1. Introduction

Exploration of renewable energy has been a continuous effort for reaching a green and sustainable world.1,2 One of the keys is related to an advanced energy storage device, namely, asymmetric supercapacitors (ASCs). ASC is composed of a positive electrode made from a faradaic, battery-like material and a negative electrode made from a non-faradaic, electric double-layer material.2,3 To date, the most effective negative electrodes are carbon-based materials.2,3 Thus, recent research interest in ASCs focuses on positive electrode materials.4–11 One of the battery-like electrode materials, i.e., metal vanadate, holds great potential owing to its layered structure and rich valence states. Common metal vanadates include Ni4–xV2O8, Zn2V2O7, BiVO4, Ni3V2O8, and Co3V2O8. Among them, cobalt vanadate (Co3V2O8) has drawn significant attention owing to its excellent stability, outstanding capacitance, low-toxicity, and simplicity of preparation.

Hydrothermally synthesized Co3V2O8 has a specific capacitance \( C_{sp} \) of 505 F g\(^{-1}\) at 0.625 A g\(^{-1}\) and an energy density \( E_{d} \) of 28 W h kg\(^{-1}\) at a power density \( P_{d} \) of 1400 W kg\(^{-1}\).12 One-pot solvothermal Co3V2O8/graphene composite showed a \( C_{sp} \) of 528.2 F g\(^{-1}\) at 0.5 A g\(^{-1}\), and 80% capacitance remaining after 5000 cycles.13 Hydrothermally synthesized Co3V2O8 nanoplate electrode shows a remarkable \( C_{sp} \) of 739 F g\(^{-1}\) at 0.5 A g\(^{-1}\) and 2000 cycles retention of 95.3%.14 Electrode based on 3D porous Co3V2O8 microflowers synthesized using a co-precipitation method exhibits a \( C_{sp} \) of 351 F g\(^{-1}\) at 1 A g\(^{-1}\) with 103% capacitance retention after 30 000 cycles.15 An \( E_{d} \) of 19 W h kg\(^{-1}\) at \( P_{d} \) of 375.8 W kg\(^{-1}\) was also reported. NiO–Co3V2O8 grown on nickel foam shows a \( C_{sp} \) of 1166 F g\(^{-1}\) at 0.5 A g\(^{-1}\) and cycle stability of 99.4% after 5000 cycles.16 The \( E_{d} \) is 38.8 W h kg\(^{-1}\) at a \( P_{d} \) of 397.9 W kg\(^{-1}\). Heterostructure of Co3V2O8–Ni3V2O8/carbon composite exhibits \( C_{sp} \) of 1731 F g\(^{-1}\) at 1 A g\(^{-1}\) and an \( E_{d} \) of 59.7 W h kg\(^{-1}\) at high \( P_{d} \) of 1970 W kg\(^{-1}\).17 The excellent SC performance is obtained due to the rich redox activities of the cobalt vanadate, and high active surface areas. On the other hand, the use of redox additive (RA) electrolyte has also been demonstrated to enhance the \( C_{sp} \).21–25

Herein, we present a room-temperature process to synthesize Co3V2O8 nanowalls on Ni foam (NF) using a template-assisted growth. Also, K3[Fe(CN)6] RA electrolyte is used to enhance ionic conductivity of electrolyte and provide additional redox reactions, targeting in the further capacitance improvements. With the use of the RA electrolyte, a capacitance of 198.1 mA h g\(^{-1}\) (1584.5 F g\(^{-1}\)) at 1 A g\(^{-1}\) is demonstrated. Furthermore, we show that an ASC having an activated carbon (AC) negative electrode, Co3V2O8 positive electrode, and the RA electrolyte provides an excellent \( E_{d} \) of 55.5 W h kg\(^{-1}\) at a \( P_{d} \) of 800 W kg\(^{-1}\) and 82% capacitance remaining after 10 000 cycles.

2. Experimental

2.1 Chemicals

All chemicals were used as received. 2-methylimidazole (2-MIM, 99%, Sigma Aldrich), cobalt nitrate hexahydrate (Co(NO3)2·6H2O, 98%, Baker Analyzed Reagent), and sodium orthovanadate (Na2VO4, ≥98%, Sigma Aldrich), and potassium hydroxide (KOH, ≥85%, Honeywell Fluka).
2.2 Synthesis of ZIF-67

ZIF-67 was synthesized by a precipitation method.26 A piece of 2 × 3 cm NF was first cleaned with 10 mL HCl 37% for 5 minutes, followed by deionized (DI) water and ethanol in sequence washing. The NF is used as the substrate for the growth of ZIF-67. To grow ZIF-67, a 20 mL solution A consisting of 2 mmol Co(NO3)2·6H2O was first made under stirring for 30 minutes to form solution A. Meanwhile, 20 mL solution B containing 16 mmol of 2-MIM was also prepared. After that, the two prepared solutions were quickly mixed. After 5 minutes of stirring, the washed NF was then deep into the prepared solution at room temperature for 3 hours. The final product was achieved after washing with DI water and ethanol, followed by drying with flowing nitrogen gas.

2.3 Synthesis of Co3V2O8

To convert the ZIF-67 into Co3V2O8, the ZIF-67@NF was immersed in 20 mL of 0.1 M Na3VO4 aqueous solution. After a three-hour ion exchange process at room temperature, the resulting NF was soaked in ethanol and DI water, then dried under a nitrogen flow. The active material on the NF was calculated to be 1.6 mg cm−2.

2.4 Material characterizations

The morphology and structure were examined utilizing transmission electron microscopy (TEM, JEOL-2100F CS STEM) and scanning electron microscopy (SEM, JSM-6701F). X-ray photoelectron spectroscopy (XPS, PHI 5000) was used to analyze the surface chemistry. Crystalline structure was examined using X-ray diffraction (XRD, Rigaku X-ray Diﬀraction) pattern (Fig. 1F) are indexed to the crystallinity Co3V2O8 (Fig. S2†). EDS elemental distribution and mappings are shown in Fig. 1H and G, respectively. The Co, V, and O uniformly distribute throughout the nanowalls. XRD analysis also indicates the formation of low-crystallinity Co3V2O8 (Fig. S2†). EDS elemental distribution and mappings are shown in Fig. 1H and G, respectively. The Co and V both exhibit multi-valence states of Co2+/Co3+ and V4+/V5+, respectively, as shown by XPS analysis (Fig. S3†).

3. Results and discussion

Co3V2O8 were grown on ZIF-67@NF where the ZIF-67 homogeneously distributes on the NF (Fig. S1A†) with a uniform thickness of 2.2 μm (Fig. S1B†) and a plate-like morphology (Fig. S1C†). After the ion exchange process, uniform coverage of the material on the NF remains, as shown in Fig. 1A. The nanoplate ZIF-67 turns into nanowall morphology (Fig. 1B). The average thickness of the nanowalls is about 30 nm (Fig. 1C), much less than that of the nanoplates. The nanowall is further examined using TEM, as illustrated in Fig. 1D. A high-resolution TEM image (Fig. 1E) shows d-spacings of 0.208 and 0.254 nm, corresponding to the (042) and (112) planes of Co3V2O8 (JCPDS no. 74-1487). Various diffraction rings in the selected area electron diffraction (SAED) pattern (Fig. 1F) are indexed to the polycrystalline Co3V2O8, confirming the formation of Co3V2O8 nanowalls. XRD analysis also indicates the formation of low-crystallinity Co3V2O8 (Fig. S2†). EDS elemental distribution and mappings are shown in Fig. 1H and G, respectively. The Co, V, and O uniformly distribute throughout the nanowalls. The Co and V both exhibit multi-valence states of Co2+/Co3+ and V4+/V5+, respectively, as shown by XPS analysis (Fig. S3†).

CV curves of the Co3V2O8 electrode evaluated using the 3 M KOH and RA electrolytes are displayed in Fig.s S4A† and 2A, respectively. Fig. 2B shows the comparison of the CV curves acquired at 5 mV s−1. With the use of the KOH electrolyte, there are two redox peaks couple, which are ascribed to the reversible redox reactions of Co(n) ↔ Co(m) (at ~0.03 and ~0.13 V) and Co(n) ↔ Co(n) (at ~0.03 and 0.43 V) reactions, respectively.27 The existence of the redox peaks indicates that the Co3V2O8 electrode is pseudocapacitive. In the case of the RA electrolyte, two redox peaks couple shifting to the positive side are seen. The couple redox peak for Co(n) ↔ Co(m) is also seen. The second redox peaks at the right are attributed to the addition of Fe(CN)6 3−/Fe(CN)6 4− (0.5 and 0.27 V vs. SCE) redox peaks.28,29

\[
\frac{m_s}{m_p} = \frac{C_p}{C_{p^+}} \times \frac{\Delta V}{\Delta V_p^+} \quad (1)
\]

where \(m_s\) and \(C_{p^+}\) are the mass, potential window, and specific capacitance, respectively; while \(\Delta V\) and \(\Delta V_p^+\) represent the negative and positive electrodes, respectively.

The \(C_p^+\) was determined using eqn (2):

\[
C_p^+ = \frac{I \times \Delta t}{m \times 3.6} \quad (2)
\]

where \(I\) is the discharge current (A), \(t\) is the discharge period (s), \(V\) is the potential window (V), \(m\) represents the active material’s weight (g), and \(I\) the discharge current (A). \(E_d\) and \(P_d\) were determined using eqn (3) and (4), respectively:

\[
E_d = \frac{1}{2} C_p (\Delta V)^2 \quad (3)
\]

\[
P_d = \frac{E_d}{\Delta V} \quad (4)
\]
The Faraday reaction of K₃Fe(CN)₆ in RA electrolyte provides additional capacitance, as shown in eqn (5) below.

\[
\text{Fe(CN)₄}^{3⁻} \leftrightarrow \text{Fe(CN)₃}^{4⁻} + e^- \tag{5}
\]

It is also seen that the RA electrolyte gives enhanced current densities, as seen in both of the redox pairs in Fig. 2B. In the first (left-hand side) redox peaks, the Co(II) \( \leftrightarrow \) Co(III) reaction is enhanced. This is attributed to the improvement of electrolyte conductivity by adding RA, which will be shown later.\(^{28,29}\) For the second redox peaks, the enhancement is primarily due to the redox reactions of K₃Fe(CN)₆. This then leads to enhanced \( C_{sp} \).

The redox reaction occurring in the RA electrolyte is explained as followed.\(^{23,30}\) During the charging process, the oxidation of Co occurs: Co\(^{2+} \) to Co\(^{3+} \) and Co\(^{3+} \) to Co\(^{4+} \), leading to the loss of electrons. The electrons then transfer to Fe(CN)\(^{3⁻} \), which then reduces to Fe(CN)\(^{4⁻} \). The reversed process takes place during the discharge process. GCD curves obtained at various current densities using the KOH and RA electrolytes are shown in Figs S4B\(^\dagger\) and 2C, respectively. Longer discharge time is seen in the GCD curves obtained using the RA electrolyte, indicating improved \( C_{sp} \). Both KOH and RA electrolytes exhibit pseudo-capacitive behaviors. The GCD curves obtained using the KOH show a plateau at about 0.05 V for Co(II) \( \leftrightarrow \) Co(III) and 0.29 V for Co(III) \( \leftrightarrow \) Co(IV).\(^{18,31}\) In the case of the RA electrolyte, the lower plateau is insensitivity. However the upper plateau is raised to a high \( V \) near 0.35 V, indicating the contribution of the redox-active K₃[Fe(CN)₆].\(^{28,29}\) The \( C_{sp} \) measured in different electrolytes was calculated using the GCD results (Fig. 2D). \( C_{sp} \) value of 109.9 mA h g\(^{-1} \) (878.9 F g\(^{-1} \)) at 1 A g\(^{-1} \) and rate retention of 58% (63.9 mA h g\(^{-1} \) (511 F g\(^{-1} \)) at 10 A g\(^{-1} \)) were obtained in the KOH electrolyte. Nearly two-fold improvement of the \( C_{sp} \) is seen when the RA electrolyte is used, giving a \( C_{sp} \) of 198.1 mA h g\(^{-1} \) (1584.5 F g\(^{-1} \)) at 1 A g\(^{-1} \) and the remaining 57% at 10 A g\(^{-1} \).

The charge storage mechanism for Co₃V₂O₈ in KOH and RA electrolytes was analyzed using the following power law equation.\(^{32,33}\)

\[
i = a\nu^b
\]

where \( a, \) and \( b \) are constants, \( \nu \) is the scan rate from CV measurement, and \( i \) is the current. The value of \( b \) is used to determine if the charge storage is diffusion-controlled or surface-controlled as follows. For surface-controlled and diffusion-controlled charge storages, the values of \( b \) are 1 and 0.5, respectively.\(^{34}\) As shown in Fig. 2E, the calculated values of \( b \) are 0.66 and 0.51 for the electrode measured in KOH and RA electrolytes, respectively. This indicates that the RA provides more diffusion-controlled charge storage, representing more
Faradaic redox reactions occurring due to the use of RA electrolyte. The additional redox reactions are ascribed to the $\text{Fe(CN)}_6^{3-}/\text{Fe(CN)}_6^{4-}$ oxidation/reduction reactions, which are shown in the CV (Fig. 2B) and GCD (Fig. 2C) curves. Thus, the significant improvement in capacitance is obtained.

EIS investigation was done and is presented in Fig. 2F. The intercept between the curve and the $x$-axis represents the solution/electrolyte resistance ($R_s$), which is associated with the electrolyte ionic conductivity. Charge transfer resistance ($R_{ct}$) is depicted by the semicircle at high frequencies. The slope at the high-frequency region represents the electrolyte diffusion resistance ($R_d$).

The Nyquist plots exhibit that the $R_s$ of RA electrolyte (1.6 $\Omega$) is slightly lower than the value in KOH electrolyte (1.8 $\Omega$). This indicates the better ionic conductivity in the RA electrolyte, which facilitates the ion movement to diffuse to the pores of the electrode. Furthermore, the $R_s$ value of Co$_3$V$_2$O$_8$ measured using the RA electrolyte is 1.5 $\Omega$, which is lower than that of measured using 3 M KOH (3.2 $\Omega$). The result indicates the faster electron transfer at the electrode/electrolyte interface in RA electrolyte and among the particle in the bulk electrode, which is beneficial for fast redox reactions. For the $R_{ct}$, it is seen that the RA electrolyte smaller slope, indicating better ions diffusion into the pores of Co$_3$V$_2$O$_8$. These reduced resistances contribute to the improvement of the electrochemical performance. Cycling performances were examined via GCD measurement at a current density of 5 A g$^{-1}$ for 5000 cycles in the KOH and 0.05 M K$_3[\text{Fe(CN)}_6]$ RA electrolytes, as shown in Fig. 2G. SEM images of the material after the cyclic test in both electrolytes are presented in Fig. S5.$^\dagger$ The Co$_3$V$_2$O$_8$ shows excellent cycle stability in both the KOH and RA electrolytes. However, the use of RA electrolyte shows lower stability than the use of KOH electrolyte. This is attributed to the crystallization of K$_3[\text{Fe(CN)}_6]$ and the aggregation of free ions during the prolonged Fe(CN)$_6^{3-}/$Fe(CN)$_6^{4-}$ redox process.$^{35,36}$ In addition, the redox additive involves intensive redox reactions at the interface of active electrode material and electrolyte, which promotes the rate of dissolution of active electrode material, leading to the cyclic retention degradation.$^{36}$

To evaluate the material for practical application, ASC was assembled and tested. The CV curves of the AC negative

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**Fig. 2** (A) CV curves obtained using RA electrolyte. (B) Comparative CV curve of the sample tested in KOH and without RA electrolytes at 5 mV s$^{-1}$. (C) GCD curves collected using RA electrolyte at different current densities. (D) $C_{sp}$ calculated based on the GCD curves. (E) Relationship between cathodic peak current with scan rates on KOH and RA electrolytes. (F) Nyquist plots and (G) Cycle performances obtained using the two different electrolytes.
electrode are displayed in Fig. S6A,† which shows no redox peak. The GCD curves show typical electrical double layer capacitor behavior of carbon (Fig. S6B†). The \( C_{sp} \) is 38.8 mA h g\(^{-1}\) (139 F g\(^{-1}\)) at 1 A g\(^{-1}\) (Fig. S6C†). Fig. S7A† shows the CV curves of the positive and negative electrodes at 5 mV s\(^{-1}\) in 3 M KOH. Fig. S7B† shows that the optimized cell voltage is 1.6 V. The CV curves of the ASC in KOH electrolyte with a cell voltage of 1.6 V is shown in Fig. S8A†. The CV curves of ASC obtained using the RA electrolyte are presented in Fig. 3A. All CV curves exhibit pseudocapacitive behavior. A higher current response is seen in the CV curves of the ASC having RA electrolyte, demonstrating the superior electrochemical performance. Fig. 3B and S8B† presented the GCD curves of the ASCs in the RA and KOH electrolytes, respectively. The discharge time of the ASC using the RA electrolyte is longer than that of the ASC using the KOH electrolyte, indicating higher capacitance in the former. Fig. 3C shows the \( C_{sp} \) derived from the GCD curves of the two ASCs. In comparison, the \( C_{sp} \) of the ASC utilizing RA

![Fig. 3](image)

(A) CV curves at various scan rates. (B) GCD curves at various current densities of Co\(_3\)V\(_2\)O\(_8\)/AC ASC in RA electrolyte. (C) \( C_{sp} \) of the two ASC calculated from GCD curves. (D) Nyquist plots of the ASCs obtained using KOH and RA electrolytes.

![Fig. 4](image)

(A) Ragone plot correlating \( E_d \) and \( P_d \) and (B) Cyclic stability of Co\(_3\)V\(_2\)O\(_8\)/AC ASC devices using KOH and RA electrolytes.
electrolyte is 69.3 mA h g\(^{-1}\) (156 F g\(^{-1}\)), more than two times higher than the ASC using KOH electrolyte (27.8 mA h g\(^{-1}\) (63 F g\(^{-1}\))). Fig. 3D show the Nyquist plots of the two ASCs. In comparison to the ASC using the 3 M KOH electrolyte (\(R_{ct} = 1.52 \Omega\)), the ASC using the RA electrolyte exhibits a reduced \(R_{ct}\) of 0.32 \(\Omega\). This indicates better charge transfer in the RA electrolyte, contributing to the improvement of the \(C_{sp}\). Also, the ASC with the RA electrolyte gives a high \(E_{d}\) of 55.5 W h kg\(^{-1}\) at a high \(P_{d}\) of 800 W kg\(^{-1}\), as shown in Fig. 4A. For comparison, the ASC using the 3 M KOH delivers an \(E_{d}\) of 22.2 W h kg\(^{-1}\) at the same \(P_{d}\). It is noted that the obtained \(E_{d}\) in this work outperforms most previously reported cobalt vanadate-based materials, such as Co\(_{3}\)Ni\(_{1}\)\(_{3}\)V\(_{2}\)O\(_{8}\)/AC (51.6 W h kg\(^{-1}\) at 850 W kg\(^{-1}\)),\(^{36}\) Co\(_{3}\)V\(_{2}\)O\(_{7}\)/rGO (19 W h kg\(^{-1}\) at 375.8 W kg\(^{-1}\)),\(^{38}\) Ni\(_{3}\)P-Co\(_{3}\)V\(_{2}\)O\(_{6}\)/AC (40.2 W h kg\(^{-1}\) at 353 W kg\(^{-1}\)),\(^{39}\) Co\(_{3}\)O\(_{x}\)-Co\(_{3}\)V\(_{2}\)O\(_{7}\)/AC (38 W h kg\(^{-1}\) at 275 W kg\(^{-1}\)),\(^{40}\) Ni\(_{3}\)V\(_{2}\)O\(_{2}\)/Co\(_{3}\)V\(_{2}\)O\(_{7}\)/AC (28 W h kg\(^{-1}\) at 1400 W kg\(^{-1}\)),\(^{41}\) and NiO-Co\(_{3}\)V\(_{2}\)O\(_{7}\)/AC (38.8 W h kg\(^{-1}\) at 379.7 W kg\(^{-1}\)).\(^{19}\) The cycle stability of the ASC in 0.05 M K\(_{3}\)Fe(CN)\(_{6}\)/RA electrolyte was determined via GCD measurement at a current density of 5 A g\(^{-1}\). As shown in Fig. 4B, the ASC exhibits 82.1% capacitance retention after 10,000 cycles. The reduction of capacitance is due to the occurrence side-reactions and the decreased activity of the redox additive during the long GCD measurement time.\(^{13,35,40,41}\)

4. Conclusion

We report cobalt vanadate nanowalls grown on nickel foam for use as an electrode of supercapacitors. The nanostructured Co\(_{3}\)V\(_{2}\)O\(_{8}\) demonstrates a high specific capacitance of 109.9 mA h g\(^{-1}\) (878.9 F g\(^{-1}\)) at 1 A g\(^{-1}\) in KOH. The use of K\(_{3}\)Fe(CN)\(_{6}\) redox additive further improves the electrochemical performance, giving nearly two-time enhancement of the capacitance (198.9 mA h g\(^{-1}\) (1584.5 F g\(^{-1}\))). ASC consisting of Co\(_{3}\)V\(_{2}\)O\(_{8}\) positive electrode, AC negative electrode, and redox additive electrolyte delivers a high energy density of 55.5 W h kg\(^{-1}\) at a power density of 800 W kg\(^{-1}\) and good cyclic stability. The excellent electrochemical performance shows that the Co\(_{3}\)V\(_{2}\)O\(_{8}\) is an excellent electrode material for the next-generation supercapacitor.

Conflicts of interest

The authors declare that there is no competing financial interest that could have appeared to influence the work reported in this paper.

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