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Current Progress on the Preparation of Binders for Electrochemical Supercapacitors

Hong-Qiang Wang[1,2], Jinchao Yin[1] , Qingyu Li[1] , Panchao Yin, PhD[3]

[1]School of Chemistry and Pharmaceutical Sciences, Guangxi Normal University, No. 15 Yucai Road, Guilin 541004, Guangxi, PR China, [2]Guangxi Experimental Centre of Science and Technology, Guangxi University, Nanning 530004, PR China, [3]Department of Polymer Science, the University of Akron, Akron, OH 44314, USA

Email: pyin@uakron.edu

Abstract

In this critical review, binders for electrochemical supercapacitors are introduced and current technologies on the preparation of binders are reviewed in detail. Different types of materials for binder preparation are reviewed by comparing their advantages, disadvantages, and performance with active materials in ES electrodes. Several new trends for the future development of binder preparation are also discussed.

Keywords: binder, energy storage, polymer, supercapacitor

Introduction

With the rapid development of the global economy, the depletion of fossil fuels and the increasing environmental pollution have been regarded as two of the major issues in this century, which urgently require efficient, clean, and sustainable energy resources, as well as new technologies for energy conversion and storage. Batteries, fuel cells, and electrochemical supercapacitors (ES) are getting more and more interest because of their high efficiencies and practical applications for electrochemical energy conversion and storage [*1*]. Especially, ES or ultracapacitors have attracted significant attention recently, mainly because of their high power density, long lifecycle, and bridging function for the power energy gap between traditional dielectric capacitors (which have high power output) and batteries/fuel cells (which have high energy storage) [*2, 3*].

ES, also known as electrochemical double-layer capacitor (EDLC), is considered as one of the most important energy storage devices nowadays [4]. In ESs, the charge is electrostatically stored at the electrode-electrolyte interface, which can be charged and discharged within seconds. The commercial available ESs display high power (up to 10 $kW \cdot kg^{-1}$) and extremely high cycle life (>500,000) [*5-9*]. These advantages render ES a large number of applications where rapid charge-discharge capability and reliability are required [*4, 10*].

An ES electrode is a composite of active materials, polymeric binder, and conductive agents (see Fig. 1). Up to now, most of the researches on EDLC are focused on electrode active materials and electrolytes while rare studies on the binders have been reported [*7, 8, 11, 12*]. Binders, actually, are important parts of electrode formulation, which can maintain the physical structure of the electrode; in other words, without a binder, the electrode would fall apart.

Theoretically, a perfect binder should have high adhesion ability for the electrode materials to the current collector, as well as the ability to form a good electric network between the active material and conductive carbon, to facilitate electron transportation and ion diffusion [*13*].

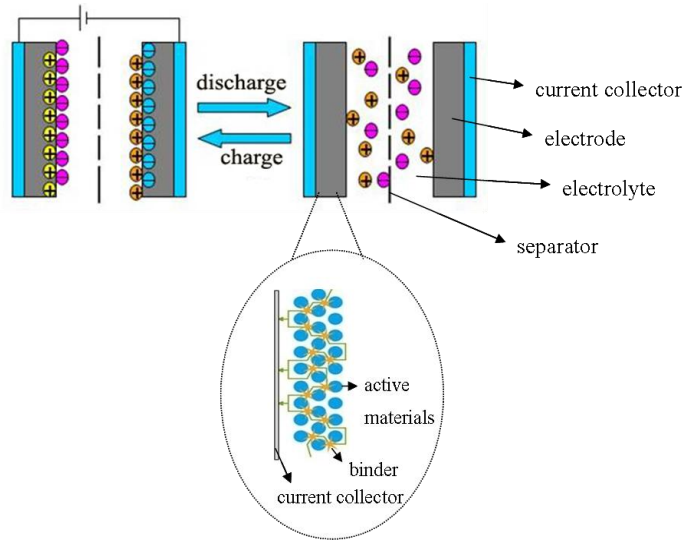

Figure 1. Schematic diagrams of ES and the function of binder in electrodes.

Classification of the binders for ESs

Non-aqueous binders

So far, non-aqueous binders, such as polyvinylidene difluoride (PVDF) [*14-16*], have been widely used and represent the state-of-the-art binders in ESs [*17*]. Recently, a few work has also been reported on the use of polyacrylic acid (PAA) and the derivatives of those above two binders, e.g. PVDF-hexafluoropropylene (PVDF-HFP) [*18*] and Nafion [*19, 20*].

PVDF is a highly inert and pure thermoplastic fluoropolymer produced by the polymerization of vinylidene difluoride. Because of its excellent resistance to varied solvents, acids, bases, and heat, PVDF exhibits high electrochemical stability and bonding strength [*21*]. Moreover, PVDF is easy to disperse [*22*], making it widely used in ESs' electrodes. However, the mixing procedure of PVDF with conductive agents and active materials requires the use of cost-expensive (and in some case toxic) organic solvents, e.g. N-methyl-2-pyrrolidone (NMP). In addition, as mentioned by Zhang et al. [*21*], PVDF is readily swollen, gelled, or dissolved by non-aqueous liquid electrolytes to form viscous fluid or gel polymer electrolyte, resulting in the shortening of capacity-fading and cycle life through desquamation of electrode particles. Moreover, the low flexibility of PVDF cannot meet the demands of long cycle life for cathode materials because of the breaking of the bonds between the active material and the conductive carbon after the durable expansion/contraction process of the active material during cycling [*23*].

PAA is a linear polymer and a superabsorbent polymer binder. It can dissolve in both water and NMP, and it can form strong hydrogen bonds with both active materials and current collectors due to its carboxylic acid functional groups [*12*]. PAA, as a binder for Sn, Si alloys [*24-28*], natural

graphite anodes [*29-32*], and LiFePO4 cathodes [*33-35*], had previously been reported. The problem of Cs (specific capacity) reduction with increasing oxide loading, as typically encountered in the MnO_2 ESs, has been solved to a great extent by combining the oxide with PAA to form composite particles [*36*]. Other than acting as a binder, PAA facilitates the homogeneous distribution of electrolytes throughout the active layer owing to its electrolyte-absorbing and swelling behaviors as mentioned by Lee et al. [*36*].

PVDF-HFP and Nafion have been used in the fabrication of solid state ESs based on polymer/gel electrolytes [*37*]. Such electrolytes play common roles of both high ionic conductor and a separator, along with their advantageous mechanical properties, including high flexibility for proper electrode-electrolyte contact and the ability to form thin films of desirable area [*37*]. Osaka et al. studied the optimized gel electrode of PVDF-HFP/PC/EC/$TEABF_4$ (23/31/35/11, mass ratio), which exhibited ionic conductivity as 5×10-3 S/cm, good mechanical strength, and excellent cycle-ability performance over 104 cycles with leakage current less than 5μA·cm^{-2} and with very good potential retention [*38*]. The all solid-state ESs with activated charcoal electrodes and PVDF-HFP based gel electrolytes with different cationic salts ($LiClO_4$, $NaClO_4$ and $TEAClO_4$) have been studied by S.A. Hashmi [*37*]. Meantime, Kang et al.[*18*] noted that the corresponding electrochemical characteristics, mechanical strength, and flexibility could be optimized by searching different weight percent of PVDF-HFP and PVDF-HFP/PVP mixed binder (weight ratio of PVDF-HFP:PVP=7:3). They found that 5% PVDF-HFP/PVP mixed binder was the optimized recipe for the electrode.

Nafion is a sulfonated tetrafluoroethylene based fluoropolymer-copolymer. In ESs, Nafion shows the double function of both binder and electrolyte, which has been used as electrolyte separator in the preparation of small scale ESs. Lufrano et al. [*19*] investigated the solid state ESs based on activated carbon material and Nafion electrolyte compared with a ES with binder as PVDF based on sulfuric acid electrolyte. They found that the ES with Nafion as binder materials shows a good affinity between electrode and current collector and fast proton transport in a smaller carbon pores [*19*].

Water-based binders

Water-based binders have drawn more and more attention in recent years because they allow the use of aqueous slurries for electrodes preparation. Additionally, the introduction of water-based binder to the film coating process of ESs can make the production process environmental friendly, reduce costs, and improve the overall safety of the ESs manufacturing process. Currently, polytetrafluoroethylene (PTFE) and sodium carboxyl methyl cellulose (CMC), and styrene–butadiene rubber (SBR) are widely adopted as water-based binders in ESs. Recently, LA135 [*8*] with the main chemical compositions as polyacrylonitrile and styrene–butadiene rubber, and Natural microcrystalline cellulose, has also been reported as water-based binders [*7*].

PTFE, as a fluorinated thermoplastic, has excellent resistance to solvents, acids, bases, and heat, rendering it excellent electrochemical stability. As ESs' binder, PTFE's aqueous dispersion (60%, wt) can be blended with active materials and conductive agents. Because of its electrochemical stability, this binder can be advantageously used for the realization of composite electrodes to be

combined with all types of electrolytes commonly used in ESs[*7*]. The binder efficiency of phenolic resin (PF) and PTFE has been studied by Li et al. [*39*]. A 1M solution of lithium perchlorate ($LiClO_4$) in a mixture of ethylene carbonate (EC) and propylene carbonate (PC) (1:1 by volume) was used as the electrolyte solution. Experimental results indicated that PTFE is a superior binder compared to PF for CNT electrodes. Nevertheless, the electrode with PTFE is not prepared by casting method, but obtained by pressing the resultant dough-like mixture onto the current collector [*40-42*] , which make it difficult to scale up such kind of ECs.

CMC and SBR have also been proposed as binders for ES electrodes during the past years. In most cases, water-soluble CMC and SBR are used jointly to provide enough adhesion [*43, 44*], yet few studies used CMC alone [*45-47*]. CMC is environmentally more friendly (fluorine-free) and cheaper (1-2€kg^{-1}, see table 1) than the state-of-the art binders [*7*]. Moreover, since CMC is soluble in water, this binder allows the use of aqueous slurries for the electrode preparation, which finally improves the overall safety of the ESs manufacturing process. Recently, previous literature showed that the performance of CMC-based electrodes is comparable with that of electrodes based on conventional, fluorinated binders in several types of electrolytes, in terms of both capacitance and cycling stability [*48-50*]. Wei et al. [*51*] compared the advantages of CMC and SBR with PVDF binders in the preparation and work efficiency of the TiO_2 electrodes. Their results showed that CMC/SBR binder is able to provide an effective three dimensional network with uniform distribution of the TiO_2 active material and the super p conductive additive and the electrode exhibits higher specific capacities, and better capacity retention. CMC/SBR as binder is also used in Si/B composite anode to improve the contact between silicon particles and copper substrate, decrease the interfacial resistance, and finally improve the cycling performance. CMC alone as binder also is used in $LiMn_2O_4$ [*12*], $LiNi_{0.4}Mn_{1.6}O_4$ [*45*], and Si anode electrodes[*52*] et al. A few literature reported the comparative study of SBR alone and CMC/SBR as binders used in graphite and nano-silicon-based negative electrodes, which finally drawn the conclusion that the latter one has good stability and good electrochemical performance [*43*].

Table 1 Comparison of some properties of polytetrafluoroethylene (PTFE), polyvinylidene difluoride (PVDF), sodium-carboxymethyl cellulose (CMC) and natural cellulose [*7*]. Reprinted with permission from ref. 7. Copyright 2013 Journal of Power Sources Publishing Group.

Binder	Average cost/(€ Kg^{-1})	Compatibility with		
		Aqueous electrolyte	Organic electrolyte	Ionic liquid electrolyte
PTFE	~15	Compatible	Compatible	Compatible
CMC	1-2	Incompatible	Compatible	Compatible
PVDF	~15	Compatible	Compatible	Compatible
Cellulose	0.5-1.5	Compatible	Compatible	Compatible

An aqueous sticky polymer (polyacrylonitrile and styrene-butadiene rubber) emulsion with the

viscosity of 15000-20000 mPa·s and the solid content of 15 wt.%, named as LA135, was reported as binder in 2013 for ES preparation[*8*]. LA135 is the kind of binder that can be possessed for mass production with the advantages of organic solvent-free, low cost (~60 CNY per kilogram), and easy availability. Sun et al. [*8*] studied the novel binder LA135 assembled ESs with different electrolytes. In his study, the electrochemical properties of ES with different binders, including PVDF, PTFE, CMC alone and CMC/SBR, were comparatively studied with LA135. In the paper, all the binders' thermal stability was analyzed (see Fig. 2). It was worth noting that the electrode with LA135 shows good thermal stability, highest specific capacitance, and moderate internal resistance.

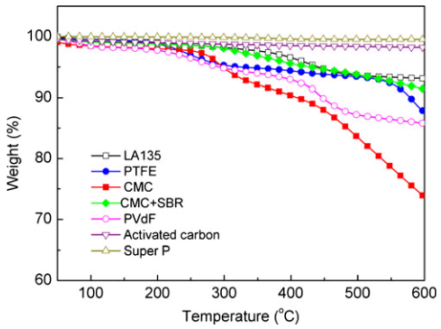

Figure 2. Thermal stability of activated carbon electrodes with different binders. Reprinted with permission from ref. 8. Copyright 2013 Journal Solid State Electrochemistry Publishing Group.

Natural, cheap, and environmentally friendly binder for ES was reported by A. Balducci [*7*]. Natural cellulose, the most abundant natural polymer, is a renewable natural resource produced from organic materials like wood and cotton. It is manufactured and regenerated in multi-ton scale every year to be used for the production of paper, tissue paper, cellophane, etc. Cellulose is a cheap material and its average production costs are estimated between 0.5 and 1.5 €kg^{-1}, depending on the yearly production [*53*]. Therefore, the introduction of cellulose as binder in ESs would represent an important contribution for the realization of cheap and environmentally friendly devices. Moreover, cellulose as binders has been successfully exploited for the realization of composite electrodes for lithium ion batteries [*53*]. Thus, the introduction of cellulose as binder for ES appears possible. A. Balducci et al. studied two different processing methods to process cellulose as ES binder. The first method is similar to that used for the preparation of cellulose-based lithiun-ion battery electrode [*53*], which is simply dissolving natural cellulose in 1-ethyl-3-methylimidazolium acetate (EMIM ac). Another method is that polyethylene oxide (PEO) is dissolved in deionized water first and the obtained solutions are added to the cellulose suspension [*7*]. Their experimental results suggest that natural cellulose as binder in ES is able to display high performance in term of specific capacitance and cycling stability as well as the conventional binders [*7*].

Other binders

In last year, some binders were also reported. However, it was difficult to synthesize and the binder cannot be used in combination with most of the active materials, so they have not been widely used in ES. Chang et al. [*54*] reported a novel liquid binder which was synthesized with acrylic acid and azodiisobutyronitrile (AIBN) to prepare electrodes from activated carbon, the electrode displayed excellent flexibility, durability, and perfect wettability.

Trends in ES binders

With increasing demands for clean, sustainable energy, the advantages of high power density,

high efficiency, and long life expectancy have made electrochemical supercapacitors one of the major emerging devices for energy storage and power supply. However, one of the key challenges for ES is their limited energy density, which has hindered their wider application in the field of energy storage. To overcome this challenge, we should be able to enhance the capacitance for material as well as the capacitance for ES electrodes. As we know, an ES electrode is a composite of active materials, polymeric binder, and conductive agents, binders are necessary for the device fabrication, and they might strongly affect the performance [*11, 46, 55-57*]. Therefore, high capacitance material and convenient binders should be applied to fabricate the ES electrodes in order to improve devices energy density.

In order to prepare high energy density ES binder, three key factors must be considered:

(1) In the process of electrode preparation, the active material and the conductive agent can spread homogeneously to form a uniform conductive network.

(2) In charging and discharging process, the binder combined closely with active material and sustained electrode structure and the conductive network integrity with it volume change repeatedly.

(3) It has good compatibility with the electrolyte.

In order to improve the performance of ES, considerably work focused on not only the development of materials with high specific capacitance, but also the inactive components especially binders. Based on the authors' experiences in working with the binders, we suggest more scientists devote to the research on the using of the complex of two or more binders in one ES, e.g. the synergistic effect of linear and point binders in gluing the particles of active materials while at the same forming network among all the particles. They are also encouraged to develop new binders with both high binding activity and conductivity, which could decrease electric resistance and therefore enhance the performance of ES.

Acknowledgments

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References

1. G. Wang, L. Zhang, J. Zhang, *Chem. Soc. rev.* **41**, 797-828 (Jan 21, 2012).
2. C. Largeot *et al.*, *J. Am. Chem. Soc.* **130**, 2730-2731 (2008/03/01, 2008).
3. S. G. Kandalkar, D. S. Dhawale, C.-K. Kim, C. D. Lokhande, *Synthetic Metals* **160**, 1299-1302 (2010).
4. J. R. Miller, P. Simon, *Science* **321**, 651-652 (Aug 1, 2008).
5. A. K. Shukla, *Reson* **6**, 49-62 (2001/11/01, 2001).
6. A. Burke, *Electrochimica Acta* **53**, 1083-1091 (2007).
7. N. Böckenfeld, S. S. Jeong, M. Winter, S. Passerini, A. Balducci, *J. Power Sources* **221**, 14-20 (2013).
8. X. Sun, X. Zhang, H. Zhang, B. Huang, Y. Ma, *Journal of Solid State Electrochemistry* **17**, 2035-2042 (2013/07/01, 2013).
9. A. K. Shukla, A. Banerjee, M. K. Ravikumar, A. Jalajakshi, *Electrochimica. Acta.* **84**, 165-173 (2012).
10. B. A., *J. Power Sources* **91**, 37-50 (2000).
11. J. Xu, S.-L. Chou, Q.-f. Gu, H.-K. Liu, S.-X. Dou, *J. Power Sources* **225**, 172-178 (2013).

12. Z. Zhang, T. Zeng, Y. Lai, M. Jia, J. Li, *J. Power Sources* **247**, 1-8 (2014).
13. H. Zheng, R. Yang, G. Liu, X. Song, V. S. Battaglia, *J. Phys. Chem. C* **116**, 4875-4882 (2012/02/23, 2012).
14. T.-H. Wu, Y.-H. Chu, C.-C. Hu, L. J. Hardwick, *Electrochem. Commun.* **27**, 81-84 (2013).
15. M. Minakshi, D. R. G. Mitchell, *Electrochimica. Acta.* **53**, 6323-6327 (2008).
16. P. K. C. P. C. Murall Dhar, *J. Mater. Sci. Lett.* **6**, 33-34 (1987).
17. P. Kurzweil, in *Encyclopedia of Electrochemical Power Sources,* J. Garche, Ed. (Elsevier, Amsterdam, 2009), pp. 634-648.
18. K.-M. Kim, J.-W. Hur, S.-I. Jung, A.-S. Kang, *Electrochimica. Acta.* **50**, 863-872 (2004).
19. F. Lufrano, P. Staiti, *Electrochimica. Acta.* **49**, 2683-2689 (2004).
20. J. Balach, M. M. Bruno, N. G. Cotella, D. F. Acevedo, C. A. Barbero, *J. Power Sources* **199**, 386-394 (2012).
21. s. s. X. Zhang, K. Jow, T. R., *J. Power Sources* **138**, 226-231 (2004).
22. S. Hu *et al.*, *Chem. Engineer. J.* **237**, 497-502 (2014).
23. A. Guerfi, M. Kaneko, M. Petitclerc, M. Mori, K. Zaghib, *J. Power Sources* **163**, 1047-1052 (2007).
24. J. Li, D.-B. Le, P. P. Ferguson, J. R. Dahn, *Electrochimica. Acta.* **55**, 2991-2995 (2010).
25. S. Komaba *et al.*, *J. Phys. Chem. C* **115**, 13487-13495 (2011/07/14, 2011).
26. N. Yabuuchi *et al.*, *Adv. Energy Mater.* **1**, 759-765 (2011).
27. A. Magasinski *et al.*, *ACS appl. mater. & interf.* **2**, 3004-3010 (2010/11/24, 2010).
28. Z.-J. Han *et al.*, *Energy & Environ. Sci.* **5**, 9014-9020 (2012).
29. S. Komaba, T. Ozeki, K. Okushi, *J.Power Sources* **189**, 197-203 (2009).
30. S. Komaba *et al.*, *Electrochem. Solid-State Lett.* **12**, A107-A110 (2009).
31. S. Komaba *et al.*, *Journal of Power Sources* **195**, 6069-6074 (2010).
32. K. Ui, S. Kikuchi, F. Mikami, Y. Kadoma, N. Kumagai, *J. Power Sources* **173**, 518-521 (2007).
33. Z. P. Cai, Y. Liang, W. S. Li, L. D. Xing, Y. H. Liao, *J. Power Sources* **189**, 547-551 (2009).
34. Z. Zhang *et al.*, *Electrochimica. Acta.* **80**, 440-444 (2012).
35. Z. Zhang *et al.*, *ECS Electrochem. Lett.* **1**, A74-A76 (2012).
36. K.-T. Lee, C.-B. Tsai, W.-H. Ho, N.-L. Wu, *Electrochem. Commun.* **12**, 886-889 (2010).
37. S. A. Hashmi, A. Kumar, S. K. Tripathi, *Ionics* **10**, 213-220 (2004/05/01, 2004).
38. X. L. Tetsuya Osaka, Masashi Nojima, and Toshiyuki Momma, *J. Electrochem. Soc.* **5**, 1724-1729 (1999).
39. L. Chensha *et al.*, *Prog. in Nat. Sci.* **15**, 453-457 (2005/05/01, 2005).
40. X. Sun, X. Zhang, H. Zhang, D. Zhang, Y. Ma, *J. Solid State Electrochem.* **16**, 2597-2603 (2012/08/01, 2012).
41. M. Stoller *et al.*, *J. Appl. Electrochem.* **41**, 681-686 (2011/06/01, 2011).
42. Y. Chen *et al.*, *RSC Advances* **2**, 7747-7753 (2012).
43. H. Buqa, M. Holzapfel, F. Krumeich, C. Veit, P. Novák, *J. Power Sources* **161**, 617-622 (2006).
44. S. Liu *et al.*, *J. Solid State Electrochem.* **16**, 1631-1634 (2012/04/01, 2012).
45. Z. Wang *et al.*, *Electrochimica. Acta.* **62**, 77-83 (2012).
46. S. Pejovnik, R. Dominko, M. Bele, M. Gaberscek, J. Jamnik, *J. Power Sources* **184**, 593-597 (2008).
47. S. F. Lux, F. Schappacher, A. Balducci, S. Passerini, M. Winter, *J. Electrochem. Soc.* **157**, A320-A325 (2010).
48. A. Krause *et al.*, *J. Power Sources* **196**,

8836-8842 (2011).
49. A. Brandt, P. Isken, A. Lex-Balducci, A. Balducci, *J. Power Sources* **204**, 213-219 (2012).
50. A. Krause, A. Balducci, *Electrochem. Commun.* **13**, 814-817 (2011).
51. X. Yan *et al.*, *J. Power Sources* **246**, 95-102 (2014).
52. H. S. Kim, K. Y. Chung, B. W. Cho, *J. Power Sources* **189**, 108-113 (2009).
53. S. S. Jeong, N. Böckenfeld, A. Balducci, M. Winter, S. Passerini, *J. Power Sources* **199**, 331-335 (2012).
54. L. Chang, Y. Yu, X. Duan, W. Liu, *Separation Sci. & Tech.* **48**, 359-365 (2012).
55. I. Kovalenko *et al.*, *Science* **334**, 75-79 (2011).
56. L. Gong, M. H. T. Nguyen, E.-S. Oh, *Electrochem. Commun.* **29**, 45-47 (2013).
57. F. M. Courtel, S. Niketic, D. Duguay, Y. Abu-Lebdeh, I. J. Davidson, *J. Power Sources* **196**, 2128-2134 (2011).