

Charge Up in Wired Covalent Organic Frameworks

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Crystalline porous covalent organic frameworks (COFs) with suitable redox-active sites were found to be useful as electrodes for capacitive energy storage.^{1–4} However, the bottleneck issues of COFs, i.e., their poor electrical conductivity and instability, greatly limit their practical implementation. Now, a strategy has been developed to overcome these obstacles and enable the use of COFs for high performance energy storage.⁵

Conducting polymers, such as polyacetylene, polyaniline, polypyrrole, and polyethylenedioxythiophene (PEDOT), have been widely used as pseudocapacitive electrode materials.⁶ However, these polymers usually show low cycle stability as a result of repeated swelling and shrinking during charge–discharge cycles. By confining these polymers within porous frameworks such as metal–organic frameworks, cycling stability can be improved while retaining their electrical conductivity and mechanical stability. By virtue of well-defined one-dimensional open channels, two-dimensional (2D) COFs are suitable candidates for encapsulating conducting polymers within their pores. The function of such spatial confinement in COFs is 2-fold. One is that the stability of the conjugated polymers can be enhanced. Another one is that the conductivity of the COFs can be improved. These two effects play a vital role in capacitive energy storage.

Recently, Dichtel and co-workers have explored this strategy by using a PEDOT-modified redox-active COF (DAAQ-TFP COF) to achieve extremely high-rate charging and high volumetric energy storage capacity, as reported in *ACS Central Science*.⁵ The DAAQ-TFP COF is chemically stable and possesses anthraquinone redox-active sites on each edge of the hexagonal polygons. The ordered DAAQ-TFP COF film was grown on gold electrode with controlled thickness ($\sim 1 \mu\text{m}$), and then 3,4-ethylenedioxythiophene (EDOT) was electropolymerized within the pores to prepare

Dichtel and co-workers dramatically improve electrochemical performance of conductive polymers, as explained here by Jiang and co-workers.

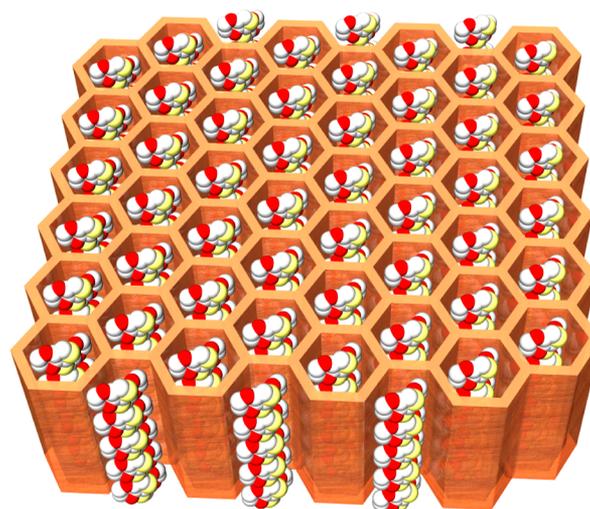


Figure 1. Redox-active COFs (orange frame) wired with conducting PEDOT chains confined within the nanopores for energy storage.

PEDOT-modified COF films (Figure 1). Interestingly, the PEDOT-modified DAAQ-TFP COF composite films exhibited a dramatically enhanced current response in cyclic voltammetry compared with the pristine DAAQ-TFP COF film. The improved current response was attributed to the wiring effect that PEDOT chains facilitate for the electron transport between electrodes and the redox-active sites of the DAAQ-TFP COF, while vertical ordered pore channels help to improve ion transport by shortening the diffusion distance. The composite COF film ($1 \mu\text{m}$ thick) exhibited

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faradaic charge storage capacity of up to 9.3 mC, corresponding to an accessibility of 97% anthraquinone redox-active sites for charge storage. Moreover, the composite COF film retained their well-defined redox responses and charge densities at a scan rate up to 500 mV s⁻¹. By contrast, the unmodified COF film showed only 0.23 mC, corresponding to accessibility of only 3% redox-active sites at a low scan rate of 20 mV s⁻¹. Therefore, the PEDOT-modified COF films exhibited a 40-fold increased charge storage capacity compared to the unmodified film.

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discharged at a very high rate of 100 C that corresponds to a charging or discharging time of only 36 s, can retain 80% capacitance of those charged or discharged at 10 C (360 s charging or discharging time). The volumetric capacitance of COF composite retains 50% of its maximum capacitance (350 F cm⁻³) even at an extremely high charging rate of 1600 C, corresponding to a complete charge time of only 2.25 s. By contrast, the unmodified COF film showed a low volumetric capacitance of 20 F cm⁻³ at 10 C, which decreased further at high charge–discharge rates. Compared to activated carbons, carbon nanotubes, carbon spheres, porous carbons and graphene (volumetric capacitance <200 F cm⁻³),^{7–10} the volumetric capacitance of the COF system is impressive. Notably, the COF composite showed stable performance over 10000 charge–discharge cycles.

This strategy offers a way to overcome the major issues in developing COFs for capacitive energy storage. Especially, the synergistic structural effects of the composite materials, i.e., the crystalline redox-active frameworks and the confined conducting PEDOT chains within the channels, enable the composite films to achieve outstanding performance in energy storage. The COF films upon introduction of PEDOT chains became less porous or even nonporous. As a future issue, leaving sufficient porosity in the composite film for promoting ion transport deserves further investigation. Another issue is to achieve high power and energy densities; designing 2D COFs with dense redox-active sites is promising and deserves further study. For practical application, large-scale synthesis and cost-effective performance have to be considered in the future.^{6,7}

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