

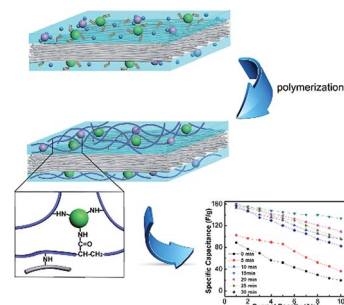
COMMUNICATION

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Controllable preparation of an eggshell membrane supported hydrogel electrolyte with thickness-dependent electrochemical performance

Xinhua Liu, Chengyao Yin, Jie Yang, Meiyang Liang, Junjie Wei, Ziyang Zhang, Huanlei Wang and Qigang Wang*

The controllable preparation of eggshell-hydrogels provides a new insight into composite material preparation from extensive life waste in energy devices with thickness-dependent electrochemical performances.



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Controllable preparation of an eggshell membrane supported hydrogel electrolyte with thickness-dependent electrochemical performance†

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The preparation of thin gel electrolyte membranes with controllable thickness is important to explore the thickness-dependent electrochemical behaviors; this can further guide the fabrication of energy devices. Here we employ an *in situ* polymerization method to prepare a BSA-PDMS-SiO₂ cross-linked nanocomposite hydrogel on surfaces of eggshell membranes, which can be used as integrated separator and electrolyte in a supercapacitor after absorbing the electrolyte. The novel controlled thickness of the coated hydrogel therefore offers superior space utilization essential for all-solid-state devices. The composite gel can reach a high ionic conductivity of 8.8 mS cm⁻¹ and a resulting C_{sp} value of 161 F g⁻¹ at the current density of 1 A g⁻¹ when assembled in the supercapacitor, while the eggshell membrane based device has limited values of 2.7 mS cm⁻¹ and 88 F g⁻¹. A new insight into hybrid material preparation from low-cost natural life waste is presented in this work to obtain high performance gel electrolytes in energy devices.

The all-solid-state supercapacitors, with desirable properties of controllable size, intrinsic safety, and long lifetimes, have great potential to be next generation power devices.¹⁻⁸ The selection of electrolytes and separators is the key factor for the fabrication of flexible supercapacitors to achieve high electrochemical performances.⁹⁻¹² The gel electrolyte materials including polyvinyl alcohol (PVA) gel and tough nanocomposite gel have been developed to prevent the conduction of electrons between two electrodes of supercapacitors because of their mechanical integrity.¹³⁻¹⁵ The self-supported gel should have suitable thickness and mechanical strength to cooperatively ensure the puncture and compressive forces of the tightly assembled devices.¹⁶ The resulting thickness bottleneck of the gel

electrolyte can hinder the further optimized design of a high performance supercapacitor.

The utilization of a tough porous material to support the gel electrolyte should be an alternative choice to control the whole device thickness and its electrochemical performance. The PP/PE (polypropylene/polyethylene) separators have demonstrated the ability to support a thin coating of ceramic materials for the improvement of safety.¹⁷⁻²⁰ However, the hydrophobic PP separator is not easy to be coated by the hydrophilic gel. Inspired by the pioneering work, the hydrophilic membrane coating with a controllable thickness gel layer can combine the advantages of a flexible polymer gel and the mechanical toughness of the membrane thus can overcome these issues and be used to design all-solid-state energy devices with adjustable performance. Herein, chicken eggshell membranes with about 80 μm thickness are selected as the scaffold to grow gel electrolytes due to their high porosity and mechanical strength.²¹

With non-toxicity and low-cost properties, eggshells are one of the most abundant materials in life wastes.^{21,22} More importantly, the eggshell membranes contain various collagen types I, V, and X which possess a large number of functional groups (-COOH, -NH₂) and have a great potential for the material design.^{23,24} In this work, we employed the *in situ* polymerization approach to prepare a composite eggshell membrane-BSA-PDMS-SiO₂ (bovine serum albumin-poly *N,N*-dimethylacrylamide-SiO₂) hydrogel. The eggshell membrane and BSA have many -NH₂ groups which can be acryloylated by a reaction with *N*-acryloxysuccinimide (NAS) to generate vinyl groups and allow for the effective growth of the BSA-PDMS-SiO₂ nanocomposite hydrogel.^{25,26} The SiO₂ nanoparticles within the polymer chains and proteins can act as physical crosslinkers and therefore can maintain the mechanical strength of the as-prepared sample. Fig. 1a-c show the photographs of chicken egg, eggshell, and eggshell membrane, respectively. The XRD spectra of the eggshell membranes (Fig. S1†) show the disappeared characteristic peaks of CaCO₃ after 1 M HCl treatment. In a typical preparation process, 0.2 g NAS was dissolved in 10 mL DI water (solution A). Then, eggshell membranes were put in solution A for 2 h to be

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† Electronic supplementary information (ESI) available: The detailed experimental procedures, sample pre-treatments and various characterizations are provided. See DOI: 10.1039/c6ta07341g

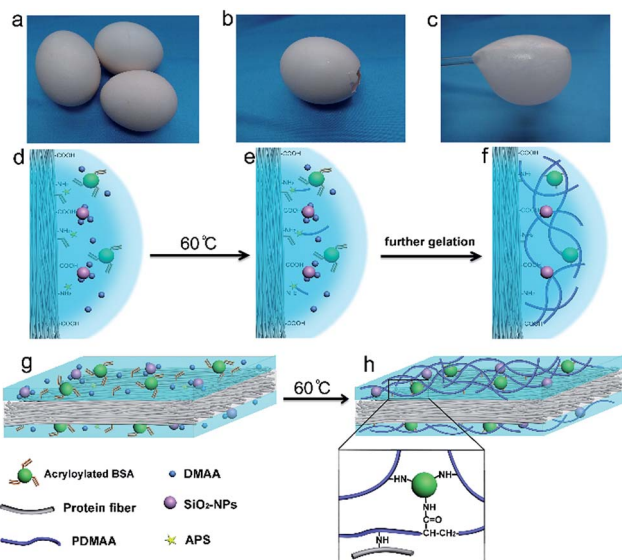


Fig. 1 Images and schematic illustration of eggshell and polymerization process. Photographs of (a) eggs, (b) an eggshell, and (c) a free-standing eggshell membrane. (d)–(f) Hydrogel grows with time on the surface of the eggshell membrane at 60 °C. (g) Acryloylated eggshell membrane in a precursor solution. (h) Eggshell membrane with tough hydrogel coatings and a magnified image of the mechanism.

acryloylated by the reaction with NAS to generate vinyl groups. Solution B can be prepared from a homogeneous aqueous solution of BSA (with 7.5 wt% NAS), SiO₂ nanoparticles (SiO₂-NPs, 13 nm), *N,N*-dimethylacrylamide (DMAA), and DI water with the mass ratio of 3 : 3 : 15 : 79. Then the eggshell membranes were suspended in precursor solution B, and ammonium persulfate (APS, 1.5%) was added and absorbed on the surfaces of the acryloylated eggshell membranes (Fig. 1d). Finally, the hydrogel can grow directly from the surfaces of the eggshell membranes at 60 °C along with time (Fig. 1e and f).

It can be further proved by FT-IR investigation (Fig. S2†). The bands of 1650 cm⁻¹ and 3400 cm⁻¹ indicate the presence of –NH₂ groups in the pure eggshell, followed by the disappearance of the –NH₂ from the modified eggshell. When the eggshell is suspended in the precursor solution, the added monomers can be polymerized on the eggshell membrane. Herein, the monomers were not fully polymerized. The double bonds of the monomers can be simply deduced from the wide bands in the wave number range 900–1050 cm⁻¹. With prolonged time, the bands become weaker; thus a continuous and more complete polymerization and a thicker hydrogel coating can be achieved. Therefore, the eggshell membrane with hydrogel coatings can be prepared (Fig. 1g and h), and the thickness of the hydrogel can be further controlled by the polymerization time. The SiO₂-NPs can serve as physical crosslinking points within the PDMAA chains and proteins *via* supermolecular effects. The nanocomposite hydrogel can grow on the acryloylated eggshell membrane surface, while the acryloylated BSA can act as crosslinkers within the polymer networks. The magnified image in Fig. 1h shows the preparation mechanism of the coated nanocomposite hydrogel.

As can be seen from Fig. 2a and b, the eggshell membrane contains protein fibres that can form three dimensional porous structures, which can facilitate the ion transport and enable its application as a supercapacitor separator. In the precursor solution, the BSA–PDMAA–SiO₂ nanocomposite hydrogel can grow from the surfaces of the acryloylated eggshell membrane. In a short polymerization time of 5 min, only a thin layer of hydrogel is formed on the eggshell membrane surface (Fig. 2d). Furthermore, a thicker hydrogel coating can be achieved by prolonging the polymerization time (Fig. 2e–i). The average single layer thicknesses of coated hydrogels along with time are shown in Fig. 2c. The thickness of a single layer hydrogel increases with the polymerization time. With a polymerization time of 30 min, the thickest layer of 260 μm can be achieved. Further extend the polymerization time, the eggshell membrane and the precursor will turn into a whole. The coated hydrogel membranes can retain the mechanical strength and increase the liquid retention ability of the eggshell membrane scaffold.

As shown in Fig. S3,† the BSA–PDMAA–SiO₂ nanocomposite hydrogels possess excellent mechanical strength. For the hydrogels with 3 wt% BSA and 15 wt% DMAA, the Young's modulus sharply increases from 13 kPa to 41 kPa and 44 kPa as the amount of SiO₂-NPs increases from 1% to 3% and 5%, respectively. The increase in the mechanical properties of the nanocomposite hydrogels with the amount of SiO₂-NPs can be attributed to the enhanced effect from nanofillers SiO₂-NPs *via* additional hydrogen bonding with polymer and protein. The excessive SiO₂-NP crosslinking points could not increase the strength sharply due to the difficulty in dispersion. Similarly, the increase of the DMAA monomer at the starting stage is beneficial in enhancing the crosslinking with BSA (Fig. S4†). The further increase in DMAA can increase the compressive

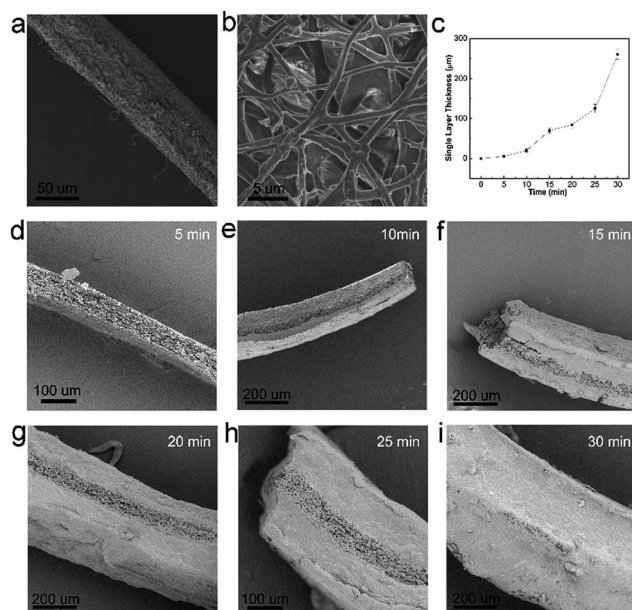


Fig. 2 (a) SEM images of the eggshell membrane in section. (b) The porous structure on the eggshell surface. (c) The time dependent thickness of a coated hydrogel. (d)–(i) Composite eggshells with hydrogel coating layers at various polymerization times.

modulus but decrease the broken strain due to the high cross-linking density. Although the increase in the polymer content can enhance the mechanical strength, the low contents of PDMAA and BSA would benefit the ion mobility and the resulting electrochemical performance. Therefore, the optimized composition to form tough BSA–PDMAA–SiO₂ should be 15 wt% DMAA, 3 wt% BSA, and 3 wt% SiO₂, respectively. The optimized composition of the hydrogel was used for the subsequent contrast experiments. Fig. 3a shows the tensile stress–strain curves for the eggshell membrane and the hybrid eggshell membrane with hydrogel coatings after absorbing sufficient electrolyte, where it is possible to notice that the composite gel possesses a larger elongation (14%) than the pure eggshell membrane (10%). Although the pure hydrogel has a low tensile strength of 257 kPa (Fig. S5†), the composite gel can maintain a similar stress value (1098 kPa) but a larger strain to the pure eggshell membrane (1112 kPa). The addition of the hydrogel can maintain a high tensile strength because of the copolymerization between the hydrogel and the eggshell membrane.

In order to investigate the electrochemical properties of the as prepared nanocomposite gel electrolytes, the ionic conductivity was determined based on their own electrolyte retention after being immersed in a 0.6 M Na₂SO₄ aqueous solution for 2 h at room temperature to absorb sufficient electrolyte (Fig. 3b). The pure eggshell membrane possesses a limited ionic conductivity value of 2.7 mS cm⁻¹ because it can only absorb a small amount of electrolyte. The coated hydrogel can enhance the liquid retention ability, and thus can achieve improved ionic conductivity (from 4.3 mS cm⁻¹ to 8.8 mS cm⁻¹) at the early polymerization stage from 5 min to 15 min. The coated hydrogel can host the ions within its 3D porous polymer networks, while the hydrogel layer is beneficial in maintaining the large amount

of free ions in the porous eggshell membrane. The ionic conductivity exhibits obvious enhancement at an early polymerization stage and tends to be stable when the hydrogel layers reach a greater thickness. Similarly, the resistances of the as-prepared samples increase with the polymerization time (Fig. S6†); at the same time, the resistivity decreases (Fig. S7†). Therefore, the eggshell membrane with 15 min polymerization of hydrogel coating (composite sample) was selected for subsequent tests.

The pure eggshell membrane and composite sample both swell in the Na₂SO₄ aqueous solution because of their hydrophilic property. The swell ratio was determined by the changes in volume with different storage times according to eqn (S1)†. As shown in Fig. 3c, the swell ratios of the eggshell membrane and composite sample remain around 10% and 15%, respectively. The swell ratio of the composite sample can still maintain a low level and is stable after a long time of 30 days.

Furthermore, the water absorption coefficient changes of the samples with various storage times were monitored to evaluate their stabilities (eqn (S2)†). The samples dried at 80 °C for 24 h were selected as standards. Fig. 3d presents the water absorption coefficients of the samples. The pure eggshell membrane can only absorb about 10% electrolyte, indicating a low wettability and limited ionic conductivity of the membrane. Compared to the pure eggshell membrane, the composite membrane can absorb a higher level of 55% electrolyte. The hydrogel possesses both the mechanical toughness and the electrochemical properties because the 3D porous polymer structures can ensure the mechanical integrity and the ion transport. The long term stability, low swelling degrees, and high ionic conductivity of the composite gels indicate them to be potential candidates for integrated separators in supercapacitors.^{27–29}

More importantly, the single layer thickness of the hydrogel coating can be accurately controlled by the polymerization time. The low thickness varies from 5 μm to 260 μm with a short polymerization time of 5–30 min. The hydrogel coated eggshell membrane possesses great advantages over other modified separators: (1) the composite gel electrolytes can be used in all-solid-state supercapacitors because the hydrogel itself can be a flexible gel electrolyte while other modified separators are still dependent on the liquid electrolyte; (2) the flexible hydrogel can grow from both surfaces of eggshell membranes while the friable ceramic coating is only loaded on one side; (3) the composite gel electrolytes with low and controllable thickness coatings of hydrogels are expected to exhibit adjustable electrochemical performances which are difficult for other modified separators to achieve.

In this work, activated carbon (YP 80F) with a specific surface area of about 2100 m² g⁻¹ was used as a supercapacitor electrode material. Two activated carbon electrodes and one eggshell membrane/composite gel electrolyte were sandwich assembled in a supercapacitor. The charge/discharge curves of the eggshell membrane and composite gel electrolyte (with 15 min polymerization time) based supercapacitors are presented in Fig. 4a, which can directly show their capacitive performances. The composite gel electrolyte based

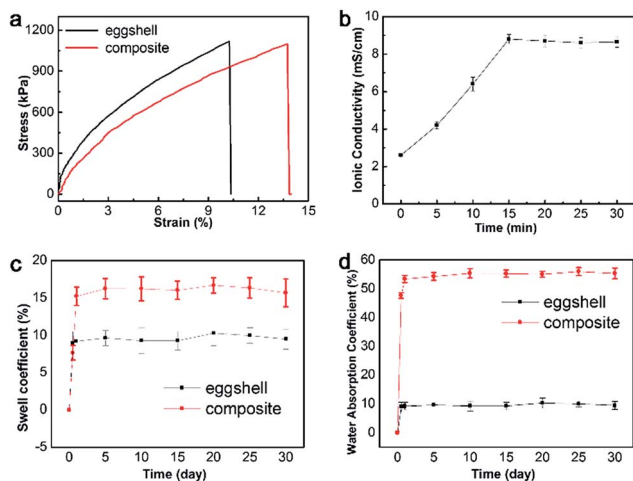


Fig. 3 (a) Tensile stress–strain curves of eggshell membrane and composite gel after absorbing sufficient electrolyte. (b) Ionic conductivities of composite gel electrolytes at various polymerization times after absorbing the electrolyte. The swell coefficient (c) and liquid absorption coefficient (d) of pure eggshell membrane and composite gel with 15 min polymerization in a 0.6 mol L⁻¹ Na₂SO₄ aqueous solution at room temperature.

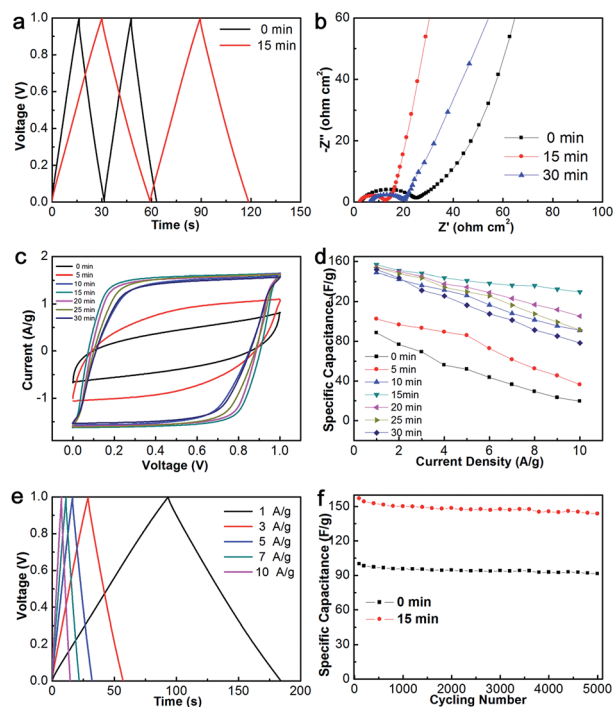


Fig. 4 (a) The charging–discharging curves of the eggshell based supercapacitors with 0 min and 15 min polymerization coating of the hydrogel in $0.6 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ at the current density of 2 A g^{-1} . (b) Impedance spectroscopy of the eggshell based supercapacitors with various electrolytes. (c) The cyclic voltammograms of the eggshell based supercapacitors at various coating times and thicknesses in $0.6 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$. (d) The charging–discharging curves of the gel electrolyte (15 min polymerization) based supercapacitors at various current densities. (e) The gravimetric capacitances of eggshell based supercapacitors at various polymerization times measured at various current densities. (f) Long-term cycling performance of supercapacitors employing eggshell and composite electrolytes at the current density of 1 A g^{-1} .

supercapacitor can achieve a high specific capacitance (C_{sp}) value of 152 F g^{-1} at the current density of 2 A g^{-1} , while the pure eggshell membrane based device exhibited a limited value of 10 F g^{-1} . The composite gel electrolyte-based supercapacitor exhibits more rectangular cyclic voltammogram (CV) curves than the eggshell membrane based device (Fig. 4c), indicating the electrochemical enhancement of the composite

device. With further increase in the thickness of the hydrogel coating, it tends to be stable with a slight decline. As an important factor, the current density can directly characterize the capacitive properties of the supercapacitor. It is obvious from Fig. 4d that the composite gel electrolyte based device performed better in maintaining higher specific capacitance values at higher current densities than the pure eggshell membrane. Among them, the device with the composite gel electrolyte with 15 min polymerization shows the best C_{sp} maintenance. Its charging–discharging curves are highly linear and symmetric at various current densities from 1 to 10 A g^{-1} , implying the excellent electrochemical reversibility and capacitive behaviors (Fig. 4e).

The enhanced electrochemical performance of the composite hydrogel based device can be attributed to the abundant free ions which are hosted within the porous eggshell membrane and hydrogel. During the charging–discharging process, the ions can easily get transferred within the composite gel electrolyte and between the electrode/electrolyte interfaces. In contrast, the pure eggshell membrane can only maintain a small amount of electrolyte which cannot fully wet the electrodes. Impedance spectroscopy of supercapacitors with various electrolytes further illustrates the electrochemical enhancements of the composite gel electrolyte based devices. In Fig. 4b, the impedance plots show an arc at higher frequency and a spike at lower frequency. The different semicircles at the high frequency range correspond to the charge transfer resistance (R_{ct}) which is caused by the double layer capacitance on the surface. The R_{ct} of the eggshell membrane based device is poorer than that of the composite based device because of the wetting issue. Therefore, the composite gel electrolyte based supercapacitor has stable and higher C_{sp} values than the eggshell membrane based device even after a long time (Fig. 4f). Furthermore, we compared the Nyquist plots of the supercapacitor using composite gel electrolyte and PP separators (Fig. S8†). Clearly, the R_s and R_{ct} of the supercapacitor with the composite eggshell-based gel electrolyte are much smaller than those of the supercapacitor with the commercial PP separator, which indicates that the eggshell-based gel electrolyte is a superior separator material for supercapacitor. Therefore, the composite gel electrolyte based supercapacitor can achieve enhanced electrochemical behaviours than both the pure eggshell and PP membrane based devices.

Table 1 Comparison of various electrolytes reported in the literature

Electrolyte	Electrolyte state	Electrode	Specific capacitance (F g^{-1})	Tensile strength (kPa)	Ref.
Eggshell-hydrogel	Gel	Activated carbon	161 (at 1 A g^{-1})	1098	This work
Pure eggshell	Liquid	Activated carbon	88 (at 1 A g^{-1})	1112	
PP	Liquid	Activated carbon	100 (at 0.5 A g^{-1})	6590	21
PVC-PEO	Gel	No data available		77–228	32
PHEMA-CS	Gel	Activated carbon	4–104 (at 25 mV s^{-1}) 13–140 (at 0.5 A g^{-1})	73–95	33 and 34
TiO ₂ -PHEMA	Gel	Activated carbon	102 F g^{-1} (at 5 mV s^{-1})	23–177	35
PMMA	Gel	No data available		50–160	36
PAA	Gel	No data available		3–8	37
PVA	Gel	Activated carbon	80 (at 2 A g^{-1})	No data available	38

The hydrogel coated eggshell membrane exhibits not only excellent electrochemical performance but also high mechanical strength compared to other kinds of modified separators (Table 1). The tensile value of the gel electrolyte can reach a high tensile strength of 1098 kPa, which is similar to that of the pure eggshell (Table 1 and Fig. 3a). Compared to the well-known commercial PP separator, the hydrogel coated eggshell membrane can reach a little lower tensile value but maintain better electrochemical performance.^{21,30,31} More importantly, the composite gel electrolyte can be used as integrated separator and electrolyte while the PP and eggshell based supercapacitors still need a liquid electrolyte. Additionally, the effective combination of polymer and electrolyte is paving the way for a promising family of gel electrolytes for the application in all-solid-state energy storage devices relative to traditional aqueous and organic ones. It is worth mentioning that both the specific capacitance and the tensile strength of the composite gel electrolyte are much higher than most of the values of gel electrolytes from reported papers.^{32–38} Applying the same electrode material, the composite gel electrolyte based supercapacitor can achieve a higher specific capacitance than the PVA–H₂SO₄ based device which has poor mechanical strength.^{34,38}

In conclusion, we present a promising approach to prepare the eggshell membrane supported hydrogel layers by surface polymerization. Meanwhile, the thicknesses of the coated hydrogel layer can be controlled applying various polymerization times. The excellent mechanical performance and high liquid retention ability of the composite gel can benefit its application as an electrolyte in a tightly assembled supercapacitor. The final supercapacitors exhibit adjustable specific capacitances, which are affected by the various thicknesses of the gel electrolyte membranes. The composite gel electrolytes have great potential to serve as the integrated electrolytes and separators for the facile fabrication of energy devices.

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Notes and references

- 1 P.-C. Chen, G. Shen, Y. Shi, H. Chen and C. Zhou, *ACS Nano*, 2010, **4**, 4403–4411.
- 2 Z. Xiong, C. Liao, W. Han and X. Wang, *Adv. Mater.*, 2015, **27**, 4469–4475.
- 3 L.-F. Chen, Z.-H. Huang, H.-W. Liang, W.-T. Yao, Z.-Y. Yu and S.-H. Yu, *Energy Environ. Sci.*, 2013, **6**, 3331–3338.
- 4 K. Jost, G. Dion and Y. Gogotsi, *J. Mater. Chem. A*, 2014, **2**, 10776–10787.
- 5 H. Lin, L. Li, J. Ren, Z. Cai, L. Qiu, Z. Yang and H. Peng, *Sci. Rep.*, 2013, **3**, 1353.
- 6 Z. Yang, J. Deng, X. Chen, J. Ren and H. Peng, *Angew. Chem., Int. Ed.*, 2013, **52**, 13453–13457.

- 7 H. Yu, J. Wu, L. Fan, K. Xu, X. Zhong, Y. Lin and J. Lin, *Electrochim. Acta*, 2011, **56**, 6881–6886.
- 8 J. Ren, L. Li, C. Chen, X. Chen, Z. Cai, L. Qiu, Y. Wang, X. Zhu and H. Peng, *Adv. Mater.*, 2013, **25**, 1155–1159.
- 9 A. Izadi-Najafabadi, S. Yasuda, K. Kobashi, T. Yamada, D. N. Futaba, H. Hatori, M. Yumura, S. Iijima and K. Hata, *Adv. Mater.*, 2010, **22**, E235–E241.
- 10 S. Saricilar, D. Antiohos, K. Shu, P. G. Whitten, K. Wagner, C. Wang and G. G. Wallace, *Electrochem. Commun.*, 2013, **32**, 47–50.
- 11 S. Pan, J. Deng, G. Guan, Y. Zhang, P. Chen, J. Ren and H. Peng, *J. Mater. Chem. A*, 2015, **3**, 6286–6290.
- 12 A. Izadi-Najafabadi, S. Yasuda, K. Kobashi, T. Yamada, D. N. Futaba, H. Hatori, M. Yumura, S. Iijima and K. Hata, *Adv. Mater.*, 2010, **22**, E235–E241.
- 13 K. Wang, Q. Meng, Y. Zhang, Z. Wei and M. Miao, *Adv. Mater.*, 2013, **25**, 1494–1498.
- 14 F. Meng and Y. Ding, *Adv. Mater.*, 2011, **23**, 4098–4102.
- 15 D. Ge, L. Yang, L. Fan, C. Zhang, X. Xiao, Y. Gogotsi and S. Yang, *Nano Energy*, 2015, **11**, 568–578.
- 16 Y. Wang, Y. Shi, L. Pan, Y. Ding, Y. Zhao, Y. Li, Y. Shi and G. Yu, *Nano Lett.*, 2015, **15**, 7736–7741.
- 17 D. Takemura, S. Aihara, K. Hamano, M. Kise, T. Nishimura, H. Urushibata and H. Yoshiyasu, *J. Power Sources*, 2005, **146**, 779–783.
- 18 J.-A. Choi, S. H. Kim and D.-W. Kim, *J. Power Sources*, 2010, **195**, 6192–6196.
- 19 J. Wang, Z. Hu, X. Yin, Y. Li, H. Huo, J. Zhou and L. Li, *Electrochim. Acta*, 2015, **159**, 61–65.
- 20 X. Zhu, X. Jiang, X. Ai, H. Yang and Y. Cao, *ACS Appl. Mater. Interfaces*, 2015, **7**, 24119–24126.
- 21 H. Yu, Q. Tang, J. Wu, Y. Lin, L. Fan, M. Huang, J. Lin, Y. Li and F. Yu, *J. Power Sources*, 2012, **206**, 463–468.
- 22 S. H. Chung and A. Manthiram, *Adv. Mater.*, 2014, **26**, 1360–1365.
- 23 J. E. Dennis, D. A. Carrino, K. Yamashita and A. I. Caplan, *Matrix Biol.*, 2000, **19**, 683–692.
- 24 Z. Li, Z. Xu, X. Tan, H. Wang, C. M. Holt, T. Stephenson, B. C. Olsen and D. Mitlin, *Energy Environ. Sci.*, 2013, **6**, 871–878.
- 25 J. Kim and J. W. Grate, *Nano Lett.*, 2003, **3**, 1219–1222.
- 26 D. Tada, T. Tanabe, A. Tachibana and K. Yamauchi, *Mater. Sci. Eng., C*, 2007, **27**, 870–874.
- 27 B. Choi, J. Hong, W. Hong, P. Hammond and H. Park, *ACS Nano*, 2011, **5**, 7205–7213.
- 28 J. Zhou, J. Cai, S. Cai, X. Zhou and A. Mansour, *J. Power Sources*, 2011, **196**, 10479–10483.
- 29 F. Meng and Y. Ding, *Adv. Mater.*, 2011, **23**, 4098–4102.
- 30 E. Kontou and P. Farasoglou, *J. Mater. Sci.*, 1998, **33**, 147–153.
- 31 S. Kundu, L. Simon, M. Fowler and S. Grot, *Polymer*, 2005, **46**, 11707–11715.
- 32 S. Ramesh, T. Winie and A. K. Arof, *Eur. Polym. J.*, 2007, **43**, 1963–1968.
- 33 X. Liu, Z. Wen, D. Wu, H. Wang, J. Yang and Q. Wang, *J. Mater. Chem. A*, 2014, **2**, 11569–11573.

1	34 X. Liu, D. Wu, H. Wang and Q. Wang, <i>Adv. Mater.</i> , 2014, 26 , 4370–4375.	37 B. Chen, J. Lu, C. Yang, J. Yang, J. Zhou, Y. Chen and Z. Suo, <i>ACS Appl. Mater. Interfaces</i> , 2014, 6 , 7840–7845.	1
	35 X. Liu, B. He, Z. Wang, H. Tang, T. Su and Q. Wang, <i>Sci. Rep.</i> , 2014, 4 , 6673.	38 Y. Kang, H. Chung, C. Han and W. Kim, <i>Nanotechnology</i> , 2012, 23 , 065401.	
5	36 M. Li, J. Li, H. Na and J. J. Vlassak, <i>Soft Matter</i> , 2014, 10 , 7993–8000.		5
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