# Boosting the voltage and specific energy of aqueous supercapacitors via Janus membrane

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## Abstract

A compact Janus membrane, which consists of sulfonated polystyrene and quaternized polystyrene, is used as the separator to assemble a novel carbon-based supercapacitor. The aqueous acidic and alkaline electrolyte solutions can be simultaneously used in one supercapacitor device. The carbon-based aqueous supercapacitor can not only run at a high cell voltage of 2.2 V, but also deliver a specific energy of 20.06 Wh kg-1. Moreover, such a supercapacitor with specific energy of 40-50 Wh kg-1 can be predicted after further optimization.

## Full Text

### Boosting the Voltage and Specific Energy of Aqueous Supercapacitors via Janus Membrane

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**Author Contributions:** N. Liang and Y. Ji contributed equally to data curation. J. Xu led formal analysis, investigation, and writing of the original draft, and provided funding support. D. Zuo supported formal analysis and writing of the original draft. D. Chen supported formal analysis and review & editing. H. Zhang led conceptualization, project administration, and validation.

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## Abstract

A compact Janus membrane consisting of sulfonated polystyrene and quaternized polystyrene is employed as the separator to assemble a novel carbon-based supercapacitor. Aqueous acidic and alkaline electrolyte solutions can be simultaneously used within a single device. The carbon-based aqueous supercapacitor operates at a high cell voltage of 2.2 V and delivers a specific energy of 20.06 Wh kg-1. Moreover, further optimization could yield supercapacitors with specific energy of 40-50 Wh kg-1.

**Keywords:** Energy conversion, Membranes, Aqueous electrolyte, Specific energy, Voltage

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## 1. Introduction

Energy storage serves as a key enabler for modern society, with essential applications in portable electronics, electric vehicles, and grid-scale storage. Supercapacitors and lithium-ion batteries (LIBs) represent two highly desirable energy storage technologies today [1]. Compared with LIBs, supercapacitors exhibit high specific power (10 kW kg-1) and long cycle life but suffer from low specific energy (only 5-10 W h kg-1) [2]. Consequently, resolving the specific energy limitation of supercapacitors has become a global research priority.

According to the formula E=1/2CV2, two primary strategies exist to enhance supercapacitor specific energy [3]. The first involves increasing capacitance through exploring new carbon-based materials with large surface area and high nitrogen doping levels [4-6], adopting pseudocapacitive materials with high specific capacitance [7], or adding redox species to the electrolyte [8-10]. The second strategy focuses on increasing voltage via non-aqueous electrolytes to achieve operating voltages above 3.0 V [11-13], assembling asymmetric supercapacitors with capacitor-type and battery-type electrodes [14-16], balancing electrode mass loading [17], or adjusting cutoff potentials for the two electrodes [18]. However, these methods for increasing capacitance and/or cell voltage each entail distinct disadvantages, including flammability, low ionic mobility, time-consuming fabrication, or high cost. Therefore, developing a facile approach to boost both specific energy and voltage in aqueous supercapacitors remains a significant challenge.

A Janus membrane exhibits opposing properties (e.g., hydrophilicity/hydrophobicity and positive/negative charges) on each side, showing promise for diverse applications including nanofiltration, catalytic contactors, demulsification, emulsification, aeration, fog harvesting, osmotic energy harvesting, and batteries [19,20]. A supercapacitor comprises three key components: electrode, electrolyte, and separator. All previously mentioned modification methods target the electrode and electrolyte. Herein, we propose a separator-based approach to increase both specific energy and cell voltage. A compact Janus membrane consisting of sulfonated polystyrene (SPS) on one side and quaternized polystyrene (QPS) on the other serves as the separator in a novel supercapacitor configuration (Scheme 1).

In this supercapacitor, two activated carbon electrodes are separated by the compact Janus membrane. The compartments on the SPS side and QPS side contain 1 M H2SO4 and 2 M KOH aqueous solutions, respectively. Notably, the supercapacitor still operates via the electrical double-layer mechanism and is classified as an electrical double-layer capacitor (EDLC). As shown in Scheme 1, during charging, K+ cations and SO4 2- anions accumulate at the surfaces of activated carbon on the negative and positive electrodes, respectively. Simultaneously, OH- and H+ ions migrate toward the Janus membrane and meet at the SPS-QPS interface to form H2O molecules. The discharge process proceeds conversely.

This EDLC configuration exploits the different stable potential windows of the positive and negative electrodes and their overpotentials, enabling a high operating voltage of up to 2.2 V. Consequently, its specific energy reaches at least five times that of conventional EDLCs using only 1 M H2SO4 or 2 M KOH aqueous solution. The stable potential windows of an activated carbon electrode are -1.2 to 0 V (vs. NHE) in 2 M KOH and 0 to 1.0 V (vs. NHE) in 1 M H2SO4 (Figure S1). For EDLC assembly using a Janus membrane, it is crucial that the electrode on the SPS side serves exclusively as the positive electrode and the electrode on the QPS side as the negative electrode. Otherwise, the EDLC performs poorly and exhibits a large voltage drop (~1 V) because transference of K+ cations and SO4 2- anions through the Janus membrane is blocked (Figure S2).

The capacitive performance of this EDLC is displayed in Figure 1 [Figure 1: see original paper]. Comparison of cyclic voltammetry (CV) curves under different voltage windows at a scan rate of 50 mV s-1 demonstrates that the EDLC can harness the potential windows of activated carbon electrodes in 2 M KOH and 1 M H2SO4 solutions to achieve a high cell voltage of 2.4 V (Figure 1a). The EDLC exhibits rectangular CV curves across a broad cell voltage range from 0 to 2.2 V, which is twice that of conventional carbon-based EDLCs using KOH or H2SO4 solutions (~1 V). However, the current increases significantly when the cell voltage exceeds 2.3 V, corresponding to water decomposition [21]. Galvanostatic charge-discharge (GCD) curves collected under different voltage windows at a specific current of 1 A g-1 further evaluate the electrochemical performance (Figure 1b). The discharge curves show a nearly linear relationship between voltage and time, indicating capacitor-like behavior. The absence of obvious voltage drop reflects low internal resistance. Furthermore, all specific capacitances calculated from these GCD curves are approximately 34 F g-1 (based on the total weight of anode and cathode active materials).

Figure 1c presents CV curves of the EDLC at scan rates ranging from 5 to 100 mV s-1 under 2.2 V. The CV curve at 5 mV s-1 shows a rectangular shape without noticeable redox peaks, revealing ideal capacitive behavior. Moreover, the CV curve maintains a distinct rectangular shape without obvious distortion even at 100 mV s-1, implying excellent reversibility and good rate performance. This is consistent with the nearly symmetric and linear GCD curves. The specific capacitances at various current densities under 2.2 V are plotted in Figure 1d. The specific capacitance gradually decreases with increasing current density because electrolyte ions have insufficient time to access the interior of activated carbon particles, utilizing only the outer active surfaces for charge storage at high rates. The specific capacitances are 45.8, 36.9, 34.4, 31.4, and 29.4 F g-1 at current densities of 0.1, 0.5, 1, 2, and 3 A g-1, respectively. This represents retention of approximately 64% of the original capacitance when the specific current increases from 0.1 to 3 A g-1, demonstrating high rate capability.

Figure 1e provides the Ragone plot of the EDLC under 2.2 V. The device exhibits specific energy of 12.65-28.07 Wh kg-1 and specific power of 36.46-916.56 W kg-1. At a specific current of 1 A g-1, the specific energy reaches 20.06 Wh kg-1, which is more than five times that of conventional EDLCs using only 1 M H2SO4 or 2 M KOH solution (Figure S3). This value represents one of the highest specific energies reported for carbon//carbon EDLCs in the literature (Table S1). A charged EDLC using a Janus membrane can power a green light-emitting diode (LED) for 80 s (inset of Figure 2e [Figure 2: see original paper] and Video S1) or drive a mini-fan for 39 s (Video S2), while a charged conventional EDLC with 1 M H2SO4 can only drive the mini-fan for 14 s (Video S3).

The long-term cycle stability was evaluated at a specific current of 1 A g-1 in the voltage window of 0-2.2 V (Figure 1f). The specific capacitance decreases to 96% of the initial value during the first 100 cycles, then remains above 90% of the initial value after 1500 cycles. Thereafter, the capacitance shows considerable reduction, retaining only 62% of the initial value after 2200 cycles. This degradation is primarily attributed to the deterioration of quaternary-ammonium groups on the Janus membrane via Hofmann degradation or SN2 substitution under strongly alkaline conditions [22]. Nyquist plots obtained from electrochemical impedance spectroscopy (EIS) before and after cycling are shown in the inset of Figure 1f. In the low-frequency region, the straight line nearly parallel to the imaginary axis represents ideal capacitive behavior and good ion diffusion. In the high-frequency region, the equivalent series resistance increases from 3.85 to 4.89 Ω after cycling, also attributed to degradation of quaternary-ammonium groups, which increases resistance. However, the charge-transfer resistance remains nearly unchanged (0.82-0.84 Ω) after cycling, indicating retained high charge-transfer rates between electrolyte and active materials.

It has been demonstrated that adding redox-active mediators to electrolytes can boost the specific energy of supercapacitors [9,10]. Consequently, p-phenylenediamine and hydroquinone were added to the 2 M KOH and 1 M H2SO4 compartments of the Janus membrane EDLC to further increase specific energy. This modified EDLC delivers a specific energy of 48.4 Wh kg-1 at 1 A g-1 in the 0-2.2 V window (Figure S4a) and can drive the mini-fan for 112 s (Video S4). Unfortunately, its capacitive performance seriously deteriorates, with specific capacitance retention falling below 80% after 700 cycles at 1 A g-1 (Figure S4b).

In summary, replacing the porous separator of conventional EDLCs with a com-

pact Janus membrane enables simultaneous use of KOH and H2SO4 electrolyte solutions. This EDLC not only maintains the high ionic mobility of both electrolyte solutions but also exploits the different stable potential windows of the positive and negative electrodes. The device successfully operates at 2.2 V and delivers a specific energy of 20.06 Wh kg-1 at 1 A g-1, which is over five times that of conventional EDLCs using only 1 M H2SO4 or 2 M KOH aqueous solution. This investigation provides a novel guideline for boosting the specific energy and voltage of aqueous supercapacitors based on activated carbon electrodes.

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## References

[1] N.-S. Choi, Z. Chen, S. A. Freunberger, X. Ji, Y.-K. Sun, K. Amine, G. Yushin, L. F. Nazar, J. Cho, P. G. Bruce, Angew. Chem. Int. Ed. 2012, 51, 9994-10024. [2] Y. Ma, H. Chang, M. Zhang, Y. Chen, Adv. Mater. 2015, 27, 5296-5308. [3] Z. Huaping, L. Long, V. Ranjith, L. Yong, Advanced Science 2017, 4, 1700188. [4] T. Lin, I.-W. Chen, F. Liu, C. Yang, H. Bi, F. Xu, F. Huang, Science 2015, 350, 1508-1513. [5] Y. Mei, Z. Zhen, Advanced Science 2017, 4, 1600408. [6] Z. Chen, Y. Yuan, H. Zhou, X. Wang, Z. Gan, F. Wang, Y. Lu, Adv. Mater. 2014, 26, 339-345. [7] V. Augustyn, P. Simon, B. Dunn, Energy Environ. Sci. 2014, 7, 1597-1614. [8] S.-E. Chun, B. Evanko, X. Wang, D. Vonlanthen, X. Ji, G. D. Stucky, S. W. Boettcher, Nature Communications 2015, 6, 7818. [9] R. Silvia, B. Clara, G. Marcos, M. Rosa, S. Ricardo, Angew. Chem. Int. Ed. 2011, 50, 1699-1701. [10] J. Wu, H. Yu, L. Fan, G. Luo, J. Lin, M. Huang, J. Mater. Chem. 2012, 22, 19025-19030. [11] E. Mourad, L. Coustan, P. Lannelongue, D. Zigah, A. Mehdi, A. Vioux, Stefan A. Freunberger, F. Favier, O. Fontaine, Nat. Mater. 2016, 16, 446. [12] R. Na, C.-W. Su, Y.-H. Su, Y.-C. Chen, Y.-M. Chen, G. Wang, H. Teng, Journal of Materials Chemistry A 2017, 5, 19703-19713. [13] H.-C. Huang, Y.-C. Yen, J.-C. Chang, C.-W. Su, P.-Y. Chang, I. W. Sun, C.-T. Hsieh, Y.-L. Lee, H. Teng, Journal of Materials Chemistry A 2016, 4, 19160-19169. [14] J. Yan, Z. Fan, W. Sun, G. Ning, T. Wei, Q. Zhang, R. Zhang, L. Zhi, F. Wei, Adv. Funct. Mater. 2012, 22, 2632-2641. [15] K. Qingqing, G. Cao, Z. Xiao, Z. Minrui, Z. Yong-Wei, C. Yongqing, Z. Hua, W. John, Adv. Mater. 2017, 29, 1604164. [16] N. Jabeen, A. Hussain, Q. Xia, S. Sun, J. Zhu, H. Xia, Adv. Mater. 2017, 29. [17] J. H. Chae, G. Z. Chen, Electrochim. Acta 2012, 86, 248-254. [18] M. Yu, D. Lin, H. Feng, Y. Zeng, Y. Tong, X. Lu, Angew. Chem. Int. Ed. 2017, 56, 5454-5459. [19] Y. Hao-Cheng, H. Jingwei, C. Vicki, X. Zhi-Kang, Angew. Chem. Int. Ed.

2016, 55, 13398-13407. [20] Y. Hao-Cheng, X. Yunsong, H. Jingwei, C. A. K., C. Vicki, D. S. B., Adv. Mater., 0, 1801495. [21] K. Fic, M. Meller, E. Frackowiak, J. Electrochem. Soc. 2015, 162, A5140-A5147. [22] G. Couture, A. Alaaeddine, F. Boschet, B. Ameduri, Prog. Polym. Sci. 2011, 36, 1521-1557.

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