

Project title: High-energy  $Mn_2V_2O_7//C$  asymmetric supercapacitors in aqueous/organic hybrid electrolytes

Industry partner(s): Atlas Power Technologies

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**Introduction & Background:**

The demand for advanced energy storage devices, such as high-energy density supercapacitors (SCs), has spurred efforts to develop new environmentally friendly and efficient electrode materials and electrolyte solutions for sustainable development. Asymmetric supercapacitors (ASCs), a combination of pseudocapacitive and electric double layer capacitor (EDLC) electrodes have emerged as promising candidates for efficient energy storage technologies stimulating sustainable energy due to their high-power density, rapid charge/discharge rates, and long cycle life [1]. The pseudocapacitive electrode facilitates rapid and reversible surface-controlled redox reactions for storing charge through intercalation or adsorption of electrolyte ions on or near the surface of the electrode resulting in improved energy density [2, 3]. However, the EDLC stores charge through physical adsorption/desorption process responsible for enhancing the power density. Transition metal oxides (TMOs) emerged as the potential pseudocapacitive electrodes due to their rich redox behavior, high abundance, environment-friendliness, ease of accessibility, remarkable electrochemical properties, and high theoretical capacitance [4]. Widening the operating voltage window of ASCs is an additional approach to improving energy density. Hybrid aqueous/organic electrolytes, referred to as hybrid electrolytes, marry the merits of aqueous and organic electrolytes to obtain a balanced operating voltage window and safety. This research aimed to develop dimanganese divanadate ( $Mn_2V_2O_7$ , MVO) particles, which were synthesized *via* a hydrothermal process and used as pseudocapacitive electrodes for ASCs. The pseudocapacitive MVO electrode offered synergistic advantages of reversible surface or near-surface Faradaic reactions for charge storage. Moreover, the influence of the annealing temperature on the phase formation, the structural and morphological features, and the electrochemical characteristics was investigated. It was observed that tailoring of the electrode material improves capacitance, and selecting an appropriate electrolyte (5 M  $NaClO_4$  in AN:  $H_2O$ ) widens the voltage window and enhances the energy density of the ASCs. The ASCs show a stability across a 2.2 V voltage window and exhibit a specific capacitance of  $156.9 F g^{-1}$  at  $0.1 A g^{-1}$  with an energy density of  $87 Wh kg^{-1}$ . Moreover, the ASCs show an impressive high-rate capability and cyclic stability for over 50,000 CV cycles. To demonstrate scalability and performance beyond proof-of-concept coin cells, pouch cells show the promising application of the MVO pseudocapacitive electrode for commercial use.

**Relevance to Circular Economy:**

Developing the MVO electrodes for ASCs with an exceptional electrochemical stability over 50,000 cycles minimizes the material degradation and extends the lifespan of electrodes. The optimized hybrid electrolyte expands the voltage window > 2.0 V, enhancing the energy density beyond symmetric EDLCs. Moreover, the use of hybrid electrolyte reduces the overall cost of the device due to low cost of ingredients and easy device fabrication. The pouch cell configuration of the MVO electrode demonstrates practical applicability in sustainable energy storage. Exploring the electrode recyclability and the materials recovery would facilitate a closed loop utilization. This recycle strategy will reduce the dependency on raw materials and advance circular strategies for next generation ASCs.

**Methodology:**

High purity chemicals were used for synthesis and electrolyte solutions that included manganese acetate tetrahydrate ( $MnO_4C_4H_6 \cdot 4H_2O$ ) (Sigma Aldrich, > 99%), ammonium vanadate ( $NH_4VO_3$ ) (Sigma Aldrich, >99%), citric acid ( $C_6H_8O_7$ ) (VWR, > 98%), Pluronic® 127 ( $C_7H_{16}O_4$ ) (Sigma Aldrich), polytetrafluoroethylene (PTFE) (VWR), acetonitrile ( $C_2H_3N$ ) (Sigma Aldrich, (99.8%), and sodium perchlorate ( $NaClO_4$ ) (Sigma Aldrich, > 98%). An adequate hydrothermal route was used for the synthesis of MVO particles, and the obtained powder was further annealed in argon atmosphere to develop the required MVO ( $Mn_2V_2O_7$ ) phase as shown in Figure 1a. Figure 2 shows the summary of different characterization techniques XRD, SEM, and TEM/HRTEM, used to investigate the structural, morphological, and surface features of developed MVO powders (VM-500, VM-600, and VM-700).

The electrochemical performance of MVO//C was assessed in both coin cells (CR2032) and pouch cells. MVO electrodes were prepared by mixing MVO powder with AB and PTFE (70:22:8 wt.%), forming a slurry with isopropyl alcohol, and rolling it into sheets. Coin cell electrodes (12 mm) were placed on Ti collectors, while pouch cell electrodes (3x3 cm) were sealed in polyethylene and aluminium casings. A 5 M  $NaClO_4$  hybrid electrolyte (AN: $H_2O$  = 2:1) was used as electrolyte with Whatman™ GF/F as separators.

**Materials Synthesis**



Figure 1 Schematic representation of the synthesis procedure of MVO powders

**Materials characterization**

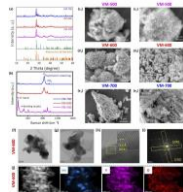


Figure 2 Structural and morphological features of developed MVO powders (a) XRD pattern, (b) Raman spectra, SEM micrographs of (c<sub>1</sub>-c<sub>2</sub>) VM-500, (d<sub>1</sub>-d<sub>2</sub>) VM-600, (e<sub>1</sub>-e<sub>2</sub>) VM-700, (f-g) TEM micrographs, (h) HRTEM image, (i) SAED pattern and (j) HAADF and mapping pattern of VM-600.

**Results & Discussion**

MVO//C-ASCs performs better than the C//C symmetric device as shown in Figure 3. Electrochemical impedance spectroscopy (EIS) reveals that the VM-600//C exhibits a low charge transfer resistance ( $R_{ct} = 8.6 \Omega$ ), enhancing ion transport due to its porous structure (Figure 3a). The quasi rectangular cyclic voltammetry (CV) curves (Figure 3b) reveals the rapid charge transfer and pseudocapacitive behaviour of the electrodes. The higher area under the CV curves than the C//C devices suggests the superior charge storage capability of VM-600//C. Galvanostatic charge-discharge (GCD) profile (Figure 3c-d) confirms superior capacitance for VM-600//C ( $156.9 F g^{-1}$  at  $0.1 A g^{-1}$ ), surpassing C//C ( $85.5 F g^{-1}$ ). The developed device exhibits an excellent rate capability to withstand at higher applied currents (Figure 3e). More importantly, the electrode shows an electrolyte stability window of 3.0 V and the device shows an operating voltage of 2.2 V with the hybrid electrolyte (Figure 3g-h). Moreover, the energy density of the developed ASCs is superior to C//C and other supercapacitor devices.

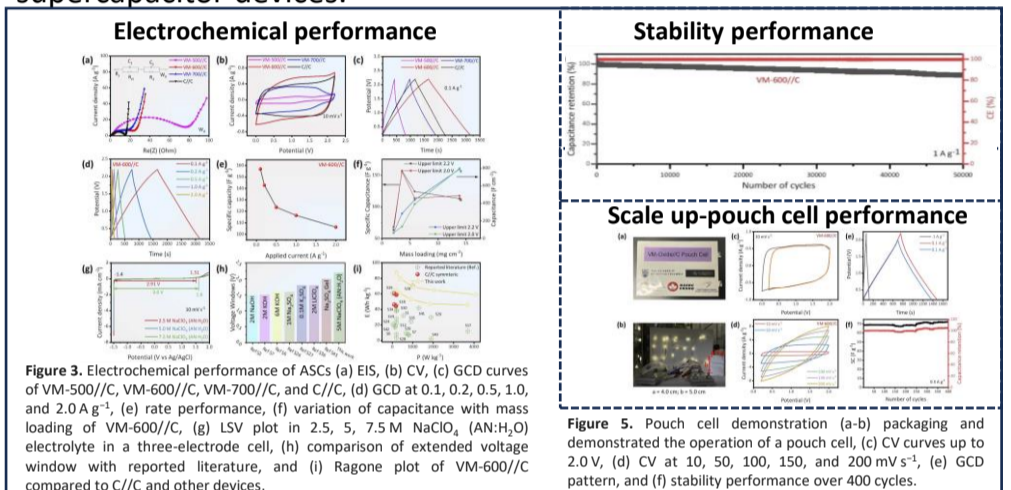


Figure 3. Electrochemical performance of ASCs (a) EIS, (b) CV, (c) GCD curves of VM-500//C, VM-600//C, VM-700//C, and C//C, (d) GCD at 0.1, 0.2, 0.5, 1.0, and 2.0  $A g^{-1}$ , (e) rate performance, (f) variation of capacitance with mass loading of VM-600//C, (g) LSV plot in 2.5, 5, 7.5 M  $NaClO_4$  (AN: $H_2O$ ) electrolyte in a three-electrode cell, (h) comparison of extended voltage window with reported literature, and (i) Ragone plot of VM-600//C compared to C//C and other devices.

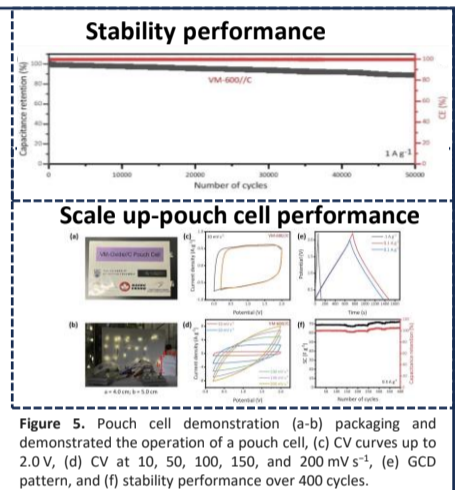


Figure 5. Pouch cell demonstration (a-b) packaging and demonstrated the operation of a pouch cell, (c) CV curves up to 2.0V, (d) CV at 10, 50, 100, 150, and 200  $mV s^{-1}$ , (e) GCD pattern, and (f) stability performance over 400 cycles.

Long term stability is an essential parameter for the practical application of any energy storage device. The VM-600//C exhibits a stability over 50,000 cycles (Figure 4). The results of the developed ASCs are summarized in Table 1. Moreover, the fabricated device exhibited a very low self-discharge making it a potential candidate for practical applications.

Table 1. Electrochemical parameters of the ASCs and symmetric C//C devices

Electrode material	Mass loading ( $mg cm^{-2}$ )	Voltage window (V)	Electrolyte	$R_s (\Omega)$	$R_{ct} (\Omega)$	SC ( $F g^{-1}$ )	E ( $Wh kg^{-1}$ )	Retention (%)
VM-600//C	3.26	0.2-2.2	5M $NaClO_4$ (AN: $H_2O$ )	2.4	8.6	156.9	87.2	80 % over 50,000 cycles
VM-600//C	3.26	0.2-2.0	5M $NaClO_4$ (AN: $H_2O$ )			144.6	65.1	92% over 20,000 cycles-
Symmetric C//C	3.35	0.2-2.2	5M $NaClO_4$ (AN: $H_2O$ )	1.0	10.8	85.4	58.9	-

The mechanistic studies reveal that the rapid redox surface reaction mechanism plays a key role in enhancing the energy density of the developed ASCs. The developed MVO electrode shows scalable potential, demonstrated by a pouch cell powering an LED with a stable performance over 400 cycles (Figure 5). The electrode exhibits excellent rate capability, stability and suitability for large scale applications.

**Conclusion & Next Steps**

MVO nanostructures were synthesized through a hydrothermal method, with reaction temperature influencing phase and morphology. The developed MVO was employed as a pseudocapacitive electrode to produce high energy density ASCs. A tailored hybrid electrolyte ( $NaClO_4$  in AN and  $H_2O$ ) expanded the operating voltage window and improved the energy density of the developed ASCs. The nanostructures improved charge transfer and capacitance. CV and GCD confirmed pseudocapacitive behavior, with no phase changes during cycling. The ASCs device outperformed symmetric EDLCs in energy density, and the samples showed exceptional cyclic stability for over 50,000 cycles. The optimized electrode was employed in a pouch cell to illuminate LED lights, confirming the promising application of the developed electrode for commercial use.

**References:**

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Further reading: R. A. Mir, J. Xu, L. Tao, E. J. Hansen, A. Khosrozadeh, M. B. Miller and J. Liu, "High-energy  $Mn_2V_2O_7//C$  asymmetric supercapacitors in aqueous/organic hybrid electrolytes", Nano Energy, 2025, 133, 110446 (doi.org/10.1016/j.nanoen.2024.110446)