Supercapacitors

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Supercapacitors are a category of energy-storage devices based on high-speed electrostatic or Faradaic electrochemical processes. The charge is mainly stored at the electrode−electrolyte interface of the active materials, such as high surface porous carbons, metal oxides, or conducting polymers. They consist of one positive electrode and one negative electrode soaked in an electrolyte and separated by an ion-permeable, electronically insulating separator.Compared with batteries, supercapacitors can supply much faster charge and discharge rates within seconds or minutes time scales but lower specific energy. Besides the high power densities, supercapacitors also have some other advantages over batteries, such as high operating safety, long cycling life, high efficiency, and high performance stability.

Keywords: Supercapacitors ; Mofs ; Mofs-Derived Porous Carbon

1. Introduction

To meet the portable demand of all kinds of electronics, it is essential to develop an efficient and green energy storage technology. Among various energy storage devices, supercapacitors (SCs) have drawn much attention due to its feature of high power density and rapid charge-discharge capability [1][2][3][4][5][6].

SCs work mainly through two types of charge storage mechanisms: (i) adsorption of charge and (ii) redox reactions associated with chemical changes. Carbon materials (graphene, activated carbon, carbon nanotubes, etc.) with superior electrical conductivity and excellent chemical stability, usually work in the first mechanism as the SCs electrode materials, yielding large power density and long cycling life, but flat energy density. Transition metal oxides/hydroxide and conducting polymers normally work in the second mechanism, presenting high energy density but poor cycling stability due to the distortion of the microstructure in electrode materials resulting from the continuous redox reactions [7][8][9][10]. Hence, to develop advanced SC electrode materials, especially in the case of solving the problems of low energy density and poor cycling stability and pursuing high capacitance, is of vital significance.

In essence, the fast adsorption/desorption of electrolyte ions or rapid reversible oxidation–reduction reaction in SCs requires electrode materials to present short charge/ions transfer channel and abundant active (adsorption/desorption and redox) sites. MOFs [11][12][13] and their derived materials (carbon, metal oxides/sulfides, etc.) with inheriting MOFs pore structure, can provide adequate adsorption/reactive sites due to their large specific surface area and adjustable porous structure; in addition, their wide varieties and promising electrochemical activity make them suitable for SC electrode materials [14]. Tremendous efforts go into the research of MOFs and their derivatives' applications in SCs in the past few years, where M-BTC (BTC = 1,3,5-benzenetricarboxylate), M-PTA (PTA = p-benzenedicarboxylate, also called terephthalate, i.e., 1,4-benzenedicarboxylate 1,4-BDC) and zeolitic imidazole frameworks (ZIFs) are the most investigated MOF series.

Due to the rapid development of this filed and ever-growing research interests, it is impossible to include all the relevant works in the present review. Consequently, in this paper, we mainly discuss and summarize the recent development of MOFs and MOFs derivatives as electrodes in SCs since 2020 where the earlier corresponding works have been reviewed in References [15][16][17][18]. Specifically, their active constituents (such as activated carbon, transition metals, metal oxides and conducting polymers), synthesis process and electrochemical performance are given. We also present an outlook and the development direction in the near future.

2. Investigations on Mofs, Mofs-Derived Porous Carbon, etc.

(i) MOFs derived metal sulfide displayed an extraordinary electronic performance, especially the trimetal sulfide composites. Binder-free Ni foam (providing Ni source)-supported NiCo-S/NF (a mixture of $NiCo_2S_4$, $Co(OH)_2$ and Ni_3S_2) derived from ZIF-67 exhibits the highest specific capacitance of 3724 F g−1, at a current density of 1 A g−1, among all the

discussed materials in the work [19], lower than recently reported MnMoO4/NF with a super-high specific capacitance of 4609 F g−1 at a current density of 1 A g−1, synthesized from non-MOF-involved hydrothermal procedure (reactants: MnCl2·4H2O and Na2MoO4·2H2O) [20];

(ii) MOFs-derived metal oxide manifested a remarkable electronic performance, as well. Notably, the Ni/Mn-PTA//AC SC device (assembled by the flower-like ultrathin MnNi2O4 nanosheet derived from Ni/Mn-PTA as the positive electrode and AC as the negative electrode) yielded the largest energy density of 142.8 Wh kg−1 at the power density of 800 W kg−1, overwhelming most previously reported SCs electrode materials [98];

(iii) most of MOFs-derived porous C exhibits specific capacitance smaller than 1000 F g−1, while a combination with metal sulfide (MoS2, NiS, etc.) can enhance its behavior; for instance, NiS@C can reach a specific capacitance up to 1827 F g−1 [21];

(iv) Binder-free-supported composites exhibit a better performance than MOFs or MOF derivative alone, partially due to the decreased “dead volume” in the binder-free composites, resulting in the smaller resistance.

Since two materials derived from MOF-5, i.e., Zn-PTA subfamilies, were used for the electrodes of SC (Ni–Zn–Co oxide/hydroxide yields capacitance of 946 F g−1 at 2 mV s−1 [22]; nanoporous carbons exhibits specific capacitance of above 100 F g−1 at 5 mV s−1 [23]) in 2010, great progress has been made over the years. The gravimetric capacitance of MOFs derivatives increased from above 100 F g−1 at 5 mV s−1 to 3724 F g−1 at a current density of 1 A g−1. Notwithstanding these achievements, challenges still exist for the practical utilization of MOFs and MOFs-derived materials in SCs, limiting their application in our daily life: (i) For economic consideration, it is expected that MOFs are facilely synthesized in the air. Therefore, their stability in the air should also be promoted; (ii) to obtain higher capacitance and rate property for SCs, enhancing the electrical conductivity of MOFs and MOFs-derived materials is highly in urgent. For most of the present MOFs/derivatives, the rate performance is unsatisfactory; (iii) an in-depth investigation is essential to uncover the synergetic effect in composites. First-principle calculations, together with machine-learning method [24], may be needed to find out the controlling factor and favor the future rational design of MOFs/derivatives as SCs electrodes. Lots of previous works have proved that first-principle calculation method is an effective tool to investigate the synergetic effect [25][26][27]. Machine-learning methods, such as SSISSO (sure independence screening and sparsifying operator) method, developed by Ouyang et al. [28][29], have succeeded in revealing the effects of temperature and composition on materials synthesizability and stability of inorganic compounds by figuring out the best descriptor equation of Gibbs energy, to generate thousands of temperature-dependent phase diagrams [30]. Similarly, SISSO may identify the descriptor equation of a specific capacitance, using the features (band gap, pore size, surface area, density, void fraction, etc.) of known materials, and then use the descriptor equation to predict the materials capacitance directly, once their features data are available.

The investigations show that vacancies such as Ni vacancies in Ni/NiO nanoparticle derived from Ni-PTA [31], oxygen vacancies in Co3O4 or ZnO derived from the ZIF subfamily [32] showed a positive improvement in charge storage. CeO2−x films with volumetric oxygen vacancies rendering Ce3+ concentrations as high as ~60 at% yielded the highest volumetric capacitance of 1873 F cm−3 among the reported works [33]. Therefore, to create the vacancies in MOFs derivatives and investigate the influence of vacancies on the electronic performance of MOFs derivatives as the SC electrode materials could be an interesting research topic.

References

1. Dang, T.; Zhang, G.; Li, Q.; Cao, Z.; Zhang, G.; Duan, H. Ultrathin hetero-nanosheets assembled hollow Ni-Co-P/C for hybrid supercapacitors with enhanced rate capability and cyclic stability. J. Colloid Interface Sci. 2020, 577, 368–378.
2. Yin, X.; Li, H.; Han, L.; Yuan, R.; Lu, J. NiCo2O4 nanosheets sheathed SiC@CNTs core-shell nanowires for high-performance flexible hybrid supercapacitors. J. Colloid Interface Sci. 2020, 577, 481–493.
3. Wang, J.G.; Ren, L.; Hou, Z.; Shao, M. Flexible reduced graphene oxide/prussian blue films for hybrid supercapacitors. Chem. Eng. J. 2020, 397, 125521.
4. Wang, P.; Wang, R.; Lang, J.; Zhang, X.; Chen, Z.; Yan, X. Porous niobium nitride as a capacitive anode material for advanced Li-ion hybrid capacitors with superior cycling stability. J. Mater. Chem. A 2016, 4, 9760–9766.
5. Lim, E.; Kim, H.; Jo, C.; Chun, J.; Ku, K.; Kim, S.; Lee, H.I.; Nam, I.S.; Yoon, S.; Kang, K.; et al. Advanced hybrid supercapacitor based on a mesoporous niobium pentoxide/carbon as high-performance anode. ACS Nano 2014, 8, 8968–8978.

6. Yan, Y.; Li, A.; Lu, C.; Zhai, T.; Lu, S.; Li, W.; Zhou, W. Double-layered yolk-shell microspheres with NiCo2S4-Ni9S8-C hetero-interfaces as advanced battery-type electrode for hybrid supercapacitors. Chem. Eng. J. 2020, 396, 125316.
7. Xu, S.; Su, C.; Wang, T.; Ma, Y.; Hu, J.; Hu, J.; Hu, N.; Su, Y.; Zhang, Y.; Yang, Z. One-step electrodeposition of nickel cobalt sulfide nanosheets on Ni nanowire film for hybrid supercapacitor. Electrochim. Acta 2018, 259, 617–625.
8. Xu, S.; Li, X.; Yang, Z.; Wang, T.; Xu, M.; Zhang, L.; Yang, C.; Hu, N.; He, D.; Zhang, Y. A novel Ni@Ni(OH)2 coaxial core-sheath nanowire membrane for electrochemical energy storage electrodes with high volumetric capacity and excellent rate capability. Electrochim. Acta 2015, 182, 464–473.
9. Xu, S.; Li, X.; Yang, Z.; Wang, T.; Jiang, W.; Yang, C.; Wang, S.; Hu, N.; Wei, H.; Zhang, Y. Nanofoaming to Boost the Electrochemical Performance of Ni@Ni(OH)2 Nanowires for Ultrahigh Volumetric Supercapacitors. ACS Appl. Mater. Interfaces 2016, 8, 27868–27876.
10. Hong, M.; Zhou, C.; Xu, S.; Ye, X.; Yang, Z.; Zhang, L.; Zhou, Z.; Hu, N.; Zhang, Y. Bi-metal organic framework nanosheets assembled on nickel wire films for volumetric-energy-dense supercapacitors. J. Power Sources 2019, 423, 80–89.
11. Zong, S.; Zhang, Y.; Lu, N.; Ma, P.; Wang, J.; Shi, X.-R. A DFT Screening of M-HKUST-1 MOFs for Nitrogen-Containing Compounds Adsorption. Nanomaterials 2018, 8, 958.
12. Zong, S.; Huang, S.; Shi, X.-R.; Sun, C.; Xu, S.; Ma, P.; Wang, J. Impact of linker functionalization on the adsorption of nitrogen-containing compounds in HKUST-1. Dalton Trans. 2020, 49, 12610–12621.
13. Tang, H.; Li, W.; Jiang, H.; Lin, R.; Wang, Z.; Wu, J.; He, G.; Shearing, P.R.; Brett, D.J.L. ZIF-8-Derived Hollow Carbon for Efficient Adsorption of Antibiotics. Nanomaterials 2019, 9, 117.
14. Ma, H.M.; Yi, J.W.; Li, S.; Jiang, C.; Wei, J.H.; Wu, Y.P.; Zhao, J.; Li, D.S. Stable Bimetal-MOF Ultrathin Nanosheets for Pseudocapacitors with Enhanced Performance. Inorg. Chem. 2019, 58, 9543–9547.
15. Xu, B.; Zhang, H.; Mei, H.; Sun, D. Recent progress in metal-organic framework-based supercapacitor electrode materials. Coord. Chem. Rev. 2020, 420, 213438.
16. Zhang, K.; Kirlikovali, K.O.; Le, Q.V.; Jin, Z.; Varma, R.S.; Jang, H.W.; Farha, O.K.; Shokouhimehr, M. Extended Metal-Organic Frameworks on Diverse Supports as Electrode Nanomaterials for Electrochemical Energy Storage. ACS Appl. Nano Mater. 2020, 3, 3964–3990.
17. Meng, J.; Liu, X.; Niu, C.; Pang, Q.; Li, J.; Liu, F.; Liu, Z.; Mai, L. Advances in metal-organic framework coatings: Versatile synthesis and broad applications. Chem. Soc. Rev. 2020, 49, 3142–3186.
18. Rajak, R.; Kumar, R.; Ansari, S.N.; Saraf, M.; Mobin, S.M. Recent highlights and future prospects on mixed-metal MOFs as emerging contestants for supercapacitors. Dalton Trans. 2020, 49, 11792–11818.
19. Zheng, L.; Song, J.; Ye, X.; Wang, Y.; Shi, X.; Zheng, H. Construction of self-supported hierarchical NiCo-S nanosheet arrays for supercapacitors with ultrahigh specific capacitance. Nanoscale 2020, 12, 13811–13821.
20. Xu, Z.; Sun, S.; Han, Y.; Wei, Z.; Cheng, Y.; Yin, S.; Cui, W. High-Energy-Density Asymmetric Supercapacitor Based on a Durable and Stable Manganese Molybdate Nanostructure Electrode for Energy Storage Systems. ACS Appl. Energy Mater. 2020, 3, 5393–5404.
21. Wu, J.; Wei, F.; Sui, Y.; Qi, J.; Zhang, X. Interconnected NiS-nanosheets@porous carbon derived from Zeolitic-imidazolate frameworks (ZIFs) as electrode materials for high-performance hybrid supercapacitors. Int. J. Hydrogen Energy 2020, 45, 19237–19245.
22. Wang, H.; Gao, Q.; Hu, J. Asymmetric capacitor based on superior porous Ni-Zn-Co oxide/hydroxide and carbon electrodes. J. Power Sources 2010, 195, 3017–3024.
23. Liu, B.; Shioyama, H.; Jiang, H.; Zhang, X.; Xu, Q. Metal-organic framework (MOF) as a template for syntheses of nanoporous carbons as electrode materials for supercapacitor. Carbon 2010, 48, 456–463.
24. Bartel, C.J.; Sutton, C.; Goldsmith, B.R.; Ouyang, R.; Musgrave, C.B.; Ghiringhelli, L.M.; Scheffler, M. New tolerance factor to predict the stability of perovskite oxides and halides. Sci. Adv. 2019, 5, eaav0693.
25. Su, Z.; Pang, R.; Ren, X.; Li, S. Synergetic role of charge transfer and strain engineering in improving the catalysis of Pd single-atom-thick motifs stabilized on a defect-free MoS2/Ag(Au)(111) heterostructure. J. Mater. Chem. A 2020, 8, 17238–17247.
26. Shi, X.-R.; Huang, S.; Huang, Y.; Zhang, Y.; Zong, S.; Xu, S.; Chen, Y.; Ma, P. Atomic structures and electronic properties of Ni or N modified Cu/diamond interface. J. Phys. Condens. Matter. 2020, 32, 225001.
27. Lin, Y.; Zheng, J.; Wang, C.; Qi, Y. The origin of the two-plateaued or one-plateaued open circuit voltage in Li–S batteries. Nano Energy 2020, 75, 104915.

28. Ouyang, R.; Curtarolo, S.; Ahmetcik, E.; Scheffler, M.; Ghiringhelli, L.M. SISSO: A compressed-sensing method for identifying the best low-dimensional descriptor in an immensity of offered candidates. Phys. Rev. Mater. 2018, 2, 083802.
29. Ouyang, R.; Ahmetcik, E.; Carbogno, C.; Scheffler, M.; Ghiringhelli, L.M. Simultaneous learning of several materials properties from incomplete databases with multi-task SISSO. J. Phys. Mater. 2019, 2, 024002.
30. Bartel, C.J.; Millican, S.L.; Deml, A.M.; Rumptz, J.R.; Tumas, W.; Weimer, A.W.; Lany, S.; Stevanović, V.; Musgrave, C.B.; Holder, A.M. Physical descriptor for the Gibbs energy of inorganic crystalline solids and temperature-dependent materials chemistry. Nat. Commun. 2018, 9, 4168.
31. Jiao, Y.; Hong, W.; Li, P.; Wang, L.; Chen, G. Metal-organic framework derived Ni/NiO micro-particles with subtle lattice distortions for high-performance electrocatalyst and supercapacitor. Appl. Catal. B Environ. 2019, 244, 732–739.
32. Dai, S.; Han, F.; Tang, J.; Tang, W. MOF-derived Co3O4 nanosheets rich in oxygen vacancies for efficient all-solid-state symmetric supercapacitors. Electrochim. Acta 2019, 328, 135103.
33. Mofarah, S.S.; Adabifiroozjaei, E.; Yao, Y.; Koshy, P.; Lim, S.; Webster, R.; Liu, X.; Nekouei, R.K.; Cazorla, C.; Liu, Z.; et al. Proton-assisted creation of controllable volumetric oxygen vacancies in ultrathin CeO2−x for pseudocapacitive energy storage applications. Nat. Commun. 2019, 10, 1–9.