Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Dielectric and transport properties of cationic polyelectrolyte membrane of P(NVP-*co*-DMDAAC)/PVA for solid-state supercapacitor

JinWang,*Mengde Deng, Yahui Xiao, Wentao Hao, Chengfeng Zhu

Anhui Key Laboratory of Advanced Catalytic Materials and Reaction Engineering, School of Chemistry and Chemical engineering, Hefei University of Technology, Hefei 23009, P. R. China

* Corresponding author Tel.: +86 551 62905660; fax: +86 551 62905660.

E-mail address: jinwang@hfut.edu.cn (Jin Wang)

1.Experimental

1.1 Orthogonal design

Tab.S1 Orthogonal experimental table

No.	Ratio of NVP/DMDAAC	Initiator /wt%	Crosslinker /wt%	Reaction temperature/℃	Conductivity /10^{-2} S cm^{-1}
1	a_1=3:1	b_1=0.5	c_1=0.5	d_1=60	f_1=0.1
2	a_1=3:1	b_2=1	c_2=1	d_2=65	f_2=0.229
3	a_1=3:1	b_3=1.5	c_3=1.5	d_3=70	f_3=0.27
4	a_1=3:1	b_4=2	c_4=2	d_4=75	f_4=0.08
5	a_1=3:1	b_5=2.5	c_5=2.5	d_5=80	f_5=0.109
6	a_2=2:1	b_1=0.5	c_2=1	d_3=70	f_6=0.469
7	a_2=2:1	b_2=1	c_3=1.5	d_4=75	f_7=2.26
8	a_2=2:1	b_3=1.5	c_4=2	d_5=80	f_8=0.15
9	a_2=2:1	b_4=2	c_5=2.5	d_1=60	f_9=0.34
10	a_2=2:1	b_5=2.5	c_1=0.5	d_2=65	f_{10}=0.176
11	a_3=1:1	b_1=0.5	c_3=1.5	d_5=80	f_{11}=2.86
12	a_3=1:1	b_2=1	c_4=2	d_1=60	f_{12}=0.16
13	a_3=1:1	b_3=1.5	c_5=2.5	d_2=65	f_{13}=0.499
14	a_3=1:1	b_4=2	c_1=0.5	d_3=70	f_{14}=0.63
15	a_3=1:1	b_5=2.5	c_2=1	d_4=75	f_{15}=0.38
16	a_4=1:2	b_1=0.5	c_4=2	d_2=65	f_{16}=1.38
17	a_4=1:2	b_2=1	c_5=2.5	d_3=70	f_{17}=0.43
18	a_4=1:2	b_3=1.5	c_1=0.5	d_4=75	f_{18}=0.244
19	a_4=1:2	b_4=2	c_2=1	d_5=80	f_{19}=0.81
20	a_4=1:2	b_5=2.5	c_3=1.5	d_1=60	f_{20}=0.736
21	a_5=1:3	b_1=0.5	c_5=2.5	d_4=75	f_{21}=1.32
22	a_5=1:3	b_2=1	c_1=0.5	d_5=80	f_{22}=0.67
23	a_5=1:3	b_3=1.5	c_2=1	d_1=60	f_{23}=0.49
24	a_5=1:3	b_4=2	c_3=1.5	d_2=65	f_{24}=0.57
25	a_5=1:3	b_5=2.5	c_4=2	d_3=70	f_{25}=0.527

1.2 Swelling percentage

The swelling percentage W ($g\cdot g^{-1}$) was calculated according to the following formula:[1]

$$W = \frac{W_2 - W_1}{W_1} \quad (1)$$

where W（$g\cdot g^{-1}$）is the swelling percentage, W_1（g）is the mass before absorption, W_2(g) is the quality after absorption.

1.3 Ionic conductivity

The measurement of ionic conductivity is carried out by electrochemical impedance spectroscopy (EIS) using CHI660B electrochemical workstation. The GPE was sandwiched by two pieces of stainless steel with the mode of SS/P(NVP-*co*-DMDAAC)/PVA /SS (SS notes stainless steel). The bulk ionic conductivity (σ) of the P(NVP-*co*-DMDAAC)/PVA GPE was determined from the complex impedance spectra in the frequency range between 1 Hz and 100 kHz with a perturbation of 5 mV rms using the equation:[2]

$$\sigma = \frac{d}{R_b \cdot S} \quad (2)$$

where d, S and R_b are the thickness, area, and bulk resistance (calculated from high-frequency intercept on the real impedance axis of the Cole-Cole plot), respectively.

2. Results and discussion

2.1 Orthogonal data processing

Tab.S1 is an orthogonal experimental design of four factors and five levels. There are 25 experiments in Tab.S1, and f_1...f_{25} represent the experimental results, respectively. Data processing is performed and the results were obtained in Tab.S2. A, B, C, and D were noted as the sum of the experimental results at the same level of the four factors includes monomer ratio, the initiator, the cross-linking agent, and the temperature, respectively. Take B_2 and C_3 as examples, the calculation method is $B_2 = (f_2 + f_7 + f_{12} + f_{17} + f_{22}) / 5$, $C_3 = (f_3 + f_7 + f_{11} + f_{20} + f_{24}) / 5$...and so on. Take X_3 as an example to illustrate the calculation process of X, $X_3 = \max\{C_1, C_2, C_3, C_4, C_5\} - \min\{C_1, C_2, C_3, C_4, C_5\}$. The result of the calculation is $X_3 > X_2 > X_1 > X_4$. It was concluded that the cross-linking agent had the greatest influence on the conductivity of the GPE, followed by the initiator and monomer ratio, and the temperature was the least. According to the experimental results, the best test combination is A_3, B_1, C_3, D_5, i.e., the conductivity of P(NVP-*co*-DMDAAC) is 2.86×10^{-2} S cm^{-1}.

Tab.S2 Data processing result of orthogonal experimental

No.	Conductivity/ 10^{-3} S cm^{-1}				
A	A_1=1.579	A_2=6.79	A_3=9.058	A_4=7.2	A_5=7.23
B	B_1=12.338	B_2=7.498	B_3=3.306	B_4=4.863	B_5=3.856
C	C_1=3.64	C_2=4.756	C_3=13.392	C_4=4.597	C_5=5.476
D	D_1=3.652	D_2=5.708	D_3=4.652	D_4=8.651	D_5=9.198
X	X_1=7.479	X_2=9.032	X_3=9.752	X_4=5.546	

Fig.S1 shows the swelling percentage of P(NVP-*co*-DMDAAC)/PVA IPN membrane with different contents PVA in deionized water and KOH electrolyte, respectively. Obviously, the swelling percentage increases first and then decreases with increasing the contents of PVA in both deionized water and KOH electrolyte, and P(NVP-*co*-DMDAAC)/10PVA has the maximum value of swelling percentage. Polar PVA with hydroxyl groups can bond with water molecules to form hydrogen which has better water retention. However, the proportion of water-soluble ionic monomer of DMDAAC is reduced as the dosage of PVA increase, and thus the water absorption capacity decreased. The swelling percentage in the KOH electrolyte is significantly reduced compared to that in water for the polyelectrolyte effect.[3] When in the aqueous solution, the molecular chain of cationic polyelectrolyte is fully extended for the electrostatic repulsion, the hydrodynamic volume becomes large and can absorb a large amount of water. While in the KOH salt solution, the electrostatic repulsion of cationic polyelectrolyte is weakened for the presence of a large number of salt ions, the molecular chain is curled and the hydrodynamic volume is reduced, thus the water absorption is reduced.

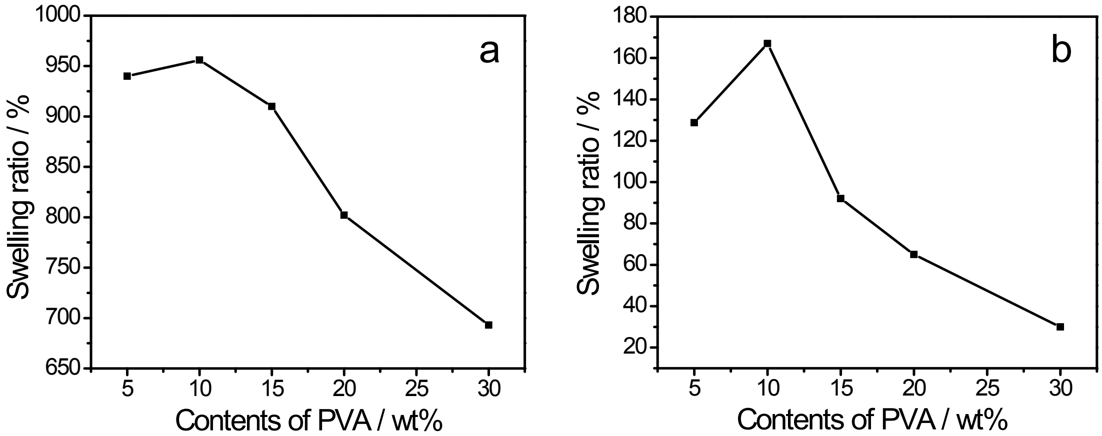

Fig.S1 Swelling percentage of P(NVP-*co*-DMDAAC)/PVA in deionized water (a) and KOH electrolyte (b) with different PVA contents

Reference:

1T.C. Nirmale, I. Karbhal, R. S. Kalubarme, M.V. Shelke, A. J. Varma and B. B. Kale,*ACS Appl. Mater. Interfaces* 2017, **9**, 34773-34782.

2 N.A. Choudhury, A.K. Shukla, S. Sampath and S. Pitchumani, *J. Electrochem. Soc.*2006, **153**, A614-A620.

3N.B. Wyatt and M. W. Liberatore, *J. App. Polym. Sci.*, 2009, **114**, 4076-4084.