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Properties of magnesium phosphate cement as electrolyte for structural supercapacitor

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The properties of cement based on magnesium phosphate (MPC) were investigated; the effect of various concentrations (3M, 6M and 9M) of alkalis LiOH, NaOH and KOH on the internal resistance, ionic conductivity and compressive strength of the structural electrolyte was studied. The results show that MPC-K9 is the optimal structural electrolyte. The maximum ionic conductivity of the MPC-K9 structural electrolyte was 16.85 $mS\cdot cm^{-1}$, which indicates its best electrochemical characteristics. An integrated structural supercapacitor is assembled with graphene electrodes and MPC-K9 structural electrolyte, and its electrochemical characteristics have been measured. The cyclic voltammetry curve was nearly rectangular in shape, indicating a typical double layer effect. The constructive supercapacitor had a surface capacity 16.72 mF/cm^2 and a compressive strength 5.9 MPa. The structural supercapacitor shows good stability and reversibility with 94.50 % capacity retention after 3000 cycles. Thus, magnesium phosphate cement can be used in the field of energy storage in buildings.

Keywords: magnesium phosphate cement, electrolyte, structural supercapacitors, compressive strength, electrochemical performance.

Властивості магнієво-фосфатного цементу як електроліту для структурного суперконденсатора. *Zhou Changshun, Wang Qidong, YU Zhouping*

Досліджено властивості цементу на основі фосфату магнію (MPC), вплив різних концентрацій (3M, 6M та 9M) лугів LiOH, NaOH і KOH на внутрішній опір, іонну провідність та міцність на стиск структурного електроліту. Результати показали, що оптимальним структурним електролітом є MPC-K9. Максимальна іонна провідність структурного електроліту MPC-K9 становила 16,85 $мСм\cdot см^{-1}$, що вказує на його найкращі електрохімічні характеристики. Інтегрований структурний суперконденсатор зібраний з графеновими електродами та структурним електролітом MPC-K9, виміряно його електрохімічні характеристики. Крива циклічної вольтамперометрії має форму, близьку до прямокутної, що вказує на типовий ефект подвійного шару. Конструктивний суперконденсатор має значення поверхневої ємності 16,72 $мФ/см^2$ та міцність на стиск 5,9 МПа. Конструкційний суперконденсатор показує хорошу стабільність та оборотність із збереженням ємності 94,50 % після 3000 циклів. Таким чином, магнійфосфатний цемент можна використовувати у галузі накопичення енергії у будинках.

Исследованы свойства цемента на основе фосфата магния (MPC), исследовано влияние различных концентраций (3M, 6M и 9M) щелочей LiOH, NaOH, KOH на внутреннее сопротивление, ионную проводимость и прочность на сжатие структурного электролита. Результаты показали, что оптимальным структурным электролитом является MPC-K9. Максимальная ионная проводимость структурного электролита MPC-K9 составляет 16,85 $мСм\cdot см^{-1}$, что указывает на его наилучшие электрохимические характеристики. Интегрированный структурный суперконденсатор собран с графеновыми электродами и структурным электролитом MPC-K9, измерены его электрохимические характеристики. Кривая циклической вольтамперометрии имеет форму, близкую к прямоугольной, что указывает на типичный эффект двойного слоя. Конструктивный суперконденсатор имеет значение поверхностной емкости 16,72 мФ/см^2 и прочность на сжатие 5,9 МПа. Конструкционный суперконденсатор показывает хорошую стабильность и обратимость с сохранением емкости 94,50 % после 3000 циклов. Таким образом, магнийфосфатный цемент можно использовать в области накопления энергии в зданиях.

1. Introduction

Recently, with the global energy shortage and pollution becoming more and more serious, researchers have developed new energy storage systems (ESSs). Traditional ESSs include batteries, dielectric capacitors and supercapacitors [1, 2]. Batteries have high energy density but low power density, while dielectric capacitors can provide high power density but limited energy density [3–5]. The electrochemical performance of supercapacitors are between batteries and dielectric capacitors [6, 7]. However, the relatively poor mechanical properties and unsatisfactory energy density limit the application of supercapacitors [8–10]. Therefore, novel electrode materials and electrolytes can be designed to enable structured supercapacitors to have the desired versatility. Among them, the structural electrode materials must have excellent structural performance and good electrochemical performance. In addition, structural electrolytes should eliminate the tension between high structural strength and a porous structure that facilitates ion movement and storage.

Graphene is a two-dimensional (2D) carbon material composed of a single layer of carbon atoms [11, 12]. It has attracted great attention due to its high mechanical strength (Young's modulus 1.0 TPa) [13], large specific area (2630 $m^2\cdot g^{-1}$) and excellent electrical conductivity (108 S/m) [14, 15]. Stoller et al. prepared a rGO based supercapacitor with a high specific capacity [16]. Zhang et al. successfully prepared a structured supercapacitor assembled by graphene electrodes with a specific capacitance of about 10 $F\cdot g^{-1}$ [17]. Therefore, graphene is considered as a potential electrode material for structuring supercapacitors.

Magnesium phosphate cement (MPC) is a cementious material based on acid-base neutralization reaction [18, 19]. MPC is a kind of high crystalline substance obtained as a result of the reaction of neutralization with acid and base when mixing raw materials, such as MgO (magnesia, sea salt, salt water, dolomite calcined), acid phosphate (KH_2PO_4, K_2HPO_4, $NH_4H_2PO_4$, $(NH_4)_2HPO_4$), retarder (sodium tripolylphosphate, boric acid, borate) and mineral admixture (fly ash, silica fume, slag, bentonite) [20–23]. MPC is especially attractive as a structural electrolyte material due to advantages of fast hardening, high early strength, good volume stability, high frost resistance, high bond strength and relatively high porosity which greatly contributes to the ionic conductivity of structural supercapacitors [24, 25].

In this paper, a novel multifunctional supercapacitor based on graphene and MPC was synthesized. The MPC alkaline structural electrolyte is sandwiched by two conductive graphene electrodes. The effects of the variety and concentration of alkali on the conductivity of the structure electrolyte are studied, and the electrochemical and mechanical properties of the integrated structure supercapacitor are evaluated.

2. Experimental

The highly conductive graphene used in this experiment was purchased from the Institute of Coal Chemistry, Chinese Academy of Sciences. Acetylene black, polyvinylidene difluoride (PVDF), N-methylpyrrolidone (NMP), LiOH, NaOH and KOH were purchased from Aladdin Chemical Reagent Co., LTD. Magnesium oxide powder (MgO), lithium dihydrogen phosphate (LDP) and borax were purchased from Sinophenol Chemical Reagent Co., LTD. MPC alkaline structure electrolyte was prepared from MgO, LDP, borax, LiOH, NaOH, KOH and deionized water. All chemicals used in the test were analytically pure.

2.1. Preparation of structural electrodes

Highly conductive graphene was mixed with acetylene black and PVDF at the mass ratio of 80:10:10, and completely ground in an agate mortar. Then an appropriate amount of NMP was added into the mixture. After uniform mixing, the resulting slurry was pasted onto nickel foam, then compressed under the pressure of 20 MPa and dried to obtain a thin plate with a thickness of about 5.5 mm. The total weight of the electrodes loaded on the nickel foam was about 1 mg/cm.

2.2. Preparation of MPC basic structural electrolytes

MPC alkaline structure electrolytes were synthesized according to the ratios shown in Table. The mass ratio of magnesium oxide to LDP (M/P) is 4. The water cement ratio

Table. Mixing ratios of alkaline structural electrolyte on magnesium phosphate cement (MPC) (g).

Sample	MgO	LDP	Borax	Water	LiOH	NaOH	KOH
MPC-Li3	2	0.5	1.25	1	0.072	–	–
MPC-Li6	2	0.5	1.25	1	0.144	–	–
MPC-Li9	2	0.5	1.25	1	0.216	–	–
MPC-Na3	2	0.5	1.25	1	–	0.12	–
MPC-Na6	2	0.5	1.25	1	–	0.24	–
MPC-Na9	2	0.5	1.25	1	–	0.36	–
MPC-K3	2	0.5	1.25	1	–	–	0.168
MPC-K6	2	0.5	1.25	1	–	–	0.336
MPC-K9	2	0.5	1.25	1	–	–	0.504

(W/C) of magnesia, LDP and borax is 0.32. Borax/magnesia (B/M) is chosen as 0.3125 in order to reduce the setting rate. Three kinds of alkali (LiOH, NaOH and KOH) were added, and the concentration was adjusted to 3M, 6M and 9M. The above mixture was mixed evenly and poured into the mold with a side length of 10 mm as the electrolyte for the structural supercapacitor. The remainder was placed in a cubic mold (30×30×30 mm^3) for mechanical testing. All samples were cured at a temperature of 20±1° and relative humidity of more than 90 % for 28 days. The final electrolyte samples were labeled as MPC-Li3, MPC-Li6, MPC-Li9; MPC-Na3, MPC-Na6, MPC-Na9; MPC-K3, MPC-K6, MPC-K9.

2.3. Assembling the integrated structural supercapacitor

The structure supercapacitor was assembled by inserting two structural electrodes into two ends of the MPC alkaline structure electrolyte obtained above until the slurry was harden. Its electrochemical performance was measured after 28 days of curing.

2.4. Characterizations and test methods

The morphology of the MPC alkaline electrolyte was characterized by a ZEISS Gemini 300 scanning electron microscope (SEM) at an accelerating voltage of 0.02–30 kV.

All electrochemical analyses were performed at the CHI660E electrochemical workstation (Chenhua Instruments, Shanghai, China). The cyclic voltammetry (CV) tests of structural supercapacitors were carried out with a scanning rate of 100 mV/S and a voltage window of −0.5 ~ + 0.5 V. Electrochemical impedance spectroscopy (EIS) tests were performed at open circuit potential with a frequency range of 0.1 Hz to 100 Hz. The areal capacitance of structural supercapacitors was calculated according to the constant current charge-discharge curve (GCD). The ionic conductivity of the MPC alkaline structure electrolyte can be calculated by the following formula:

$$\sigma = d/SR_s, \qquad (1)$$

where d is the distance between two electrodes, S is the contact area between electrode and electrolyte, and R_s is the bulk resistance of MPC alkaline structure electrolyte.

The area capacitance of structural supercapacitor is calculated by the formula:

$$C = I \cdot \Delta t/S\Delta V. \qquad (2)$$

Here C is the surface specific capacitance (F·cm^{-2}), I is the current density (A·cm^{-2}), S is the area of the active substance (cm^2), ΔV is the potential window (V), and Δt is the discharge time (s).

The compressive strength of the MPC alkaline structure electrolyte was measured on a JES 300 concrete compressive strength tester (Wuxi, China) at the loading rate 2.4 kN/s. Three samples were prepared for each group and tested under the same conditions in order to ensure the accuracy of the experimental results.

3. Results and discussion

3.1. Internal resistance and ionic conductivity analysis of MPC alkaline structure electrolyte

The internal resistance of the structural electrolyte should be kept as low as possible in order to improve its ionic conductivity. The internal resistance of the structural electrolyte is determined by the intersection point of the Nyquist curve and horizontal axis in the high frequency region of electri-

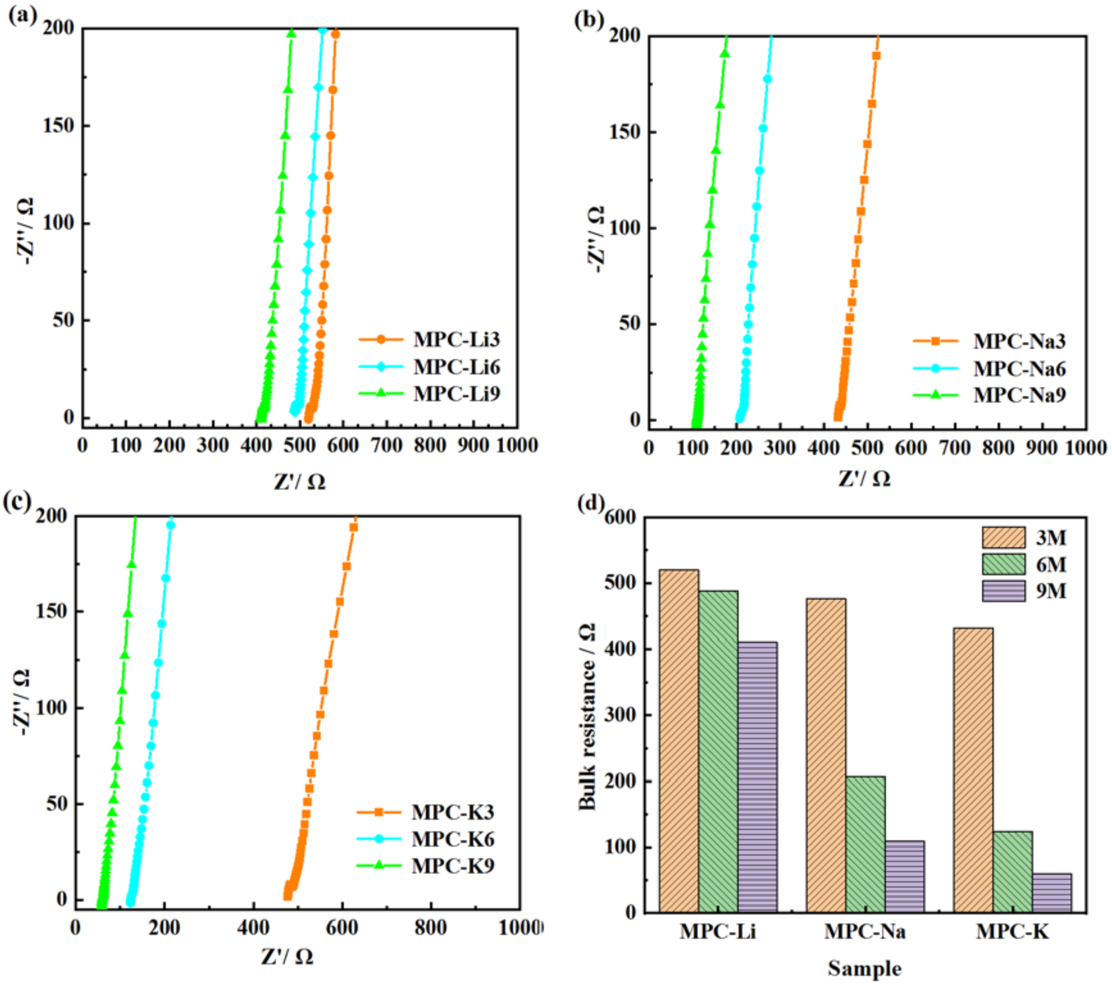

Fig. 1. (a–c) EIS spectra, (d) bulk resistances of the structural electrolytes with various contents of MPC alkaline.

cal impedance spectroscopy. As can be seen from Fig. 1, the resistance of the same type of alkali gradually decreases with increasing its concentration, that is: Rb (MPC — Li3) > Rb (MPC — Li6) > Rb (MPC — Li9); Rb (MPC — Na3) > Rb (MPC — Na6) > Rb (MPC — Na9); Rb (MPC — K3) > Rb (MPC — K6) > Rb (MPC — K9). At the same concentration, the internal resistance of MPC added with KOH electrolyte was lower. MPC-K9 exhibited the lowest internal resistance (59.34 Ω) among the nine electrolytes. This may be attributed to the addition of KOH electrolyte and more pores, which facilitates the diffusion of ions between the electrolyte and the electrode.

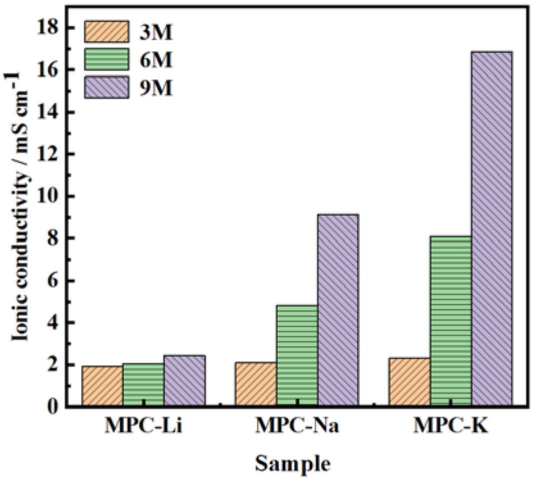

Fig. 2. Ionic conductivities of the structural electrolytes with various contents of MPC alkaline.

Fig. 2 shows the ionic conductivity of nine electrolytes. The ionic conductivity of these electrolytes added with of LiOH increased slightly with its concentration. With an increase in the concentration of NaOH electrolyte, the ionic conductivity has doubled in comparison with the initial one. Also, the ionic conductivity of electrolytes added with KOH increased sharply with KOH concentration. Therefore, the MPC-K9

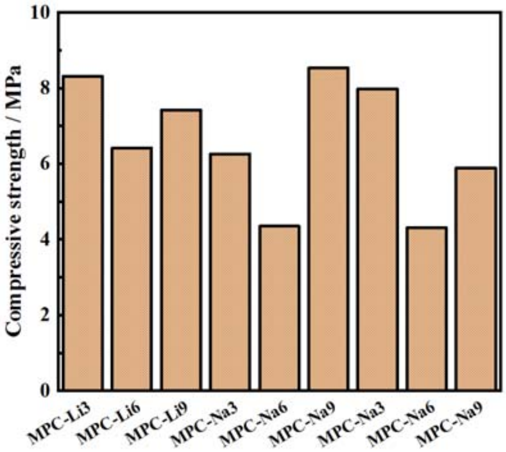

Fig. 3. Compressive strength of structural electrolytes with various MPC alkaline contents.

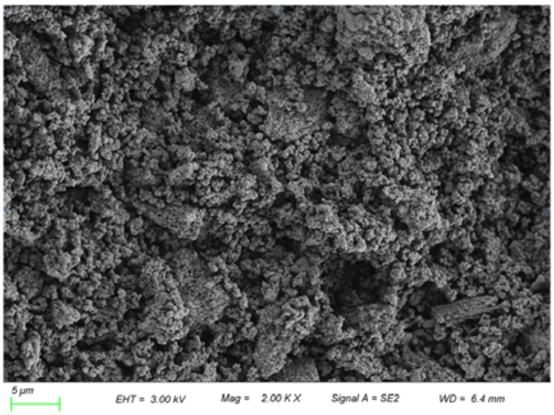

Fig. 4. SEM image of MPC-K9 structural electrolyte.

electrolyte showed the highest ionic conductivity (up to 16.85 mS·cm^{-1}), indicating that the MPC-K9 electrolyte has the best electrochemical performance and is expected to be used as an ideal electrolyte for structural supercapacitors.

3.2. Mechanical properties of MPC alkaline electrolytes

The compressive strength tests were used to evaluate the mechanical properties of the nine structural electrolytes as shown in Fig. 3. The compressive strength of these electrolytes fluctuated in the range of 4 ~ 9 MPa, which indicated that the compressive strength of these electrolytes remained at a moderate level. Structural supercapacitors must have both excellent electrochemical and mechanical properties. Therefore, the MPC-K9 alkaline electrolyte with the best electrochemical performance is selected for further analysis when there is little difference in mechanical properties.

3.3. Microstructure characterization of the MPC alkaline structure electrolyte

The morphology of MPC-K9 structural electrolyte was analyzed using a scanning electron microscope (SEM). As shown in Fig. 4, the MPC-K9 structural electrolyte was composed of irregular particles with loose structure, and a large number of holes with a diameter of 0.5–5 μm were widely distributed in the electrolyte, which can provide sufficient channels for ion migration. Therefore, the ionic conductivity of the MPC-K9 structural electrolyte is higher than for others.

3.4. Electrochemical performance of assembled structural supercapacitors

The integrated structural supercapacitor was assembled as MPC-K9 structural electrolyte sandwiched between two graphene electrodes. Cyclic voltammetry (CV), galvanostatic charge-discharge (DSC), electrochemical impedance (EIS) and cyclic stability of the structural supercapacitor were measured. Fig. 5a shows the CV curve of the structural supercapacitor based on graphene and MPC-K9. It can be seen that the curve obtained with the scanning rate of 0.01 mV/s, has a spindle shape without REDOX peaks, which indicates that the structural supercapacitor is a typical double layer capacitor and has good electrochemical reversibility. Fig. 5b shows the DSC curves when the current density is 0.1 mA·cm^{-2}, 0.2 mA·cm^{-2} and 0.3 mA·cm^{-2}. The three charge-discharge curves are triangular, indicating that the structural supercapacitor is a typical double layer capacitor. The area capacitance of the structural supercapacitor can be calculated based on the DSC curve by formula (2), and the longer the discharge time, the larger the area capacitance. Therefore, the area capacitance of the structural supercapacitor decreases with current density, as shown in Fig. 5c. Moreover, the area capacitance reached the maximum value of 16.72 mF·cm^{-2} at the current density of 0.1 mA·cm^{-2}. This may be due to the addition of a high concentration of KOH, which increases the number of charged ions, accelerates the migration rate of ions, and reduces the migration resistance of ions between the electrode and the electrolyte. Based on the resistance of the structural supercapacitor, as shown in Fig. 5d, the intersection point of impedance diagram and

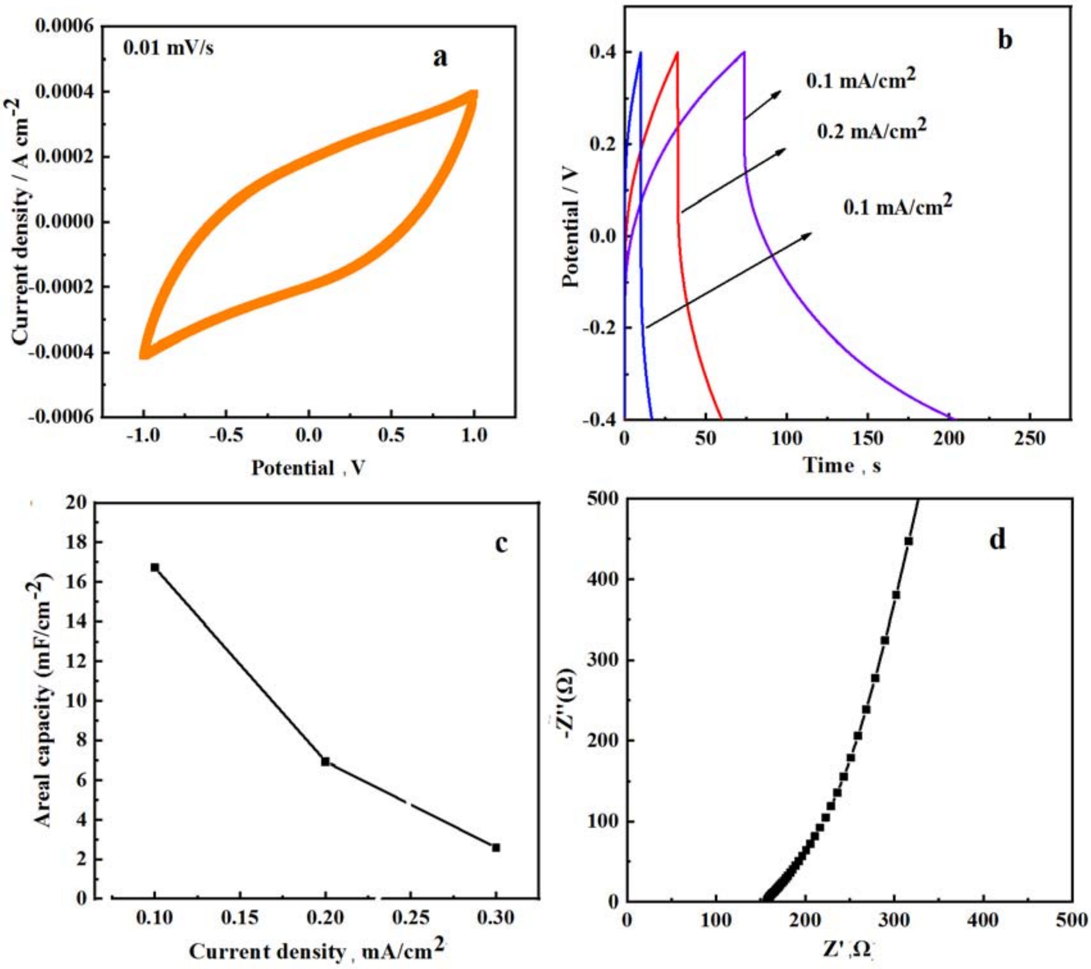

Fig. 5. (a) CV curve obtained at 0.01 mV/s scanning rate, (b) DSC curves at different current densities, (c) area capacitance and (d) EIS spectrum of the structure supercapacitor based on graphene and MPC-K9.

horizontal axis is the internal resistance of structural supercapacitor. The smaller the internal resistance value, the higher the ionic conductivity of the electrolyte and electrode. According to Fig. 5, the internal resistance of the structural supercapacitor was 156.7 Ω.

The relationship between the area capacitance and the number of cycles of the structural supercapacitor under the condition of 3000 charge-discharge cycles with the current density of 0.1 mA·cm^{-2} is shown in Fig. 6. It can be seen that the area capacitance retention rate of the structural supercapacitor was 94.50 % after 3000 cycles, indicating that the structural supercapacitor based on graphene and MPC-K9 has excellent cycling stability and reversibility. At the same time, the structural electrode and electrolyte material were stable and have good durability during the cycle. Therefore, graphene and MPC-K9 structural electrolyte can be used as ideal energy storage materials, which can provide guidance for future structural energy storage application research.

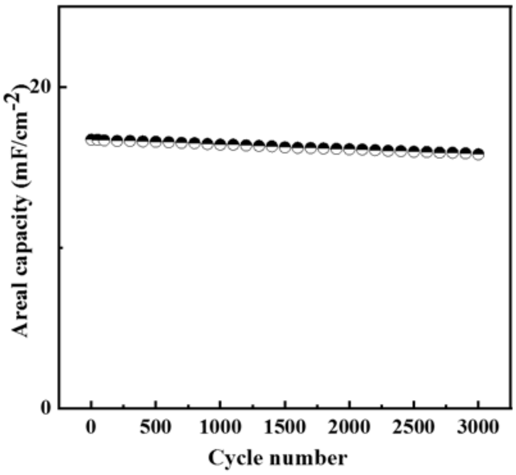

Fig. 6. Cycling stability of the structure supercapacitor based on graphene and MPC-K9 for 3000 cycles.

4. Conclusions

Thus, MPC alkaline structure electrolytes were synthesized with MgO, lithium dihydrogen phosphate, borate, LiOH, NaOH, KOH and deionized water as raw materials. The influence of different concentrations of three kinds of alkali (3M, 6M and 9M) on the internal resistance, ionic conductivity and compressive strength of the structure electrolyte was studied; it was established that the optimal structural electrolyte was MPC-K9 electrolyte. The microstructure characterization results show that the MPC-K9 electrolyte was composed of irregular particles with loose structure, and a large number of pores with a diameter of 0.5–5 μm are widely distributed in the MPC-K9 electrolyte. These pores could provide sufficient channels for ion migration. Therefore, the ionic conductivity of the MPC-K9 electrolyte was the highest, reaching 16.85 $mS\cdot cm^{-1}$. Thus, the MPC-K9 electrolyte demonstrates the best electrochemical performance and can be used as an ideal electrolyte for structural supercapacitors. The MPC-K9 structural electrolyte and graphene electrode were assembled into an integrated structural supercapacitor. The electrochemical performance analysis showed that the CV curve was close to the spindle shape, and there was no pseudo-capacitance characteristic, indicating that it was a typical double layer capacitor. In addition, the DSC curves were triangular at the current density of 0.1 $mA\cdot cm^{-2}$ and the maximum area capacitance was 16.72 $mF\cdot cm^{-2}$. EIS results showed that the internal resistance of the structural supercapacitor was 156.7 Ω. The structural supercapacitor showed good cycle stability and reversibility. Its area capacitance retention rate was 94.50 % after 3000 cycles of charge and discharge at 0.1 $mA\cdot cm^{-2}$.

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References

1. S.L.Min, H.J.Choi, J.B.Baek et al., *Appl.Energy*, **195**, 1071 (2016).
2. A.Burke, *J.Power Sources*, **91**, 37 (2000).
3. F.Beguin, E.Frackowiak, *J.Solid State Electr.*, **19**, 1253 (2015).
4. P.Simon, Y.Gogotsi, *Nat.Mater.*, **7**, 845 (2008).
5. R.Ko''tz, M.Carlen, *Electrochim.Acta*, **45**, 2483 (2000).
6. J.Yan, Q.Wang, T.Wei et al., *Adv.Energy Mater.*, **4**, 157 (2014).
7. H.M.Jeong, J.W.Lee, W.H.Shin et al., *Nano Lett.* , **11**, 247 (2011).
8. G.Wang, L.Zhang, J.Zhang, *Chem.Soc.Rev.*, **41**, 797 (2012).
9. Z.Tang, C.H.Tang, H.Gong, *Adv.Funct. Mater.*, **22**, 1272 (2012).
10. S.Giri, D.Ghosh, C.K.Das, *Adv.Funct.Mater.*, **24**, 1312 (2014).
11. K.S.Novoselov, A.K.Geim, S.V.Morozov et al., *Science*, **306**, 666 (2004).
12. Y.W.Son, M.L.Cohen, S.G.Louie, *Nature*, 444, 347 (2006).
13. M.Guo, X.Yi, G.Liu et al., *Compas. Sci. Technol.*, **97**, 27, (2014).
14. C.Lee, X.Wei, J.W.Kysar et al., *Science*, **321**, 385 (2008).
15. A.A.Balandin, S.Ghosh, W.Bao et al., *Nano Lett.*, **8**, 902 (2008).
16. M.D.Stoller, S.Park, Y.Zhu et al., *Nano Lett.*, **8**, 3498 (2008).
17. J.Zhang, J.Xu, Z.Dong, *J.Electrochem.Soc.*, **163**, E83 (2016).
18. A.Arora, B.Singh, P.Kaur, *Mater.Today Proc.*, **17**, 70 (2019).
19. X.Jia, J.Li, P.Wang et al., *Constr.Build. Mater.*, **229**, 116927 (2019).
20. Y.Du, J.Yang, B.S.Thomas et al., *Constr. Build.Mater.*, **260**, 120449 (2020).
21. Y.Zhang, S.Wang, L.Li et al., *Constr.Build. Mater.*, **262**, 119893 (2020).
22. D.Zhong, S.Wang, L.Wang, *Constr.Build. Mater.*, **264**, 120679 (2020).
23. D.Hou, D. Chen, X. Wang et al., *Constr. Build.Mater.*, **263**, 120190 (2020).
24. Y.Li, W.Bai, T.Shi, *Constr.Build.Mater.*, **142**, 459 (2017).
25. Q.Yang, B.Zhu, X.Wu, *Mater.Struct.*, **33**, 229 (2000).