)//Na\(_{0.33}\)V\(_2\)O\(_5\) device, the specific capacitance values of the devices are compared with recently reported metal oxide//metal oxide based symmetric supercapacitors. The symmetric supercapacitor based on the most authorized electrode materials such as RuO\(_2\)//RuO\(_2\), and MnO\(_2\)//MnO\(_2\) displayed specific capacitance values of 52.66 F g\(^{-1}\) and 44 F g\(^{-1}\) respectively in 1M Na\(_2\)SO\(_4\).\(^ {5,57}\) Similarly, the potential binary complex NiCo\(_2\)O\(_4\)//NiCo\(_2\)O\(_4\) and β-Co(OH)\(_2\)//β-Co(OH)\(_2\) devices showed specific capacitance value of 89 F g\(^{-1}\) and 44 F g\(^{-1}\) in 1M KOH \(^{58,59}\) and the symmetric cell of parent compound V\(_2\)O\(_5\).H\(_2\)O//V\(_2\)O\(_5\).H\(_2\)O revealed a specific capacitance of 127 F g\(^{-1}\) in 2M KCl.\(^{60}\) V\(_2\)O\(_5\)//V\(_2\)O\(_5\), flexible device exhibited a specific capacitance of 96 F g\(^{-1}\) in PVA/LiClO\(_4\) gel electrolyte.\(^{61}\) The carbon coated V\(_2\)O\(_5\)// carbon coated V\(_2\)O\(_5\) shown maximum specific capacitance of 101 F g\(^{-1}\) in 0.5M K\(_2\)SO\(_4\).\(^{62}\) The above reports clearly showed that the metal oxide based symmetric supercapacitors are endured from low specific capacitance value than that obtained in this present work. From these observations, the Na\(_{0.33}\)V\(_2\)O\(_5\) nanomaterials are excellent candidate for the fabrication of symmetric supercapacitors with better performance in all the studied aqueous neutral electrolytes.
2.3.3 Electrochemical impedance spectroscopy

**Figure 6.** (a) Nyquist plots for Na$_{0.33}$V$_2$O$_5$ symmetric supercapacitors (inset shows the equivalent circuit of fit), b) Bode plots for the Na$_{0.33}$V$_2$O$_5$ symmetric supercapacitors in LiCl, NaCl and KCl electrolytes, c) the variation of real (C') and (d) the imaginary (C'') part of capacitance values of the device with respect to frequencies.

EIS is a potential tool to analyse the performance of electrochemical capacitors in terms of their internal resistance, capacitive behaviour, charge transfer properties. **Figure 6(a)** show the Nyquist plots of Na$_{0.33}$V$_2$O$_5$ symmetric devices. The plots depict a semicircle at the high-frequency region denotes the resistive part of the device and the medium-
frequency region displays the diffusion process that is related to the morphology of the electrodes. The Na$_{0.33}$V$_2$O$_5$ symmetric devices exhibited almost a vertical line close to $-90^\circ$ in low frequency region, indicating the good capacitive behaviour of the devices. The obtained Nyquist plots were well fitted to the equivalent circuit (inset of Figure 6(a)) using Zview software and the fitted parameters are presented in Table 1. The real axis intercept at extreme high-frequency region of the Nyquist plot represents the electronic resistance of the device, similarly known as the equivalent series resistance (ESR), denoted as $R_s$, which is the sum of electrolyte resistance, active material resistance and the interface resistance between active material/current collector. The $R_s$ of Na$_{0.33}$V$_2$O$_5$ symmetric supercapacitor in LiCl, NaCl and KCl electrolytes are found to be 0.95, 0.92 and 0.87 $\Omega$ cm$^{-2}$ respectively. Thus, the device in three electrolytes have exhibited small ESR values, which distinctly indicates that these electrolytes are more feasible for contacting more intercalation/deintercalation reactions with the Na$_{0.33}$V$_2$O$_5$ electrodes. The semicircle at high frequency region was fitted to a charge transfer resistance ($R_{ct}$) and the values are 5.52, 5.54 and 5.8 $\Omega$ cm$^{-2}$, in LiCl, NaCl and KCl electrolytes respectively. This obviously shows the charge transfer process of Na$_{0.33}$V$_2$O$_5$ electrode also slightly depend upon the size of cation present in the electrolyte. The Li$^+$ and Na$^+$ ion based electrolyte exhibits nearly equal $R_{ct}$ value compared with K$^+$ ion. Because the size of K$^+$ ion larger than both Li$^+$ and Na$^+$, thus the K$^+$ ions show slightly less interaction with the electrode surface. However, the Na$_{0.33}$V$_2$O$_5$ electrodes exhibit comparable and even less $R_{ct}$ values in electrolytes represents the possibility of efficient pseudocapacitive reaction at the electrode/electrolyte interfaces and rapid build-up of electrolytic ions onto the electrode surface. 

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The sight inclination of spike at a medium frequency region denotes the existence of Warburg impedance (W) corresponds to the ionic diffusion process. The Warburg resistances (W_R) of Na_{0.33}V_2O_5 symmetric cell in LiCl, NaCl and KCl electrolytes are 15.2, 15.8 and 28 Ω cm^{-2} respectively. The Warburg lengths are in the order of LiCl< NaCl < KCl, reflecting faster ion transport at the electrode/electrolyte interface depends upon the size of the cations. Moreover, the nanorod morphology can provide slightly more positive influence by rising the diffusion and migration path of smaller Li^+ ions and facilitates more ions in the intercalation/deintercalation reaction.\(^{[49]}\) The constant phase elements CPE1 and CPE2 in the circuit demonstrating the contributions of double layer capacitance and pseudocapacitance of the symmetric supercapacitors.\(^{[56]}\)

**Table 1.** EIS fitted parameters of symmetric Na_{0.33}V_2O_5 // Na_{0.33}V_2O_5 supercapacitor in different electrolytes.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Rs (Ω cm^{-2})</th>
<th>Rct (Ω cm^{-2})</th>
<th>W_R (Ω cm^{-2})</th>
<th>CPE1 (F cm^{-2})</th>
<th>CPE2 (F cm^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCl</td>
<td>0.95</td>
<td>5.52</td>
<td>15.2</td>
<td>14.7×10^{-5}</td>
<td>0.0332</td>
</tr>
<tr>
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<td>5.54</td>
<td>15.8</td>
<td>15.5×10^{-5}</td>
<td>0.0261</td>
</tr>
<tr>
<td>KCl</td>
<td>0.87</td>
<td>5.8</td>
<td>28</td>
<td>7.57×10^{-5}</td>
<td>0.0255</td>
</tr>
</tbody>
</table>

**Figure 6(b)** display the frequency dependent phase angle (Bode plots) of the symmetric devices. In the plots, the lower frequency phase angle approaches -90°, indicating that the supercapacitor device perform as a pure capacitor.\(^{[57]}\) The Na_{0.33}V_2O_5 symmetric supercapacitor in LiCl, NaCl and KCl electrolytes show a maximum phase angle of -76.9°, -78° and -76.5° at low frequency region represents the capacitive behaviour. But, the values are relatively lesser than that of an ideal capacitors (-90°), this lower shift of
phase angle is mainly due to the pseudocapacitive nature of the electrodes.\[^{68}\] Moreover, the broad peak observed in the high-frequency region related to the diffusive resistance of the devices. The peak frequency values of supercapacitors in LiCl, NaCl and KCl electrolytes are $5.5 \times 10^3$, $6.52 \times 10^3$ and $6.2 \times 10^3$ Hz respectively. The high frequency peak of devices shows nearly comparable value with a slightly shifted to high-frequency. This indicates a low diffusive resistance involves in the present system and which can effectively enhances the electrochemical accessibility of electrolytic ions as well as the performance of the device.\[^{69}\]

In general, the supercapacitors are a series combination of a resistance and a capacitance which depend upon the applied frequency. In the low frequency region, the capacitance ($C(\omega)$) can be defined as the mixture of imaginary part of the capacitance ($C''(\omega)$) and real part of the capacitance ($C'(\omega)$), and can be expressed as Equations (5).\[^{70}\]

$$C = \frac{-1}{(\omega Z')}, \quad \text{(3)}$$

Thus, the complex form of capacitance can be also written as:

$$C = C'(\omega) - jC''(\omega), \quad \text{(4)}$$

The real part of capacitance $C' = \frac{Z'(\omega)}{\omega|Z(\omega)|^2}$ and imaginary part $C'' = \frac{Z''(\omega)}{\omega|Z(\omega)|^2}$

where $\omega$ is angular frequency $(2\pi f_0)$, $Z'$ and $Z''$ represents the real and imaginary parts of impedance and, $|Z(\omega)|$ is the modulus of impedance.\[^{71}\] Figure 6(c) presents the variation in the real part of the capacitance $C'(\omega)$ with respect to the applied frequency (Hz) for Na$_{0.33}$V$_2$O$_5$ supercapacitor in four different electrolytes. The plots show a resistive
behaviour at high frequency region and a pronounced capacitance behaviour at low frequency and the low frequency capacitance values decrease in the order of Li\(^+\) > Na\(^+\) > K\(^+\) for Na\(_{0.33}\)V\(_2\)O\(_5\) symmetric supercapacitors.

**Figure 6(d)** shows the progression of imaginary capacitance values \(C''(\omega)\) with frequencies for the symmetric cells in different electrolytes. The imaginary part established a peak frequency \(f_0\), which determines the resistive and capacitive behavior of the device. From the peak frequency, the relaxation time constant \(\tau_0\) can be evaluated as \(\tau_0 = (1/2\pi f_0)\). If, \(f > 1/\tau_0\), then the device works as a pure resistor and \(f < 1/\tau_0\) works as a pure capacitor.\(^{[72]}\) The relaxation time constant \(\tau_0\) for the symmetric cell is \(\sim 1.075\) s in LiCl, \(\sim 1.57\) s in NaCl and \(\sim 1.72\) s in KCl electrolytes respectively. This value indicating a measure of how fast the stored energy of the device can efficiently distributed.\(^{[73]}\) Thus, the Li\(^+\) ion supported supercapacitor with low \(\tau_0\) value representing high energy storage capability with high rate attributed to slightly quick intercalation/deintercalation process with the electrode material, compared to Na\(^+\) and K\(^+\) ions.

**2.3.4 Cyclic stability test**
Figure 7. (a) Cycling stability of Na$_{0.33}$V$_2$O$_5$ symmetric supercapacitors tested for LiCl, NaCl and KCl electrolytes 50,000 charging/discharging cycles at 5 A g$^{-1}$, (b) Nyquist plots of Na$_{0.33}$V$_2$O$_5$ symmetric supercapacitors after cycling stability test (inset shows the magnified portion of plots at high frequency region), (c) imaginary part of capacitance (C") of the symmetric cell in the three different electrolytes after cycling stability test.

Figure 7(a) shows the cyclic stability of the Na$_{0.33}$V$_2$O$_5$ supercapacitor in LiCl, NaCl and KCl electrolytes for 50,000 charge/discharge cycles. And shows the device in three electrolytes have better ability and retainability of specific capacitance values. The device in electrolytes LiCl, NaCl and KCl displayed specific capacitance retention of 61%, 81% and 72% after 50,000 cycles. The cyclic stability of all the studied devices are comparable.
to the carbon based EDCLs and even higher than those reported for metal oxides based supercapacitors.\textsuperscript{[74,33,75]} The above examination reveals that the supercapacitor in NaCl shows extremely good electrochemical stability and describing as a potential electrolyte for the Na\textsubscript{0.33}V\textsubscript{2}O\textsubscript{5} system with a most comparable specific capacitance value. Moreover, the LiCl electrolyte shown less stability (61\%, 50,000 cycles) than KCl electrolyte, this might be due to the slow formation of impurity phase while performing the lithiation/de-lithiation process as mentioned in Equation (6).\textsuperscript{76}

\[
\text{Na}_{x}\text{V}_2\text{O}_5 + 2 \text{Li}^+ + 2 \text{e}^- \leftrightarrow \text{Na}_x\text{V} + \text{Li}_2\text{O}
\] (6)

The stability of the symmetric supercapacitors is further investigated by performing electrochemical impedance spectroscopy (EIS) analysis after executing the 50,000-cyclic stability test. Figure 7(b) shows the resultant Nyquist plots for Na\textsubscript{0.33}V\textsubscript{2}O\textsubscript{5} symmetric supercapacitors in LiCl, NaCl and KCl electrolytes after cycling stability test. The plots were well fitted with the similar equivalent circuit (Figure 6(b)) and the fitted data are presented in Table. 2 From the fitted data, the equivalent series resistance (R\textsubscript{s}) of the device slightly shifted to higher value after GCD cycles for LiCl 0.95 to 1 Ω cm\textsuperscript{-2}, NaCl 0.92 to 0.918 Ω cm\textsuperscript{-2} and KCl 0.87 to 0.942 Ω cm\textsuperscript{-2} respectively. This negligibly small increase in the R\textsubscript{s} values after cycle stability test is mainly due to sight poisoning of electrolyte solution by repeated intercalation/deintercalation process of cations with the electrode. However, comparing the R\textsubscript{ct} values of Na\textsubscript{0.33}V\textsubscript{2}O\textsubscript{5} device before and after cyclic stability test a subsequent increase in the R\textsubscript{ct} values were observed (in LiCl 5.52 to 6.52 Ω cm\textsuperscript{-2}, NaCl 5.54 to 6.34 Ω cm\textsuperscript{-2} and KCl 5.7 to 6.81 Ω cm\textsuperscript{-2}), which indicates the electrodes are somewhat affected by the prolonged cyclic GCD tests. The Nyquist plots of the device before and after GCD test in each electrolyte are comparatively displayed in Figure S5 a), b) and c) respectively. From the variation of R\textsubscript{ct} values, all three
electrolytes highly assail the electrodes surface. Since, initially the Li$^+$, Na$^+$ and K$^+$ ions can easily perform intercalation/deintercalation with the electrode material up to a certain instant for the continuous GCD process and tends to form an impurity phases on the electrode surface due to long time contact of the electrolytic ions.$^{[38]}$ This increase in $R_{ct}$ value can be considered as a crucial factor affecting the stability of the device in LiCl and KCl electrolytes. Conversely in the case of NaCl electrolyte, the electrode materials already possess a considerable amount of sodium ions in their crystal lattice, so the intercalation of excess Na$^+$ ions from electrolyte cannot alter the surface state of the electrode or even not accommodate permanently in to the stable crystalline structure. Therefore, it is believed that the polarized electrolytic Na$^+$ ions of NaCl can effectively accomplish the intercalation/deintercalation reaction with the electrode for a long term rather than affecting the surface of the Na$_{0.33}$V$_2$O$_5$ electrode up to 50,000 cycles. Thus, the symmetric device in NaCl electrolyte shows prolonged stability than that of LiCl and KCl electrolytes in this present Na$_{0.33}$V$_2$O$_5$ crystalline system. In addition, the relaxation time constant was determined from the imaginary part of capacitance values obtained after cyclic stability test as shown in Figure 7(d).

After cycling stability test the $\tau_0$ values of the devices are found to be $\sim$ 1.789 s in LiCl, $\sim$ 1.598 s in NaCl and $\sim$ 1.94 s in KCl the aqueous electrolytes respectively. LiCl and KCl electrolytes showed the $\tau_0$ value ($\sim$ 1.789 s in LiCl and $\sim$ 1.598 s in KCl) slightly higher than its initial value, this clearly reveals that after long cyclic process the device require slightly additional time to distribute the stored energy. This can be attributed to the feeble loss of electrolytic ions permanently on the electrode surfaces (as impurity) while executing the repeated intercalation/deintercalation processes. On the other hand, in NaCl electrolytes $\tau_0$ value is nearly
same (~1.57 s and 1.598 s) even after 50,000 cycles with excellent capacitance retention, representing a promising electrolyte for the Na$_{0.33}$V$_2$O$_5$//Na$_{0.33}$V$_2$O$_5$ symmetric device.

**Table 2.** EIS fitted parameters of symmetric Na$_{0.33}$V$_2$O$_5$ // Na$_{0.33}$V$_2$O$_5$ devices after cycling stability test.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Rs (Ω cm$^{-2}$)</th>
<th>Rct (Ω cm$^{-2}$)</th>
<th>WR (Ω cm$^{-2}$)</th>
<th>CPE1 (F cm$^{-2}$)</th>
<th>CPE2 (F cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCl</td>
<td>1</td>
<td>6.52</td>
<td>18</td>
<td>14.143×10$^{-5}$</td>
<td>0.031</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.918</td>
<td>6.34</td>
<td>18</td>
<td>14.7×10$^{-5}$</td>
<td>0.0213</td>
</tr>
<tr>
<td>KCl</td>
<td>0.942</td>
<td>6.81</td>
<td>34</td>
<td>7.06×10$^{-5}$</td>
<td>0.0222</td>
</tr>
</tbody>
</table>

3. Conclusion

In summary, Na$_{0.33}$V$_2$O$_5$ nanostructured electrodes have been successfully utilized for the fabrication of the symmetric supercapacitor and studied their performances in different neutral electrolytes. It was confirmed that the different cationic species in electrolytes have individual electrochemical behavior, cycling stability and ionic diffusion/relaxation times. The Na$_{0.33}$V$_2$O$_5$ symmetric supercapacitor showed excellent specific capacitance values in the order of Li$^+ >$ Na$^+ >$ K$^+$. Furthermore, the Na$_{0.33}$V$_2$O$_5$ // Na$_{0.33}$V$_2$O$_5$ symmetric supercapacitor in NaCl electrolyte delivered extremely high cycling stability ~ 81% retention after 50,000 cycles, which is comparatively close to EDLC and better than most reported metal oxide based symmetric devices. The results clearly demonstrated that the Na$_{0.33}$V$_2$O$_5$ nanostructure is a potential electrode material for the application of symmetric supercapacitor device in neutral electrolytes. Thus, the Na$_{0.33}$V$_2$O$_5$ device in NaCl electrolyte affords a remarkable supercapacitive
performance and is a promising approach for the development of symmetric energy storage device in future.

4. Experimental Methods

4.1 Materials

The starting materials VOSO$_4$.xH$_2$O was purchased from Alfa-Aesar (Korea) and NaOH was purchased from Daejung Chemicals & Metals Co. Ltd. (Korea). The carbon black, poly-(vinylidene fluoride) (PVDF), N-methyl-2-pyrrolidone (NMP), KCl, NaCl and LiCl were obtained from Alfa-Aesar (Korea). The substrate titanium foil was purchased from Nilaco Ltd. (Japan).

4.2 Synthesis of Na$_{0.33}$V$_2$O$_5$ nanoparticles

The Na$_{0.33}$V$_2$O$_5$ nanoparticle was synthesized by simple low temperature co-precipitation technique. Briefly, 1:0.2 molar ratio of vanadyl sulfate (VOSO$_4$.xH$_2$O) and sodium hydroxide (NaOH) were mixed in deionized water and stirred at room temperature for 30 min. Then the temperature was gradually increased upto 80 °C and maintained the stirring until 20 h. After this, the mixture was slowly cool down to room temperature and the resultant precipitate was separated by centrifugation and washed in deionized water until reaches neutral pH. Then the resultant precipitate was dried in oven at 40 °C for 12 h, the dried sample displays a dark greenish color, which was used for the further characterization. The chemical reaction takes place in the synthesis process is shown in Equation (7)

$$4\text{VOSO}_4 + 2\text{NaOH} \rightarrow 2\text{Na}_x\text{V}_2\text{O}_5 + \text{H}_2\text{SO}_4 + 2\text{SO}_3 + \text{SO}_2 \xrightarrow{\text{wash}} 2\text{Na}_x\text{V}_2\text{O}_5 + 2\text{H}_2\text{O} \xrightarrow{40\,^\circ\text{C}} 2\text{Na}_{0.33}\text{V}_2\text{O}_5.\text{H}_2\text{O} \quad (7)$$
4.3 Fabrication of electrodes and symmetric supercapacitor

The supercapacitor electrodes were fabricated using titanium (Ti) substrate of area 1 × 1 cm² as current collector. Initially, the surface of Ti substrate was polished with emery paper, ultrasonically cleaned in acetone, deionized (DI) water and dried in a hot plate. The electro active slurry was prepared by grounding 75% of synthesized Na₀.₃₃V₂O₅, 20% of carbon black, 5% polyvinylidene difluoride (binder) and few drops of N-methyl pyrrolidone (NMP) in an agate mortar. Then the slurry was pasted over the pre-treated titanium substrate and dried at 70 °C for 10 h. The mass of the active material coated in the substrate was ~1.2 mg. The symmetric full-cell was fabricated utilizing the stainless-steel split test cell (EQ-STC) purchased from MTI Korea Ltd. The cell was assembled using a pair of Na₀.₃₃V₂O₅ coated Ti electrodes of nearly similar weight and arranged face-to-face by sandwiching a filter paper as separator (Whatman). Then, few drops of aqueous 1M LiCl or NaCl or KCl electrolyte was dropped in between the electrodes. The photographic representations of the symmetric cell fabrication steps are shown in Figure S1.

4.4 Structural characterization

The crystallinity and structural aspects of synthesized Na₀.₃₃V₂O₅ nanoparticle were analysed by X-ray diffraction (XRD, D/max-2400, Rigaku, Ultima IV) using a Cu Kα source operated at 40 kV and 30 mA in the 2θ range of 5-60°. The morphological features and elemental analysis (energy dispersive X-ray spectroscopy (EDX)) of Na₀.₃₃V₂O₅ nanostructure was recorded using JEOL-7500FA (Japan) and Transmission electron microscopy (TEM), JEOL model JEM-2100F (Japan) respectively. X-ray photoelectron spectroscopy (XPS) measurement was performed using the Veresprobe II spectrometer.
and pattern was collected using Al Kα radiation. Raman spectrum of the sample was recorded using micro Raman spectrometer with an excitation produced by laser beam at 525 nm wavelength.

4.5 Electrochemical Measurements

The electrochemical properties of Na$_{0.33}$V$_2$O$_5$ supercapacitors were studied using ZIVE-SP2 electrochemical workstation (Korea) at room temperature (~25 °C). The whole electrochemical experiments were performed utilizing the assembled full-cell in different aqueous electrolyte of 1M LiCl, NaCl and KCl solutions respectively. Cyclic voltammetry (CV) was performed for various scan rates from 5 to 100 mVs$^{-1}$ and the galvanostatic charge/discharge test was carried out under different charge/discharge current densities (0.5, 1, 2.5, 5, 7.5, 10, 12.5, 15 and 20 Ag$^{-1}$) at a constant potential window of 0 to 0.8 V. Electrochemical impedance spectroscopy (EIS) was measured in the frequency range between 0.01 Hz - 100 kHz at 0 V bias condition. The specific capacitance (C in F g$^{-1}$) was calculated from the CV curves according to the following Equation (8),

$$
C = 2 \left( \frac{\int_{m}^{s} \Delta v}{\Delta v} \right) \tag{8}
$$

where, $m$ is the mass of active material of one electrode (g), $s$ is the potential scan rate (mV s$^{-1}$), $i$ is the voltammetric current (A), and $\Delta V$ is the potential window (V) of CV curve.

The specific capacitance value of the symmetric supercapacitor was determined from the charge/discharge curves using Equation (9).

$$
C = 2 \left( \frac{\Delta t}{m \Delta V} \right) \tag{9}
$$
where, \( I \) is the constant discharge current (A), \( \Delta t \) is the discharge time (s), \( m \) is the mass of the one electrode (g), and \( \Delta V \) is the potential window (V).

Energy density \( (E) \) and power density \( (P) \) of symmetric supercapacitor were determined by the Equations (10) and (11),

\[
E = \frac{1}{8} C \Delta V^2 \tag{10}
\]

\[
P = \frac{E}{\Delta t} \tag{11}
\]

**Supporting information**

Supporting Information is available from the Wiley Online Library or from the author.

**Acknowledgements**

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References


Symmetric supercapacitor was fabricated utilizing Na$_{0.33}$V$_2$O$_5$ nanorods and studied their performance in Li$^+$, Na$^+$ and K$^+$ cation based aqueous electrolytes. The Na$_{0.33}$V$_2$O$_5$ symmetric supercapacitor showed better electrochemical performance with excellent cyclic stability for 50,000 charge/discharge cycles in all three electrolytes.