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Cite this article as:

Iqbal Rashid, Badshah Amir, Ma Ying-Jie, Zhi Lin-Jie. An Electrochemically Stable 2D Covalent Organic Framework for High-performance Organic Supercapacitors[J]. *Chinese J. Polym. Sci.*, 2020, 38(5): 558-564. doi: 10.1007/s10118-020-2412-z

View online: <https://doi.org/10.1007/s10118-020-2412-z>

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An Electrochemically Stable 2D Covalent Organic Framework for High-performance Organic Supercapacitors

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Electronic Supplementary Information

Abstract An electrochemically stable two-dimensional covalent organic framework, PI-COF, has been synthesized by a scalable solvothermal method. PI-COF possesses a highly crystalline structure, well-defined pores, high specific surface area, and cluster macrostructure. Thanks to these features, PI-COF can work as electrode materials in organic supercapacitors, exhibiting a specific capacitance of 163 F/g at 0.5 A/g over a wide potential window of 0–2.5 V. Moreover, PI-COF shows excellent rate performance, which can deliver 96 F/g even at a high current density of 40 A/g. Because of the high capacitance and wide potential window, PI-COF has achieved a superior energy density of 35.7 W·h/kg at a power density of 250 W/kg. Most importantly, due to the remarkable electrochemical stability, the PI-COF based device shows outstanding cycling stability with 84.1% capacitance maintained (137 F/g) after 3.0×10^4 charged/discharged cycles at 1 A/g. This work should shed light on designing new COF-based electrode materials for supercapacitors and other electrochemical devices.

Keywords 2D COFs; Electrochemically stable; Electrode materials; High energy density; Organic supercapacitors

Citation: Iqbal, R.; Badshah, A.; Ma, Y. J.; Zhi, L. J. An electrochemically stable 2D covalent organic framework for high-performance organic supercapacitors. *Chinese J. Polym. Sci.* 2020, 38, 558–564.

INTRODUCTION

Nowadays, energy demand is increasing exponentially in every sector.^[1] Many energy storage devices, including capacitors,^[2] lead batteries,^[3] fuel cells,^[4] lithium ion batteries,^[5] lithium sulfur batteries,^[6] etc., have been invented to meet the rising demand for energy storage and conversion. Among these devices, supercapacitors (SCs) have gained tremendous attentions because of their distinguishing characteristics, such as high power density, fast charge/discharge rate, long lifespan, and good safety.^[7–12] Nevertheless, the low energy density is still the key challenge for SCs, which limits their application.^[1,13–17] The energy density of SCs can be enhanced by increasing specific capacitance or potential or both of them, because the energy density is proportional to specific capacitance and the square of potential. This can be accomplished by choosing proper electrode materials, which have high specific capacitance and can work with electrolytes having broad potential.^[18,19] In the past few years, as new emerging electrode

materials for SCs, covalent organic frameworks (COFs), especially two-dimensional COFs (2D COFs), have drawn increasing attention due to their high surface area, extended π conjugated structures, crystalline frameworks, and adjustable functionality.^[20] High surface area provides high capacity for charge storage, contributing mainly the electric double layer capacitor (EDLC) behavior.^[15,21–25] Extended π conjugated structures benefit the electronic conductivity of 2D COFs.^[26,27] Well-defined pore structures facilitate the electron/ion transport and electrolyte diffusion, so as to ensure the electrochemical process occurs with high efficiency.^[28,29] Adjustable functionality enables to tune the capacitive character by atomic manipulation and generate extra capacitance from redox reactions.^[29–34] With COF-based electrode materials, significant progress has been made in improving the performance of SCs. However, COF-based electrode materials still suffer from poor rate performance and inferior cycling stability due to their low electrochemical stability.^[33,35–42]

Herein, we prepared an electrochemically stable 2D COF named PI-COF for SCs by condensation of pyrene-1,3,6,8-tetramine (PTA) with 1,2,4,5-benzenetetracarboxylic anhydride (PMDA). Pyrene-based conductive units, PTA, should facilitate the electron transport in SCs because of their large conjugated cores; PTA units provide pseudocapacitance by redox reactions of carbonyl groups. PI-COF has a highly crystalline

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Special Issue: Polymers for Energy and Electronic Devices

Received December 23, 2019; Accepted February 24, 2020; Published online March 25, 2020

structure and well-defined pores and plenty of redox groups. As a result, PI-COF delivers extraordinary capacitance with organic electrolytes in a wide potential range (0–2.5 V), giving the excellent energy density of 35.7 W·h/kg at a power density of 250 W/kg. Most importantly, PI-COF displays excellent cycling stability, which still shows a specific capacity retention of 79.3% after 3.0×10^4 charge-discharge cycles, exhibiting remarkable electrochemical stability.

EXPERIMENTAL

Synthesis of PI-COF

A Pyrex tube was charged with PMDA (52.4 mg, 0.20 mmol) and PTA (26.2 mg, 0.10 mmol) in a solution of 0.75 mL mesitylene, 0.75 mL NMP, and 0.08 mL isoquinoline. The tube was flash frozen at 77 K (liquid nitrogen bath), evacuated, and flame sealed. The reaction mixture was heated at 200 °C for 7 days, affording a brown precipitate. The precipitate was isolated by filtration over a medium glass frit and washed with anhydrous THF (50.0 mL). The product was immersed in anhydrous THF (40.0 mL) for 8 h, during which the activation solvent was decanted and replaced four times. The solvent was removed under vacuum at 80 °C to afford PI-COF as a brown powder (51.2 mg, 80%).

Electrochemical Measurement

Electrochemical measurements were done after fabrication of symmetric SCs system (a coin-type cell of 2032 size) using 1 mol/L lithium bis(trifluoromethanesulfonyl)imide [LiN(CF₃SO₂)₂, LITFSI] as the electrolyte. 1 mol/L LITFSI electrolyte

consisted of 1,3-dioxolane (DOL) and dimethoxyethane (DME) (1:1, W:W). The working electrode was made of PI-COF (80 wt%), Super P conductive carbon black (15 wt%), and polytetrafluoroethylene (5 wt%, 60% in water, and diluted to 6% before use) in an agate mortar. The electrode film was dried under vacuum at 120 °C for 12 h, and cut to circular tablets with a diameter of 9 mm and a mass of about 1–2 mg.

Two electrodes with nearly the same mass were pressed between the stainless-steel wire meshes (316L, 400 meshes, and a diameter of 15 mm), respectively, as the two symmetric working electrodes. A sulfonated polypropylene membrane was used as a separator. The assembled coin cell SCs were pressed at 0.207 MPa and kept stationary overnight so that the electrolyte could establish among all the components of the SCs. Cyclic voltammetry (CV) curves, galvanostatic charge-discharge curves, and Nyquist plots were collected on a CHI660D electrochemical workstation at room temperature (25 °C). The specific capacitance (C , F/g) was calculated from the slope of discharge curve using the formula: $C = 2It/mV$, where I (unit: A) is the discharge current, m (unit: g) is the mass of PI-COF in one electrode, t (unit: s) is the discharge time, and V (unit: V) is the discharge voltage. The energy densities (E , W·h/kg) were calculated by $E = 1/8CV^2$ (1000/3600). The power densities (P , W/kg) were calculated by $P = E/(t/3600)$.

RESULTS AND DISCUSSION

As shown in Fig. 1, PI-COF was synthesized as a brown powder

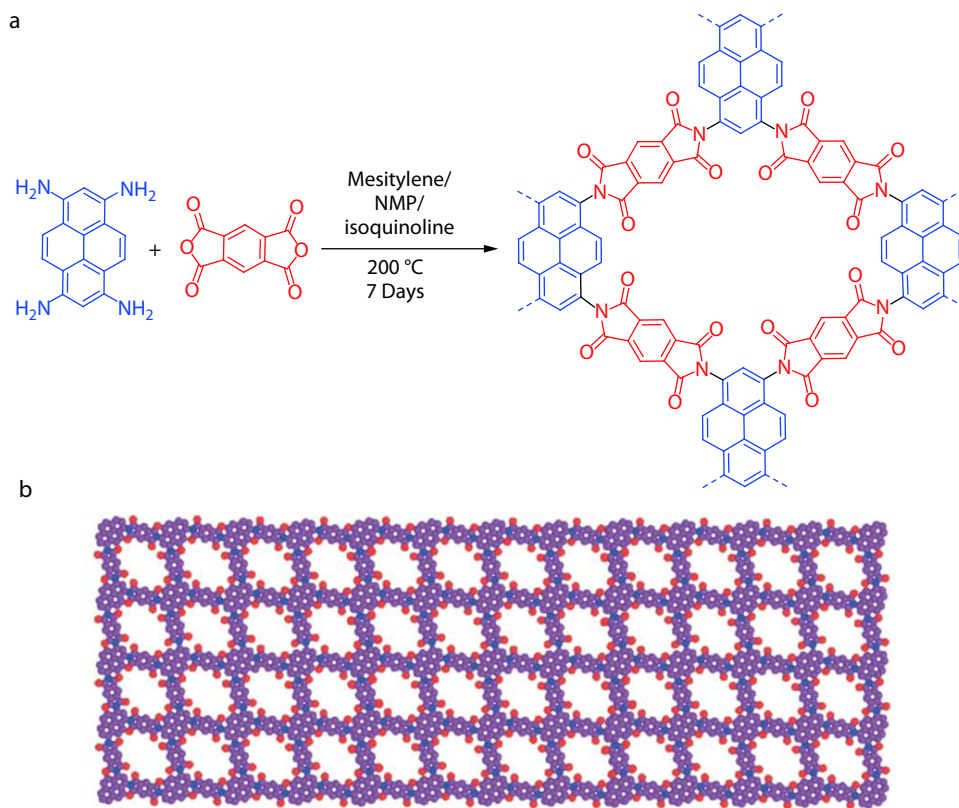


Fig. 1 Chemical structure: (a) Synthetic route to PI-COF. (b) Schematic structure of PI-COF.

by condensation of PMDA and PTA using solvothermal strategy. The detailed structure of PI-COF was analysed by Fourier-transform infrared (FTIR) spectroscopy. The FTIR spectra of PMDA, PTA, and PI-COF show that the vibration bands owing to NH_2 groups of PTA (3329 cm^{-1}) and $(\text{C}=\text{O})_2\text{O}$ units of PMDA (1622 cm^{-1}) disappeared after reaction (Fig. 2a). However, the FTIR spectrum of PI-COF indicates the formation of imide linkage with the characteristic band at 1125 cm^{-1} , confirming the framework constructed by repeating units using C–N bonds. The vibration band of conjugated benzene ring structure at 1363 cm^{-1} , and bands of carbonyl functional group at 1720 and 1744 cm^{-1} were also observed. Thus, PI-COF with the chemical structure as demonstrated in Fig. 1 was confirmed by FTIR analysis. The spectrum of ^{13}C cross-polarization magic angle spinning (CP/MAS) NMR displays two broad signals at 137 and 126 ppm, which indicates the aromatic carbon structure of benzene rings from PMDA and pyrene cores from PTA in the framework (Fig. S3 in the electronic supplementary information, ESI). The signal at 167 ppm is assigned to the carbonyl functional group from imide linkages. This characterization further proves that PI-COF contained all the required functional groups as shown in Fig. 1.

After condensation of PMDA and PTA, benzene rings and pyrene cores were periodically linked by imide linkers, affording PI-COF with the highly crystalline structure that was revealed by the XRD measurements in conjunction with structure simulation (Fig. 2b). As shown in Fig. 2(b), the strongest peaks at 1.1° and 3.5° can be assigned to the (100) and (220) facet of a regularly ordered rectangle lattice, respectively. The peak at 25.9° is assignable to the (001) facet (π - π stacking), which can be also observed by the parallel alignment (d -spacing) of 2D sheets in the TEM images (Figs. 3b and 3c). The experimental pattern (black curve) is in excellent agreement

with the simulated one (red curve), as evidenced by their negligible difference (blue curve). These results suggest that PI-COF was highly crystalline in nature and close packed. The inter layer distance of neighboring nano sheets in PI-COF was further confirmed by HRTEM, showing the d -spacing of $3.33\text{ \AA}$ ascribed to the (001) facet (Fig. 2b). Field-emission scanning electron microscopy (FE-SEM) revealed that 2D PI-COF formed into micron-grade sheets which further assembled into clusters (Fig. 3d).

Theoretically, the regularly ordered rectangle lattice of PI-COF gives rise to nano pores (diameter = 1.8 nm), which is supported by the experimental results of BET (Brunauer-Emmett-Teller) as shown in Fig. 4(a). The nitrogen sorption measurement at 77 K shows that PI-COF was microporous, displaying typical type I reversible sorption profiles and the significant uptake in the low-pressure region ($P/P_0 < 0.05$) (Fig. 4b). The BET specific surface area of PI-COF was estimated to be $375\text{ m}^2/\text{g}$.

So, it is clear that PI-COF possessed a hierarchical porous structure which consisted of nano pores and micron-grade sheets and clusters. PI-COF was highly crystalline and porous in nature, providing channels for the diffusion of electrolyte ions when it works as electrode materials. In addition, its high specific surface area should benefit the capacity of ion storage. Therefore, PI-COF is a highly promising electrode material for SCs.

The electrochemical performance of PI-COF was evaluated by cyclic voltammetry (CV), galvanic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS) in 1 mol/L LiTFSI solution using conventional two electrode system. As shown in Fig. 5(a), the electrochemical behavior of PI-COF was evaluated by CV at different scan rates from 5 mV/s to 200 mV/s over a potential window of $0\text{--}2.5\text{ V}$. Obviously, PI-

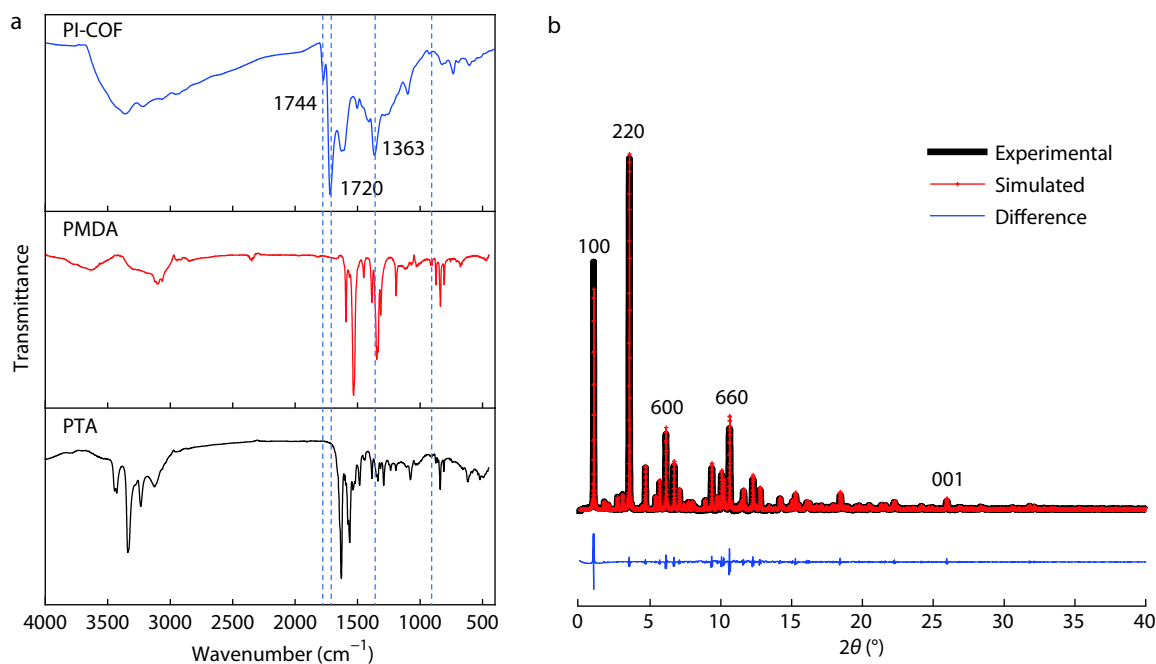


Fig. 2 (a) PXRD profile of PI-COF (black: experimentally observed XRD; red: Pawley-refined pattern simulated XRD result; blue: difference between experimental and simulated XRD). (b) FTIR spectra of PI-COF and the two monomers.

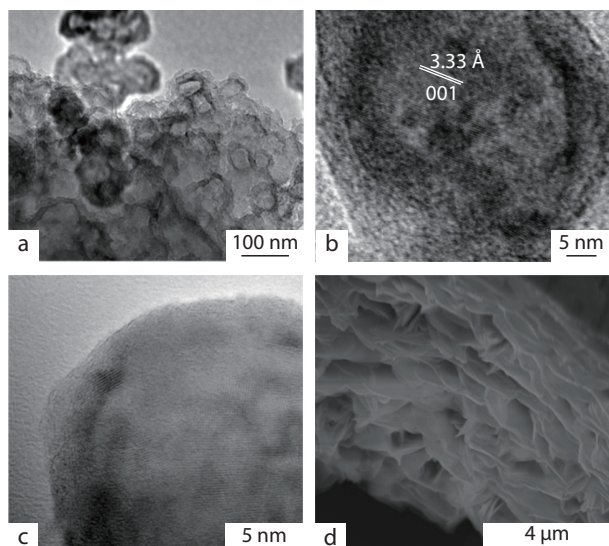


Fig. 3 (a) TEM image of PI-COF; (b, c) High-resolution TEM images of PI-COF; (d) SEM image of PI-COF.

COF displayed redox peaks at different scan rates, corresponding to the redox reaction of carbonyl groups in imide units. In the redox process, carbonyl groups in the imide rings undergo a reversible conversion to enolate functionality, contributing pseudocapacitance to the system. Moreover, the CV curves demonstrate nearly rectangular shapes even at a high scan rate of 200 mV/s, indicating the highly capacitive nature and a fast and efficient charge transfer. The GCD curves of PI-COF at various current densities ranging from 0.5 A/g to 4 A/g exhibit nearly triangular shapes, further confirming the outstanding capacitive behavior of PI-COF (Fig. 5b). Significantly, PI-COF showed admirable specific capacitance of 163 F/g at 0.5 A/g, which is, to the best of our knowledge, among the highest in the COF-based electrode materials till date. The high capacitance of PI-COF in the organic electrolyte can be attributed to the high specific surface area that ensures the high mass uptake of electroactive materials, the uniform pores that facilitate the diffusion of ions, and the redox behavior of imide units that provide extra capacitance. In addition, PI-COF showed remarkable rate capability with capacitance retention of 59% when the current density was increased from 0.5 A/g up to 40 A/g (Fig. 5c). The good rate capability of PI-COF can be ascribed to its unique structure. The cluster-like structure formed by PI-COF micron-grade sheets would benefit the efficient infiltration of the electrolyte. The highly crystalline structure and well-defined pores provide channels, allowing fast transport of ions. Moreover, the pyrene cores embedded in the framework of PI-COF ensure the fast transfer of electrons.

The capacitive behavior of the electrochemical cell was also investigated by electrochemical spectroscopy. The typical Nyquist impedance measurement has been carried out over a frequency range of 100 kHz to 100 MHz in an organic system (Figs. 5d and 5e). The Z' -intercept of the Nyquist plot is the equivalent series resistance (ESR) corresponding to the resistance of the electrolyte, internal resistance of the active material and substrate, and the contact resistance at active materi-

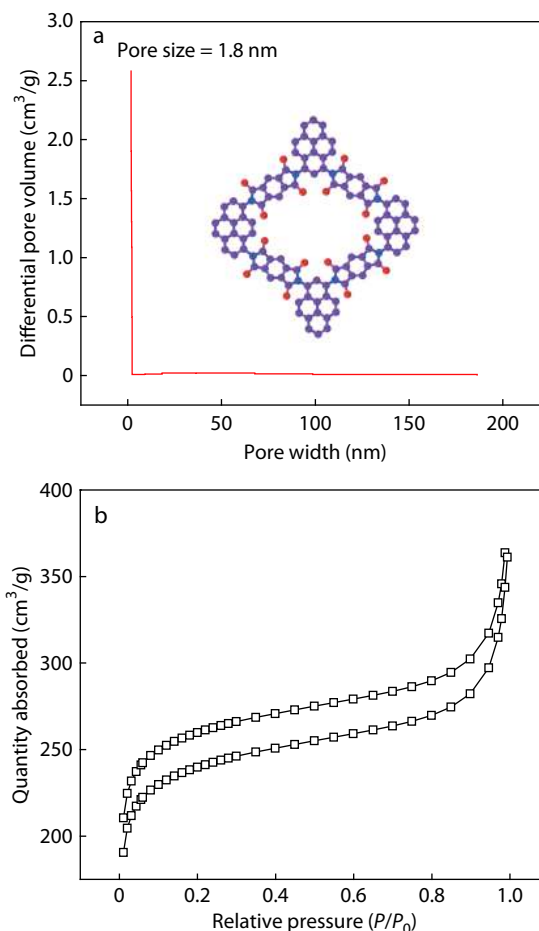


Fig. 4 BET analysis: (a) Pore size distribution of PI-COF; (b) N_2 adsorption-desorption isotherms of PI-COF at 77 K.

al-current collector interface. Initially, the ESR was 3.11 Ω , while it was increased up to 25.2 Ω after 1.0×10^4 charge/discharge cycles at 1 A/g, which is well known phenomena in SCs. The impedance spectrum shows a semi-circle in the high frequency region, whereas straight line in the low frequency region, implying that the charge transfer at the electrode electrolyte interface in the high frequency region and mass transfer process in the low frequency region.^[43] The diameter of the semi-circle indicates the charge transfer resistance (R_{ct}) of the supercapacitor. It can be observed that R_{ct} was increased from 121 Ω to 130 Ω after 1.0×10^4 charge/discharge cycles at 1 A/g, indicating that PI-COF still processes efficient charge transfer process after long-term cycling. The straight line located in the low frequency region indicates the capacitive behavior—a pure EDLC should have an ideal 90° phase angle, meaning excellent capacitive behavior without diffusion limit over the electrode electrolyte interfaces. Interestingly, after 1.0×10^4 cycles, the slopes increased towards an angle of 90° implying an increase in the phase angle, and consequently suggesting the better capacitive behavior after long-term cycling. As a result, the EIS analyses elucidate that this crystalline material provides better diffusion capability, which further leads to better rate capability.

As shown in Fig. 5(f), the overall performance of PI-COF

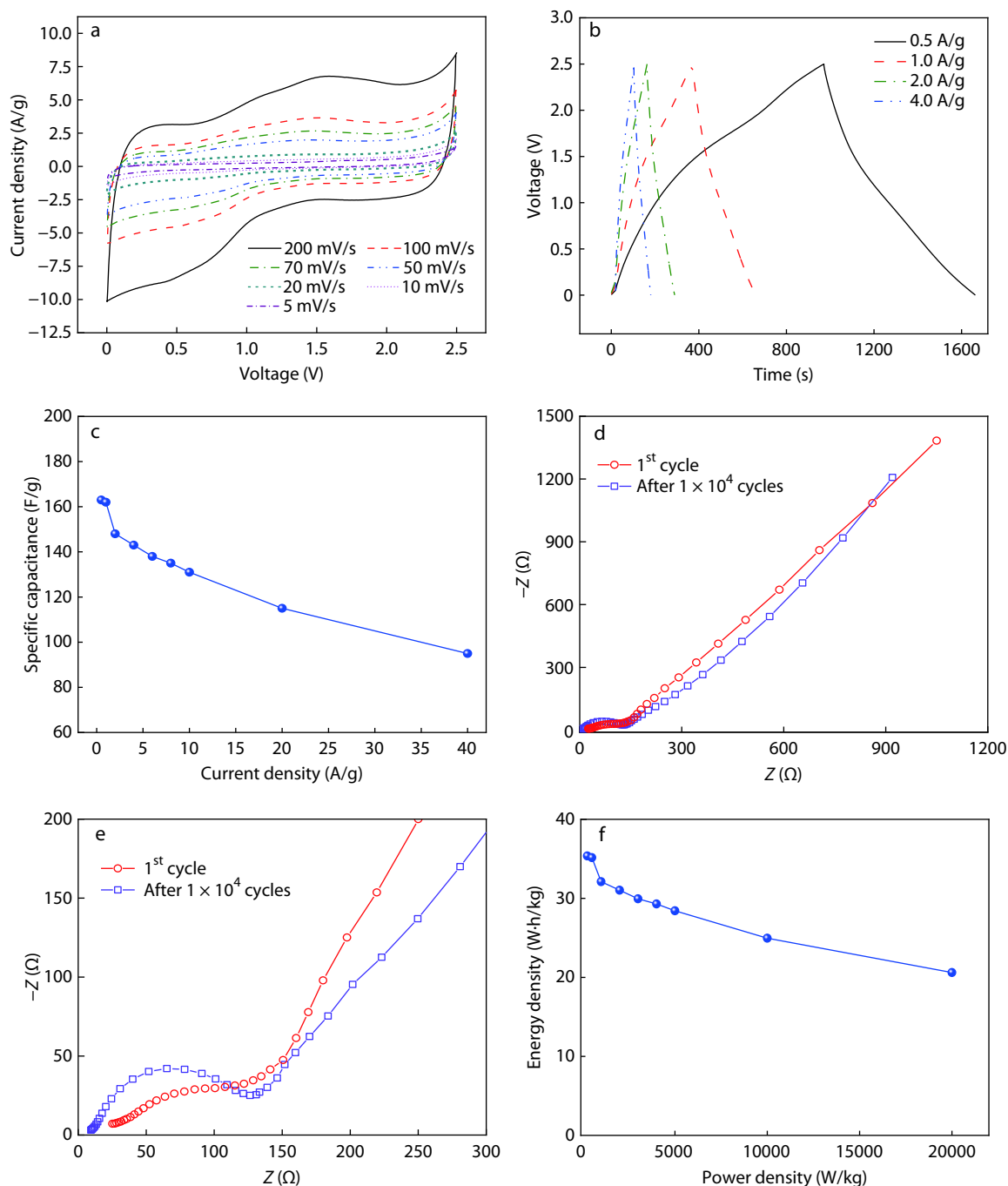


Fig. 5 Electrochemical performance of PI-COF in 1 mol/L LITFSI: (a) CV curves of PI-COF at different scan rates; (b) GCD curves of PI-COF at current densities between 0.5 and 4 A/g; (c) Specific capacitances at varying current densities; (d) EIS of PI-COF at the first and after 1.0×10^4 cycles; (e) Partial enlargement of EIS; (f) Ragone plot (energy density versus power density) of PI-COF.

was estimated by a Ragone plot. The energy density and power density were calculated based on the total mass of active materials on the cathode and anode. Remarkably, PI-COF demonstrated the outstanding energy density of 35.7 Wh/kg at a power density of 250 W/kg, which still remained 22.2 Wh/kg even when the power density was 2.0×10^4 W/kg (Fig. 5f). Furthermore, PI-COF showed outstanding cycling stability with 84.1% capacitance maintained

(137 F/g) after 3.0×10^4 charge/discharge cycles at 1 A/g as shown in Fig. 6. Notably, after 1.0×10^4 cycles at 1 A/g, the specific capacitance of PI-COF kept stable, the decrease of which was negligible in cycles 1.0×10^4 to 3.0×10^4 . Even at a higher current density of 4 A/g, its capacitance still retained 79% (112 F/g) after 3.0×10^4 charge/discharge cycles, which demonstrates that PI-COF possessed excellent electrochemical stability.

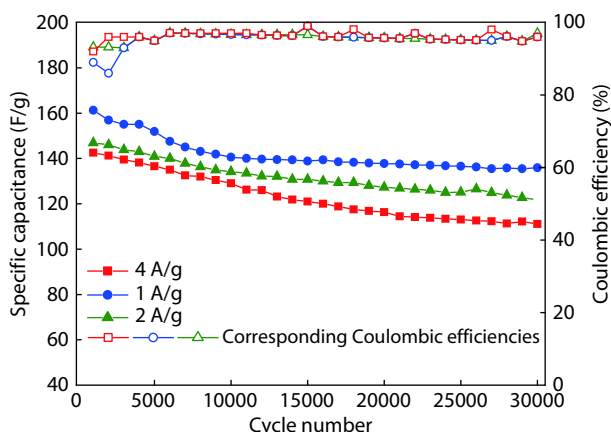


Fig. 6 Cycling stability of PI-COF: specific capacitance versus cycle number plot up to 3.0×10^4 cycles at various current densities along with corresponding coulombic efficiencies.

CONCLUSIONS

In conclusion, a 2D COF (PI-COF) has been successfully synthesized using solvothermal strategy via condensation of PMDA and PTA. By taking advantage of the unique structure of PI-COF, including highly crystalline framework, uniformed pores, high specific surface area, and porous structure, PI-COF demonstrated promising electrochemical properties as electrode materials in supercapacitors, showing a specific capacitance of 163 F/g at 0.5 A/g in the organic electrolyte, which still maintained a specific capacitance of 96 F/g even at an ultrahigh current density of 40 A/g, with a capacity retention rate of 58.9%. Benefiting from the high specific capacitance and wide potential window (0–2.5 V), PI-COF delivered a high energy density of 35.7 W·h/kg at a power density of 250 W/kg in organic electrolyte, which is among the best in the COF-based electrode materials. In addition, PI-COF showed tremendous electrochemical stability, and its capacitance retention was 84.1% (137 F/g) after 3.0×10^4 charge/discharge cycles at 1 A/g, which still remained 79.3% (112 F/g) after 3.0×10^4 charge-discharge cycles even at a high current density up to 4 A/g. We believe that this work provides new insight into designing and fabricating the COF-based electrode materials for high-performance SCs and other energy storage devices, and pushes forward the development of COF-based materials in energy storage and conversion.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-020-2412-z>.

ACKNOWLEDGMENTS

This work was financially supported by the Ministry of Science and Technology of China (No. 2012CB933403), Beijing Natural Science Foundation (No. 2182086), the National Natural Science Foundation of China (Nos. 51425302 and 51302045), CAS-TWAS President's PhD Fellowship program, the Beijing Municipal

Science and Technology Commission (No. Z121100006812003), and the Chinese Academy of Sciences.

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