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Solid-state supercapacitors based on polyoxometalate-based crystalline materials modified with polyaniline[†]

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Owing to the rapid advancement of electric energy and energy storage devices, there exists an urgent demand for solid-state supercapacitors that possess high capacitance and safety features. Polyoxometalate (POM)-based complexes are excellent candidates for electrode materials in the construction of solid-state SCs (SCs = supercapacitors), as they are capable of maintaining structural stability during the reversible redox reaction process. However, the poor conductivity of POM-based complexes cannot meet the requisite standards for solid-state SCs. In this study, two new POM-based complexes, $H_{2}\{Co_{2}Py_{4}(H_{2}O)_{4}[Co_{2}\{Co[Mo_{6}O_{12}(OH)_{3}(HPO_{4})(PO_{4})_{3}]_{2}\}]\}\cdot 4DMF\cdot 10H_{2}O$ (1) and H₆Py₂[Mn₂{Mn $[MO_6O_{12}(OH)_3(HPO_4)_4]_2]$ ·6DMF ·4H₂O (**2**) (Py = pyridine) were synthesised and the surface of POM-based electrodes were coated with a conductive polymer (PANI) via electrodeposition, resulting in a marked improvement in the transfer rates of electrolyte ions and electrons. The n@PANI-1 carbon paper electrodes were prepared and symmetrical solid-state capacitors (n@PANI-1-SCs) were assembled (in which n is the number of title complexes); their specific capacity could reach 58.166 mA h g^{-1} and 35.299 mA h g^{-1} at a current density of 0.2 A g⁻¹. Moreover, the successful powering of the red LED for a duration of 0.5 min serves as a practical demonstration of the solid-state SC's feasibility. Our new findings may provide some inspiration to develop new solid-state SCs for wearable electronics.

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Introduction

For the past few decades, fossil fuels are being used to generate secondary energy sources and this has resulted in increasingly severe environmental problems.^{1–3} Thus, new alternative forms of power generation have gained significant attention.^{4–6} Supercapacitors (SCs) are a type of novel and promising energy

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storage devices with excellent durability and low cost that they have become the primary candidates for next-generation energy storage devices.⁷⁻⁹ In traditional SCs, a shortage cannot be ignored due to the leakage of liquid electrolytes, which also limits the scope of the application of liquid SCs.¹⁰ Yet solidstate capacitors can eliminate the flaws of traditional liquid capacitors, which are made by assembling two active electrodes with a gel electrolyte. To meet the high demand for solidstate SCs with greater capacitance, it is crucial to exploit new strategies to change the status quo. Generally, there are two categories for the improvement of solid-state SCs: on the one hand, exploring new electrolyte materials with high ion-conduction in the solid state and appropriate redox potential. In 2020, our group reported solid-state SCs with polyoxometalatebased gel electrolytes, and the maximum capacitance could reach 3840 F g⁻¹ when H₃PMo₁₂O₄₀ and H₃PW₁₂O₄₀ were mixed as gel electrolytes.¹¹ On the other hand, there was the exploration for electrode materials with high conductivity and stability. Over the past decade, porous and stable crystalline materials, such as MOFs, COFs, and POM-based complexes, have been studied by researchers as suitable electrode materials.¹²⁻¹⁸ However, the capacitive performance of these crystalline materials in solid-state SCs is not outstanding, which is due to their limited conductivity. We noted that the

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introduction of conductive polymers can enhance the conductivity of electrode materials and POM-based complexes can provide electrochemically active sites.^{13,19} Therefore, we consider the preparation of excellent electrode materials by combining POM-based complexes with conductive polymers on the surface of carbon papers.

Polyoxometalates (POMs), a family of transition metaloxygen cluster anions, possess a large number of oxygen atoms on their surfaces. POM-based complexes can maintain structural stability, allowing for reversible electron transfer, which has emerged as a promising class of electrode materials.²⁰⁻²⁹ The above features enable POM-based complexes as electrode materials to effectively improve the electrochemical performance of SCs. The promising electrochemical performance of POM-based complexes may be attributed to four main reasons: (i) these complexes contain polyanions, which endow them with excellent redox properties; (ii) POM-based complexes with three-dimensional framework structure may facilitate electronic transport; (iii) POM-based complexes possess lower solubility in water and organic solvents, which is attributed to the synthetic methods and the presence of metal-POM bonds;¹⁴ (iv) the introduction of metal ions and N-based organics can modulate the conductivity and rate capability, and enhance the stability in the process of charge/discharge.³⁰

Conductive polymers (CPs), such as polyaniline (PANI) and polythiophene (PTh) are well-studied electroactive materials for enhancing the electrochemical performance of SCs with high capacitance and conductivity.^{31–33} CPs can be deposited on the surface of electrodes using chemical or electrochemical methods to prepare capacitor electrodes with excellent capacitance.^{34–38} In 2015, Li's research group presented a case of a flexible solid-state SC device assembled using MOF-based carbon cloth electrodes coated with PANI. The results revealed that the areal capacitance of PANI-ZIF-67-CC can reach 35 mF cm⁻² at the current density of 0.05 mA cm⁻², this work provides novel ideas for the development of new capacitor devices based on crystalline materials.⁹

Inspired by the outstanding previous work on utilizing crystalline materials to assemble asymmetric SC devices, in this work, we obtained two POM-based complexes by introducing N-containing organic ligands to modulate properties such as conductivity and rate capability. To improve the conductivity of electrodes and accelerate the transfer of ions and electrons, the electrode's surface was coated with PANI by electrodeposition. Furthermore, the all-solid-state SCs were prepared by assembling two electrodes with H₂SO₄ gel by using a hot-press method. The results reveal that POM-based complexes can exhibit excellent capacitive properties as electrode materials, and the technique of introducing conductive polymers to improve the capacitive performance is feasible and effective.

Results and discussion

Characterization of structure and composition of complexes

The single crystal X-ray diffraction analysis revealed that complex 1 belongs to the C/2m space group of the monoclinic

system, which contains five Co^{II} ions, four pyridine molecules, and two $[\text{H}_6\text{P}_4\text{Mo}_6\text{O}_{31}]^{6-}$ anions. The Co1 atom is six-coordinated by O19 from $[\text{H}_6\text{P}_4\text{Mo}_6\text{O}_{31}]^{6-}$ anions, N1 from pyridine molecules, and O1 W from lattice water molecules with the bond distance of Co1–N1 is 2.212 Å and the angel of O– Co–O is in the range of 79.5°–96.11°. The Co2 atom is four-coordinated by O3, O17, and O18 from different $[\text{H}_6\text{P}_4\text{Mo}_6\text{O}_{31}]^{6-}$ anions. As the structural center of anions, the Co3 is six-coordinated by O9 and O12 (Fig. 1a). The adjacent {Co $[\text{H}_6\text{P}_4\text{Mo}_6\text{O}_{31}]_2\}^{10-}$ anions are connected through $\{\text{Co}_2\text{O}_6\text{Py}_4\}$ unit to form chain structures (Fig. 1b and c). As shown in Fig. 1d, the adjacent layers are connected to the formation of a three-dimensional framework with pores of 16.7766 Å × 13.8385 Å.

The single crystal X-ray diffraction analysis revealed that complex 2 belongs to the $P\bar{1}$ space group of the triclinic system, which contains three Mn^{II}ions, two pyridine molecules, and two $[H_6P_4Mo_6O_{31}]^{6-}$ anions (Fig. 2a). The Mn1 atom is six-coordinated by O3, O7, O29 from $[H_6P_4Mo_6O_{31}]^{6-}$ anions, and the Mn2 atom is four-coordinated by O13, O14, O18 and O22 from three $[H_6P_4Mo_6O_{31}]^{6-}$ anions. Where the bond distance of Mo–O is in the range of 1.794–1.965 Å, the angles of O–Mo–O are in the range of 105.42°–123.57°. Peculiarly, the trimeric structure of $\{Mn[H_6P_4Mo_6O_{31}]_2\}^{10-}$ was formed with Mn2 as the connecting center. The trimeric structure contains three Mn1 centers arranged in a stable equilateral triangle configuration, with each corner having an approximate angle of 60° (Fig. 2b). The adjacent $\{Mn$



Fig. 1 (a) Stick view of the asymmetric unit of 1. The hydrogen atoms and crystal water molecules are omitted for clarity. (b) The one-dimensional chain structure of complex 1. (c) The $\{Co_2O_6Py_4\}$ unit. (d) The 3D open framework of 1.



Fig. 2 (a) Stick view of the asymmetric unit of **2**. The hydrogen atoms and crystal water molecules are omitted for clarity. (b) The trimeric structure of $\{Mn[H_6P_4Mo_6O_{31}]_2\}^{10-}$ units. (c)The dimer structure of $\{Mn[H_6P_4Mo_6O_{31}]_2\}^{10-}$ units. (d) The 2D layer structures with hexahedral pore-structures.

 $[H_6P_4Mo_6O_{31}]_2\}^{10-}$ units are connected by two $\{MnO_4\}$ tetrahedrons to form the dimer structure (Fig. 2c). Then, the adjacent trimeric structures are connected to each other to construct the two-dimensional layers. A large number of regular hexahedral pore-structures are contained in two-dimensional layers, the dimensions of the pores in a regular hexahedral are approximately 11.156 Å × 5.609 Å (Fig. 2d).

The schematic diagram of the two-step fabrication of n@PANI-x electrodes is shown in Fig. S1.[†] The FT-IR spectra of the complexes are shown in Fig. S2,† the characteristic peaks at 1028, 963, 752, 519 cm⁻¹ for 1, 1018, 960, 737, 500 cm⁻¹ for 2 are attributed to ν (Mo=O), ν (P-O), and ν (Mo-O-Mo) of [P₄Mo₆O₃₁]¹²⁻ polyoxoanion, respectively.³⁹⁻⁴¹ The characteristic peaks in the region of 1606, 1487 cm⁻¹ for 1, 1636, and 1466 cm⁻¹ for 2 are attributed to pyridine.⁴²⁻⁴⁴ Powder X-ray diffraction was used to verify the crystal purity of complexes 1-2, and the results are shown in Fig. S3.[†] It can be seen from the PXRD graph that complexes 1-2 have high purity. The X-Ray photoelectron spectroscopy of complexes exhibits two peaks at 231.58 eV, 234.78 eV, and 232.43 eV, 235.8 eV, which indicates that Mo atoms are in the reduced state. The characteristic peaks of 782.28 eV, 786.78 eV, 797.88 eV, and 800.28 eV correspond to Co²⁺, and 645.13 eV, 657.13 eV correspond to Mn²⁺, respectively^{45,46} (Fig. S4[†]). The SEM and EDS of the complexes are shown in Fig. S5,† the results indicate that title complexes contain P, Mo, Co (complex 1), and Mn (complex 2) elements, respectively, and are distributed in the crystal uniformly.

Electrochemical properties

The electrochemical properties of complexes 1- and 2-carbon paper electrodes (1- and 2-CPs, respectively) were studied through a three-electrode system in $0.5M H_2SO_4$ solution. The cyclic voltammograms of 1- and 2-CP at different scan rates (20 mV–250 mV) are shown in Fig. 3(a and b), three pairs of reversible peaks I–I', II–II' and III–III' can be observed in the potential range of –200 mV to +600 mV. Three reversible peaks belong to the electron transfer processes of $[P_4Mo_6O_{31}]^{12-}$ anion (eqn (S1)–(S3)†). The half-wave potentials are –62 mV, 180 mV and 343 mV for 1-CP, –72 mV, 163.5 mV and 335 mV for 2-CP⁴⁷ ($E_{1/2} = (E_{pa} + E_{pc})/2$, scan rate = 200 mV s⁻¹).

According to eqn (1) and (2), the charge storage mechanism was investigated by analyzing the peak current values at different scanning rates.^{48–50}

$$i = av^{b}$$
 (1)

$$Log (i) = b log (v) + log (a)$$
(2)

where *i* is the peak current of II–II', *v* is the scan rate, and *a* and *b* are adjustable parameters, and the electrode reaction kinetics can be characterized. The slopes of the curves (fitted *b* value) were calculated to be 0.714 and 0.685, 0.668 and 0.608 (Fig. S6†), which are between 0.5 and 1, indicating that the total capacitance includes pseudocapacitance and double-layer capacitance.

The galvanostatic charge–discharge of **n**-CP was investigated in 0.5 M H₂SO₄ electrolyte at different current densities (in which **n** is the number of complexes), the results are seen in Fig. 3(c and d). When the current density was 1 A g⁻¹, the specific capacity values could reach 157 mA h g⁻¹ for 1-CP, and 149 mA h g⁻¹ for 2-CP, respectively. The CV curve of 1-CP is



Fig. 3 (a)(b) The CV curves of 1- and 2-CPs in 0.5 M H₂SO₄ at 20, 40, 60, 80, 100, 150, 200, 250 mV s⁻¹. (c)(d)The GCD curves of complexes 1–2 at different current densities (from 1A g⁻¹ to 5 A g⁻¹). (e) The CV curves of 1- and 2-CPs at the same scan rate of 20 mV s⁻¹. (f) The EIS spectra of complexes 1- and 2-CPs.

larger than 2-CP, which also suggests that 1-CP exhibits higher capacitance (Fig. 3e). To further understand the electrochemical performances of complexes, the EIS spectra of **n**-CPs were collected and are shown in Fig. 3f. It can be clearly shown that 1-CP exhibits lower resistance than 2-CP, which shows that 1-CP possesses faster electron transfer than 2-CP. The matched circuit appropriate to fit the EIS, which consists of a Faraday capacitor (C_f) and electric double-layer capacitance (C_{dl}), and three resistons (R_s = the Ohm resistance, R_{ct} = the charge transfer resistance, Z_w = the ion diffusion resistance).⁵⁰ The results show that complex **1** with three-dimensional structures possesses greater electrochemical performance than complex **2**.

To improve the conductivity of the electrode materials, the active material PANI was coated on the surface of electrodes by electrodeposition to form n@PANI-x electrodes (x is the number of cycles). The cyclic voltammograms of \mathbf{n} @PANI-x at different scan rates (50 mV-250 mV) are shown in Fig. S7.† As shown in Fig. 4a, four PANI-modified electrodes exhibited higher capacitive performance than n-CPs. The biggest CV area of these electrodes at 20 mV s^{-1} scan rate was for 1@PANI-1, indicating that 1@PANI-1 possesses a higher capacitance than other electrodes. At the current density of 1 A g^{-1} , the specific capacity values were 383 mA h g^{-1} for 1@PANI-1, 277 mA h g^{-1} for 1@PANI-2, 285 mA h g^{-1} for 2@PANI-1, 178 mA h g^{-1} for 2@PANI-2 (Fig. 4b). Taking 2-CP as an example, we explored the effect of the electrodeposition of PANI on the capacitance performance. As shown in Fig. 4c, when only one cycle of the electrodeposition of PANI was conducted, the discharge time of the capacitor was significantly increased nearly by twice. However, when the number of electrodeposition cycles was further increased, the capacitance of electrodes was significantly reduced, which may have been caused by the following reasons: excessive polyaniline reduces the electrochemically active area and hinders the diffusion of electrolyte ions on the electrode surface.¹⁶ The trend of specific capacitance with different current densities is shown in Fig. 4d, the GCD curves at different current densities, and the EIS spectra of n@PANI-x electrodes are shown in Fig. S8 and S9.† We found that the specific capacitance of n-CPs is almost the same, but the specific capacitance of 1@PANI-x is significantly higher than that of 2@PANI-x. The result may be attributed to the threedimensional framework being more conducive to improving the performances of capacitors than the two-dimensional layer structure. The proposed mechanism of PANI is shown in Fig. S10.[†] In order to prove that the enhancement of capacitance after electrodeposition of polyaniline is attributed to the synergistic effect of polyaniline with complexes, PVDF and Ketjen black, we used bare-carbon paper, PVDF@Ketjen black to carry out the comparative experiment. Compared with the n@PANI-1, the capacitance performances of CP@PANI-1 and PVDF@Ketjen black@PANI-1 are significantly reduced, and the specific capacities were 85.39 mA h g^{-1} , 121.08 mA h g^{-1} at 1 A g^{-1} , respectively (Fig. S11[†]). The results confirmed that the enhancement of capacitance performance after electrodeposition of polyaniline can be attributed to the synergistic effect of polyaniline with complexes, PVDF and Ketjen black.

To further research the practical application of the as-prepared SCs, in this work, the symmetrical capacitors were assembled by using the **n**@PANI-1 as electrodes. The POMsbased solid-states SCs were assembled by hot-pressing two sheets of **n**@PANI-1 electrodes at 50 °C for 10 min, H₂SO₄-gel solution as the electrolyte, and namely **n**@PANI-1-SC (Fig. 5a). Fig. 5b shows the cyclic voltammogram curve of **1**@PANI-1-SC with the operating window of -0.2 to 0.6 V at a scan rate of 20–250 mV s⁻¹, the shape of CV curves remained stable at different scan rates. Fig. 5c is the GCD curves of **1**@PANI-1-SC at the different current densities from 0.2 to 0.5 A g⁻¹, and the corresponding specific capacity were 58.166, 48.901, 49.917,



Fig. 4 (a)The CV curves of n-CPs and n@PANI-*x* at 20 mV s⁻¹. (b) The GCD curves of n@PANI-*x* at 1 A g⁻¹. (c) the discharge time of 2-CP, 2@PANI-1, and 2@PANI-2 at 1 A g⁻¹. (d)The trend of specific capacity with a current density of n@PANI-*x* at varied current density.



Fig. 5 (a) Schematic illustration for the assembled structure of n@PANI-1-SC device. (b) CV curves of 1@PANI-1-SC device at different scan rates from 20 mV s⁻¹ to 250 mV s⁻¹. (c)GCD curves of 1@PANI-1-SC device at different current densities from 0.2 A g⁻¹ to 0.5 A g⁻¹. (d) Variation of C_s and C_a of 1@PANI-1-SC device as a function of the current density. (e) Capacitance retention of the 1@PANI-1-SC devices at 0.5 A g⁻¹. (f) A red LED powered by three devices in series.



Fig. 6 A Ragone plot of the as-synthesized devices.

37.681 mA h g⁻¹ for 1@PANI-1-SC, respectively. According to the GCD curves, the specific capacity and areal capacitance $(C_{\rm a})$ of SC were 58.166 mA h g⁻¹ and 1200 mF cm⁻² at 0.2 A g⁻¹ and remain quite high (specific capacity = $37.681 \text{ mA h g}^{-1}$, areal capacitance = 759 mF cm⁻²) at 0.5 A g⁻¹ showing a rate capability of 63% (Fig. 5d). Meanwhile, the maximum energy density and power density of 1@PANI-1-SC and 2@PANI-1-SC were 25.39 W h $\rm kg^{-1},~45.7~W~kg^{-1},~and~15.7~W~h~kg^{-1}$ and 34.95 W kg⁻¹ at a current density of 0.1 A g⁻¹, respectively (the GCD curve of n@PANI-1-SC is shown in Fig. S13[†]). The Ragone plot of the comparison with the previous report on the POMbased supercapacitor indicates that the as-synthesized devices exhibit excellent electrochemical performance (Fig. 6).51-57 Fig. 5e shows the charge-discharge cycle test of 1@PANI-1-SC at 0.5 A g^{-1} , the capacitance retention can reach 72.46% after 1000 cycles, and the comparison of capacitance retention with other solid-state SCs is shown in Table S3.† As shown in Fig. 5f, a commercial light-emitting diode (LED) was fed with three SCs in series. This result demonstrates that 1@PANI-1-SC device can be used for energy storage. The same experiment was carried out for 2@PANI-1-SC device and the results are shown in Fig. S12.†

Conclusions

In brief, two novel Hourglass-type POM-based complexes were synthesized using the solvothermal method. The synergistic effect of POM-based complexes and conductive polymer PANI was employed to enhance the capacitive performance of solid-state SCs. A feasible method for designing and assembling solid-state SCs is to interweave POM-based complexes and electrochemically polymerized PANI on cloth paper. The resulting n@PANI-1 electrode possesses excellent electrochemical performance, and the solid-state SCs n@PANI-1-SC delivered outstanding specific capacitance, the specific capacity of solid-state SCs could reach

58.166 mA h g⁻¹ and 35.299 mA h g⁻¹ at the current density of 0.2 A g⁻¹, respectively. In addition, the capacitance retention of 1@PANI-1-SC was 72.46% after 1000 cycles at 0.5 A g⁻¹. This work provides a distinctive demonstration for improving the capacitive performance of solid-state SCs and a general strategy to be applied in other energy storage devices.

Conflicts of interest

There are no conflicts to declare.

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