

Designing organic pseudocapacitors through molecular hybridization

Alae Eddine Lakraychi¹ and Yan Yao^{1,*}

In this issue of *Joule*, Dincă and co-workers showcase a fused aromatic organic electrode material that exhibits remarkable physicochemical properties, such as high electrical conductivity, rapid ion transport, and insolubility in the electrolyte. As a result, the material functions as an excellent pseudocapacitive material that can efficiently store and discharge energy in a short period of time.

Organic electroactive molecules (OEMs) present a credible alternative to conventional energy storage systems, thanks to their abundance of constituent elements, high design flexibility, and high capacity.¹ However, their practical application as the main active material in energy storage has been largely hindered by high solubility in the electrolyte and poor intrinsic electronic conductivity, leading to inferior electrochemical performances compared to their inorganic counterparts. To address these challenges, several molecular engineering strategies have been developed, but they often compromise specific energy and fail to meet all required figure of merits.^{2–4}

Molecular hybridization offers a new approach to designing high-performance organic electrode materials that can fulfill all primary requirements. This strategy involves combining two or more active molecules to create a new compound with improved properties, and the richness of organic chemistry allows for a vast array of possible combinations. This concept has been explored in medicinal chemistry and involves combining multiple molecular features into a single chemical compound that can achieve multiple targets simultaneously.⁵

In their paper, "High-rate, high-capacity electrochemical energy storage in hydrogen bonded fused aromatics," published in this issue of Joule, Dincă and co-workers employed molecular hybridization strategy to design oligomer poly(bis-tetraaminobezoguinone) (pBTABQ) as an organic electrode material.⁶ pBTABQ can be synthesized in gram-scale amounts through a two-step process using tetraaminobenzoquinone (TABQ) as the precursor, as shown in Figure 1A. This organic material possesses several key molecular features that are not typically found in other conventional organic electrode materials. First, its repeat unit BTABQ has a planar fused tricyclic aromatic backbone with extended conjugation that contains two diaminobenzoquinone moieties (acceptor) bridged by a dihydro-pyrazine core (donor). Second, the high density of carbonyl (C=O) and imine (C=N) groups within the molecule serve as redox active centers for a multi-electron redox reaction, as illustrated in Figure 1B. Finally, the presence of amines as ending groups and donor-acceptor (D-A) moieties allow for the formation of a strong polymeric network through hydrogen bonding and π - π stacking, which facilitates further extended conjugation (Figure 1C).

The unique molecular features of pBTABQ combine synergistically to make it an excellent candidate as an electrode material (Figure 1D). The insolubility in aqueous and organic electrolytes, due to the joint hydrogen bonding and π - π stacking, is highly



desirable for long-term cycling stability. Moreover, these interactions enable significant intermolecular electronic delocalization across the polymeric network. The partial oxidation of pBTABQ units generates the formation of organic free radicals in the fused aromatic backbone, contributing to the high bulk electrical conductivity of 0.40 \times 10⁻⁶ S cm⁻¹ measured at room temperature, which is several orders of magnitude higher than most organic materials. Furthermore, through continuous rotation electron diffraction and cryogenic electron microscopy, the authors demonstrated that the oligomeric pBTABQ units crystallize as stacked two-dimensional layers, with an interlayer spacing of 3.14 Å that could serve as open channels for facile Li-ion diffusion. These physicochemical properties, combined with the high theoretical capacity (389 mAh q^{-1}), make pBTABQ a promising candidate for high-rate electrochemical energy storage. The stable network, high electrical conductivity, open channels, and facile ionic transport could be key enablers for high-rate energy storage.

In terms of electrochemical performance, pBTABQ exhibited unexpected electrochemical properties in an aqueous neutral electrolyte. Unlike most OEMs, cyclic voltammograms (CVs) displayed quasi-rectangular curves at scan rates ranging from 0.2 to $30 \, \text{mV s}^{-1}$, and galvanostatic charge-discharge measurements revealed triangular voltage profiles at current densities ranging from 2 to 10 A g^{-1} . These electrochemical properties are highly unusual among OEMs and indicate a capacitive-like charge storage mechanism known as pseudocapacitive.

¹Department of Electrical and Computer Engineering and Texas Center for Superconductivity at the University of Houston, University of Houston, Houston, TX 77204, USA *Correspondence: yyao4@uh.edu

https://doi.org/10.1016/j.joule.2023.04.012

Previews

Joule

CellPress



Figure 1. Pseudocapacitive charge storage in poly(bis-tetraaminobezoquinone)

(A) Molecular design and syntheses employed in the fabrication of pBTABQ. 5,7,12,14-pentancetetrone (PT) is shown for comparison.

(B) Schematic depiction of redox centers carbonyl/enolate and imine/amine involved in the charge storage.

(C) Illustration of the polymeric network composed of oligomeric pBTABQ units, highlighting the hydrogen bonding and D-A π - π stacking. (D) A molecular hybridization for organic pseudocapacitive charge storage.

Adapted from Chen et al.⁶

According to Conway, a pseudocapacitive charge storage mechanism occurs when reversible redox reactions take place at or near the surface of the electrode material, leading to an electrochemical response that resembles capacitive storage in electrochemical double-layer capacitors (EDLCs), a non-faradaic process.⁷ This is in contrast to OEMs that store energy via charge compensation involving conversion reaction or intercalation of metal cations in a host. These systems are characterized by plateaus in the electrochemical response.^{8,9}

In the case of pBTABQ, the pseudocapacitance originates from the delocalization of charges stored intramolecularly within the fused aromatic backbones of pBTABQ units and intermolecularly through H-bonding and π - π stacking across the polymeric network. The simultaneous existence of all these features is essential for achieving pseudocapacitive charge storage in pBTABQ. This was further supported by the battery-like electrochemical behavior of TABQ, which only displays intermolecular H-bonding but lacks extended conjugation, and 5,7,12,14-pentancetetrone (PT), which is composed of only an extended π -conjugated system but lacks H-bonding (Figure 1A). The charges stored in both molecules are localized at the molecular level, resulting in well-defined redox features.

Pseudocapacitive charge storage can be classified into two categories: fast surface reactions and non-diffusionlimited intercalation reactions. The authors utilized a combination of characterization techniques, such as *in situ* wide-angle X-ray scattering, powder X-ray diffraction, energydispersive X-ray spectroscopy, and angle-resolved X-ray photoelectron spectroscopy, to demonstrate that pBTABQ's pseudocapacitance was governed by the intercalation mechanism. This was supported by the material's low specific surface area (20 m² g^{-1}) and its ability to intercalate various hydrated alkali and alkaline earth ions (Li⁺, Na⁺, and Mg²⁺), but not tetraethylammonium (TEA⁺), likely due to its relatively larger size. The material delivered a capacitance of 510 F g-1 at 0.2 mV s⁻¹ and 300 F g⁻¹ at 10 mV s⁻¹ upon prolonged cycling (20,000 cycles) without any change in particle size or morphology. These capacitance values are comparable to a recently reported organic pseudocapacitive material, perylene diimide-hexaazatrinaphthylene (PHATN), which stores charges through surface reactions.¹⁰



The authors also investigated the pseudocapacitance of pBTABQ in aqueous electrolytes at different pH values. They found that the specific capacity increased when the material was cycled in low pH (0-1) or high pH (>13) electrolytes, reaching 310 and 272 mAh g^{-1} , respectively. The corresponding CVs revealed the presence of broad redox peaks, but the redox process was not limited by diffusion. This suggests that the material stores more charges, and the pseudocapacitance process is maintained in these extreme acidic and alkaline aqueous electrolytes. To increase the operating voltage, the authors explored the compound in a water-in-salt electrolyte (WiSE). They obtained similar capacitance values to those recorded in aqueous neutral electrolyte at different mass loadings (up to 6.0 mg cm^{-2}) with excellent capacitance retention over prolonged cycling (40,000 cycles). Interestingly, the utilization of WiSE increased the capacity from 160 to 225 mAh g^{-1} as compared to aqueous neutral electrolyte, due to the intercalation of a larger number of metal cations. Moreover, the material achieved an impressive rate capability, delivering a specific capacity of 100 mAh g^{-1} within 60 s. Overall, pBTABQ's outstanding electrochemical performances make it a promising candidate for bridging the gap between batteries and capacitors.

The results presented by the authors demonstrate that competitive electrode materials can be designed from earth-abundant elements (C, H, O, N, and S). Molecular hybridization is emerging as an efficient design strategy to create organic electrode materials with unprecedented physicochemical and electrochemical properties. Despite being in its infancy, the field of organic batteries presents a promising and unexplored chemical playground for the development of efficient and competitive energy storage systems.

ACKNOWLEDGMENTS

The work presented herein was funded in part by the Advanced Research Projects Agency-Energy (ARPA-E), US Department of Energy, under award number DE-AR0001548.

DECLARATION OF INTERESTS

Y.Y. is a co-founder of LiBeyond LLC and Solid Design Instruments LLC.

REFERENCES

- Poizot, P., Gaubicher, J., Renault, S., Dubois, L., Liang, Y., and Yao, Y. (2020). Opportunities and Challenges for Organic Electrodes in Electrochemical Energy Storage. Chem. Rev. 120, 6490–6557.
- Renault, S., Gottis, S., Barrès, A.-.L., Courty, M., Chauvet, O., Dolhem, F., and Poizot, P. (2013). A green Li–organic battery working as



a fuel cell in case of emergency. Energy Environ. Sci. *6*, 2124–2133.

- Liang, Y., Chen, Z., Jing, Y., Rong, Y., Facchetti, A., and Yao, Y. (2015). Heavily n-Dopable m-Conjugated Redox Polymers with Ultrafast Energy Storage Capability. J. Am. Chem. Soc. 137, 4956–4959.
- Rambabu, D., Lakraychi, A.E., Wang, J., Sieuw, L., Gupta, D., Apostol, P., Chanteux, G., Goossens, T., Robeyns, K., and Vlad, A. (2021). An Electrically Conducting Li-Ion Metal–Organic Framework. J. Am. Chem. Soc. 143, 11641–11650.
- Ivasiv, V., Albertini, C., Gonçalves, A.E., Rossi, M., and Bolognesi, M.L. (2019). Molecular Hybridization as a Tool for Designing Multitarget Drug Candidates for Complex Diseases. Curr. Top. Med. Chem. 19, 1694–1711.
- Chen, T., Banda, H., Yang, L., Li, J., Zhang, Y., Parenti, R., and Dincă, M. (2023). High-rate, high-capacity electrochemical energy storage in hydrogen-bonded fused aromatics. Joule 7, 986–1002. https://doi. org/10.1016/j.joule.2023.03.011.
- Simon, P., and Gogotsi, Y. (2020). Perspectives for electrochemical capacitors and related devices. Nat. Mater. 19, 1151–1163.
- Dong, H., Tutusaus, O., Liang, Y., Zhang, Y., Lebens-Higgins, Z., Yang, W., Mohtadi, R., and Yao, Y. (2020). High-power Mg batteries enabled by heterogeneous enolization redox chemistry and weakly coordinating electrolytes. Nat. Energy 5, 1043–1050.
- Lee, M., Hong, J., Lopez, J., Sun, Y., Feng, D., Lim, K., Chueh, W.C., Toney, M.F., Cui, Y., and Bao, Z. (2017). High-performance sodium-organic battery by realizing foursodium storage in disodium rhodizonate. Nat. Energy 2, 861–868.
- Russell, J.C., Posey, V.A., Gray, J., May, R., Reed, D.A., Zhang, H., Marbella, L.E., Steigerwald, M.L., Yang, Y., Roy, X., et al. (2021). High-performance organic pseudocapacitors via molecular contortion. Nat. Mater. 20, 1136–1141.