Supporting information

Proton conductivities of three Mn-MOFs containing different water molecules synthesized by time-induced single-crystal-to-single-crystal transformation

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Table S1 The parameters of hydrogen bonds in compound **1**.

D-H···A	H···A	D···A	<(DHA)
O12-H···O11^{i}	2.03	2.880(19)	178.2
O12-H···O1	2.34	3.051(16)	141.7
O11-H···O1	2.38	3.175(14)	156.9
O11-H···O4^{ii}	2.17	2.987(12)	160.6
O8-H···O6	2.09	2.778(6)	137.3
O8-H···O2^{iii}	2.20	2.901(6)	139.5
O7-H···O2^{iv}	2.08	2.839(6)	149.2
O7-H···O3^{v}	1.93	2.734(6)	156.5
O10-H···O6^{vi}	2.58	3.276(10)	140.2
O10-H···O3^{vii}	2.33	2.773(10)	112.8
O10-H···O3^{viii}	2.29	2.995(10)	141.0
O9-H···O3^{v}	2.34	2.833(7)	117.2
O9-H···O4^{v}	2.60	3.352(7)	148.9

Symmetry code: i -x+1, -y+1, -z+1; ii x-1, y-1, z; iii x-1, y, z-1; iv x, y, z-1; v -x+2, -y+2, -z+1; vi -x, -y+1, -z; vii x-1, y-1, z-1; viii -x+1, -y+2, -z+1.

Table S2 The parameters of hydrogen bonds in compound **1**.

D-H···A	H···A	D···A	<(DHA)
O11-H···O1^{i}	2.34	3.143(12)	157.5
O11-H···O5^{ii}	2.45	3.241(12)	155.2
O10-H···O11	1.84	2.628(15)	154.4
O10-H···O1	1.81	2.599(11)	154.1
O9-H···O2^{iii}	2.06	2.769(4)	140.9
O9-H···O3^{iv}	1.91	2.709(4)	154.9
O8-H···O6^{v}	1.99	2.737(4)	146.6
O8-H···O2^{iv}	2.08	2.926(5)	171.4
O7-H···O8^{ii}	2.56	3.245(6)	138.2
O7-H···O11	1.89	2.695(10)	158.7

Symmetry code: i -x+1, -y, -z; ii x, y-1, z; iii x+1, y+1, z+1; iv -x+1, -y+1, -z; v -x+1, -y+2, -z+1

Table. S3.Selected bond lengths (Å) and band angles (°) for compounds **1**

Bond lengths for compounds **1**		Band angles for compounds **1**	
Mn(2)-O(3)#1	2.149(3)	O(3)#1-Mn(2)-O(7)	165.89(10)
Mn(2)-O(7)	2.203(3)	O(3)#1-Mn(2)-O(6)#2	79.67(9)
Mn(2)-O(6)#2	2.235(2)	O(7)-Mn(2)-O(6)#2	93.51(10)
Mn(2)-O(2)#3	2.266(2)	O(3)#1-Mn(2)-O(2)#3	87.79(9)
Mn(2)-O(6)	2.267(2)	O(7)-Mn(2)-O(2)#3	79.95(9)
Mn(2)-N(1)	2.287(3)	O(6)#2-Mn(2)-O(2)#3	91.08(9)
Mn(1)-O(5)	2.138(2)	O(3)#1-Mn(2)-O(6)	100.92(9)
Mn(1)-O(5)#4	2.138(2)	O(7)-Mn(2)-O(6)	88.92(9)
Mn(1)-O(2)#5	2.227(2)	O(6)#2-Mn(2)-O(6)	74.28(9)
Mn(1)-O(2)#6	2.227(3)	O(2)#3-Mn(2)-O(6)	161.10(9)
Mn(1)-O(4)#7	2.239(2)	O(7)-Mn(2)-N(1)	111.54(11)
Mn(1)-O(4)#8	2.239(2)	O(6)#2-Mn(2)-N(1)	136.59(10)
O(2)-Mn(1)#6	2.227(2)	O(2)#3-Mn(2)-N(1)	126.82(10)
O(2)-Mn(2)#3	2.266(2)	O(6)-Mn(2)-N(1)	71.49(9)
O(4)-Mn(1)#7	2.239(2)	O(5)-Mn(1)-O(5)#4	178.44(15)
O(6)-Mn(2)#2	2.235(2)	O(5)-Mn(1)-O(2)#5	88.85(9)
		O(5)#4-Mn(1)-O(2)#5	92.16(9)
		O(5)-Mn(1)-O(2)#6	92.16(9)
		O(5)#4-Mn(1)-O(2)#6	88.85(9)
		O(2)#5-Mn(1)-O(2)#6	99.02(14)
		O(5)-Mn(1)-O(4)#7	80.92(9)
		O(5)#4-Mn(1)-O(4)#7	97.92(9)
		O(2)#5-Mn(1)-O(4)#7	167.35(9)
		O(2)#6-Mn(1)-O(4)#7	88.85(10)
		O(5)-Mn(1)-O(4)#8	97.92(10)
		O(5)#4-Mn(1)-O(4)#8	80.92(9)

Symmetry transformations used to generate equivalent atoms: #1 -x+3/2,-y+1/2,-z+2

#2 -x+1,y,-z+3/2 #3 -x+2,-y,-z+2

#4 -x,y,-z+3/2 #5x-1,-y,z-1/2 #6 x-1,-y,z-1/2

#7 -x+1/2,-y+1/2,-z+2 #8 x-1/2,-y+1/2,z-1/2

Table. S4.Selected bond lengths (Å) and band angles (°) for compounds **2**

Bond lengths for compounds **2**		Band angles for compounds **2**	
Mn(1)-O(9)#1	2.142(3)	O(9)#1-Mn(1)-O(9)	180.000(1)
Mn(1)-O(9)	2.142(3)	O(9)#1-Mn(1)-O(5)	89.93(11)
Mn(1)-O(5)	2.164(2)	O(9)-Mn(1)-O(5)	90.07(11)
Mn(1)-O(5)#1	2.164(2)	O(9)#1-Mn(1)-O(5)#1	90.07(11)
Mn(1)-O(8)	2.166(3)	O(9)-Mn(1)-O(5)#1	89.93(11)
Mn(1)-O(8)#1	2.166(3)	O(5)-Mn(1)-O(5)#1	180.000(1)
Mn(2)-O(4)#2	2.156(3))	O(9)#1-Mn(1)-O(8)	92.52(14)
Mn(2)-O(6)	2.183(3)	O(9)-Mn(1)-O(8)	87.48(14)
Mn(2)-O(3)#3	2.185(3)	O(5)-Mn(1)-O(8)	86.02(11)
Mn(2)-O(2)#4	2.187(3)	O(5)#1-Mn(1)-O(8)	93.98(11)
Mn(2)-O(7)	2.223(4)	O(9)#1-Mn(1)-O(8)#1	87.48(14)
Mn(2)-N(1)	2.280(3)	O(9)-Mn(1)-O(8)#1	92.52(14)
O(2)-Mn(2)#4	2.187(3)	O(5)-Mn(1)-O(8)#1	93.98(11)
O(3)-Mn(2)#5	2.185(3)	O(5)#1-Mn(1)-O(8)#1	86.02(11)
O(4)-Mn(2)#2	2.156(3)	O(8)-Mn(1)-O(8)#1	180.000(1)
		O(4)#2-Mn(2)-O(6)	88.58(12)
		O(4)#2-Mn(2)-O(3)#3	1 91.26(11)
		O(6)-Mn(2)-O(3)#3	93.09(11)
		O(4)#2-Mn(2)-O(2)#4	99.28(12)
		O(6)-Mn(2)-O(2)#4	172.03(13)
		O(3)#3-Mn(2)-O(2)#4	85.44(11)
		O(4)#2-Mn(2)-O(7)	172.62(14)
		O(6)-Mn(2)-O(7)	84.15(15)
		O(3)#3-Mn(2)-O(7)	87.89(14)
		O(2)#4-Mn(2)-O(7)	87.97(15)
		O(4)#2-Mn(2)-N(1)	96.30(11)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+2,-z+1 #2 -x,-y+1,-z #3 x,y,z+1

#4 x,-y,-z #5 x,y,z-1 #6 -x+1,-y,-z

Table. S5.Selected bond lengths (Å) and band angles (°) for compounds **3**

Bond lengths for compounds **3**		Band angles for compounds **3**	
Mn(2)-O(3)#1	2.149(3)	O(3)#1-Mn(2)-O(7)	165.89(10)
Mn(2)-O(7)	2.203(3)	O(3)#1-Mn(2)-O(6)#2	79.67(9)
Mn(2)-O(6)#2	2.235(2)	O(7)-Mn(2)-O(6)#2	93.51(10)
Mn(2)-O(2)#3	2.266(2)	O(3)#1-Mn(2)-O(2)#3	87.79(9)
Mn(2)-O(6)	2.267(2)	O(7)-Mn(2)-O(2)#3	79.95(9)
Mn(2)-N(1)	2.287(3)	O(6)#2-Mn(2)-O(2)#3	91.08(9)
Mn(1)-O(5)	2.138(2)	O(3)#1-Mn(2)-O(6)	100.92(9)
Mn(1)-O(5)#4	2.138(2)	O(7)-Mn(2)-O(6)	88.92(9)
Mn(1)-O(2)#5	2.227(2)	O(6)#2-Mn(2)-O(6)	83.27(15)
Mn(1)-O(2)#6	2.227(3)	O(2)#3-Mn(2)-O(6)	161.10(9)
Mn(1)-O(4)#7	2.239(2)	O(3)#1-Mn(2)-N(1)	81.42(10)
Mn(1)-O(4)#8	2.239(2)	O(7)-Mn(2)-N(1)	111.54(11)
O(2)-Mn(1)#6	2.227(2)	O(6)#2-Mn(2)-N(1)	136.59(10)
O(2)-Mn(2)#3	2.266(2)	O(2)#3-Mn(2)-N(1)	126.82(10)
O(3)-Mn(2)#1	2.149(3)	O(6)-Mn(2)-N(1)	71.49(9)
O(4)-Mn(1)#7	2.239(2)	O(5)-Mn(1)-O(5)#4	178.44(15)
O(6)-Mn(2)#2	2.235(2)	O(5)-Mn(1)-O(2)#5	88.85(9)
		O(5)#4-Mn(1)-O(2)#5	92.16(9)
		O(5)-Mn(1)-O(2)#6	92.16(9)
		O(5)#4-Mn(1)-O(2)#6	88.85(9)
		O(2)#5-Mn(1)-O(2)#6	99.02(14)
		O(5)-Mn(1)-O(4)#7	80.92(9)
		O(5)#4-Mn(1)-O(4)#7	97.92(9)
		O(2)#5-Mn(1)-O(4)#7	167.35(9)
		O(2)#6-Mn(1)-O(4)#7	88.85(10)
		O(5)-Mn(1)-O(4)#8	97.92(10)
		O(5)#4-Mn(1)-O(4)#8	80.92(9)

Symmetry transformations used to generate equivalent atoms:

#1 -x+3/2,-y+1/2,-z+2 #2 -x+1,y,-z+3/2 #3 -x+2,-y,-z+2

#4 -x,y,-z+3/2 #5 x-1,-y,z-1/2 #6 -x+1,-y,-z+2

#7 -x+1/2,-y+1/2,-z+2 #8 x-1/2,-y+1/2,z-1/2

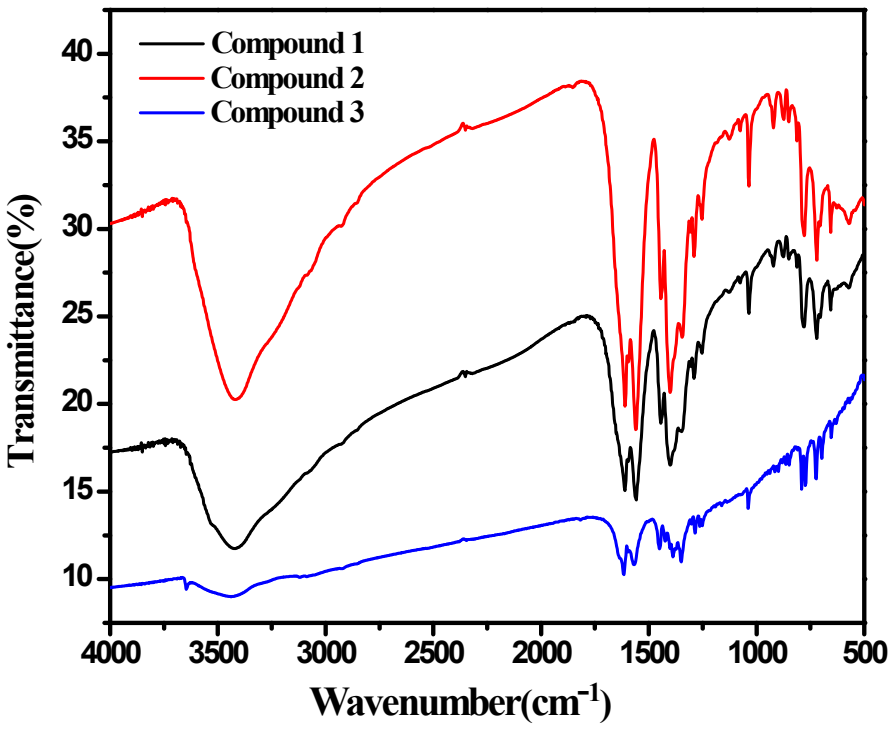


Fig. S1 IR spectra of compounds **1-3**.

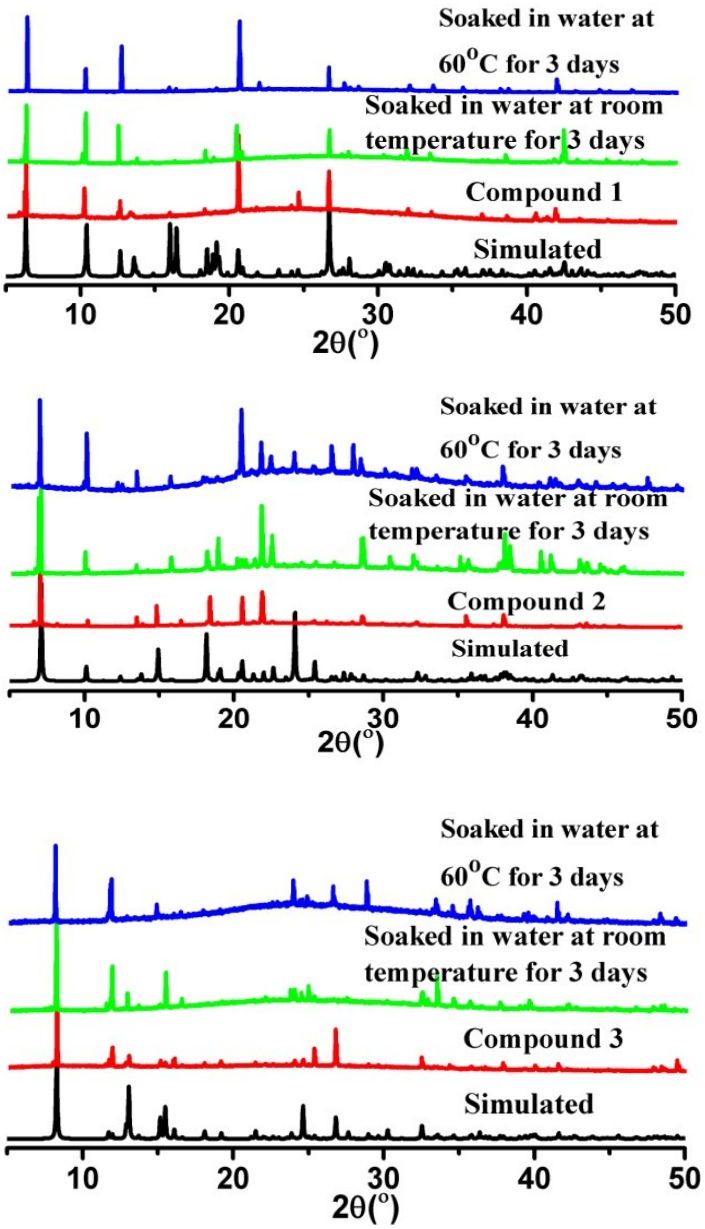
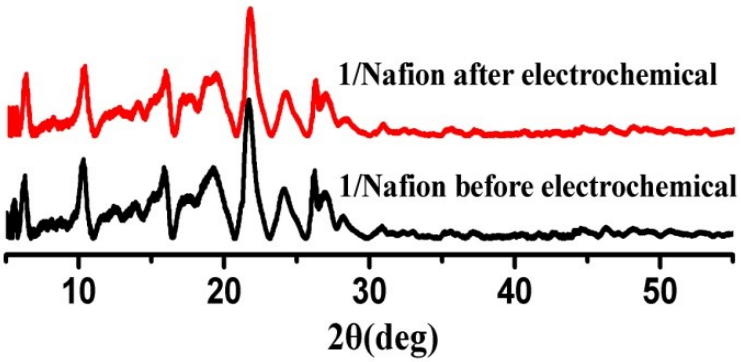
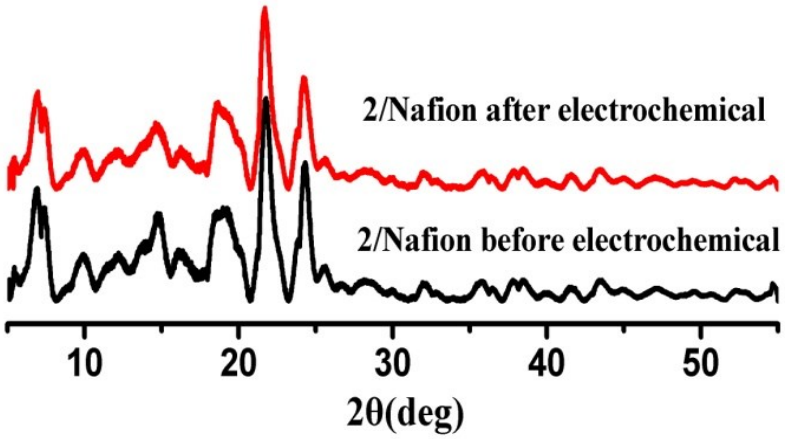


Fig. S2 The simulated, experimental, and water treatment samples PXRD patterns of compounds 1-3.



(a)



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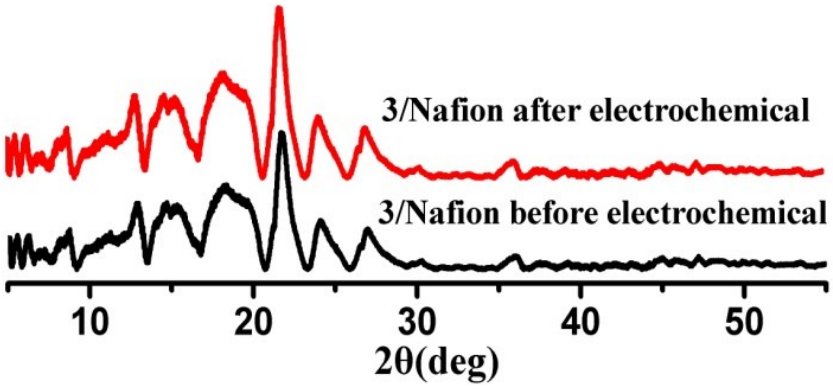

(c)

Fig. S3 The PXRD patterns of **1-3**/Nafion before and after electrochemical experiment.

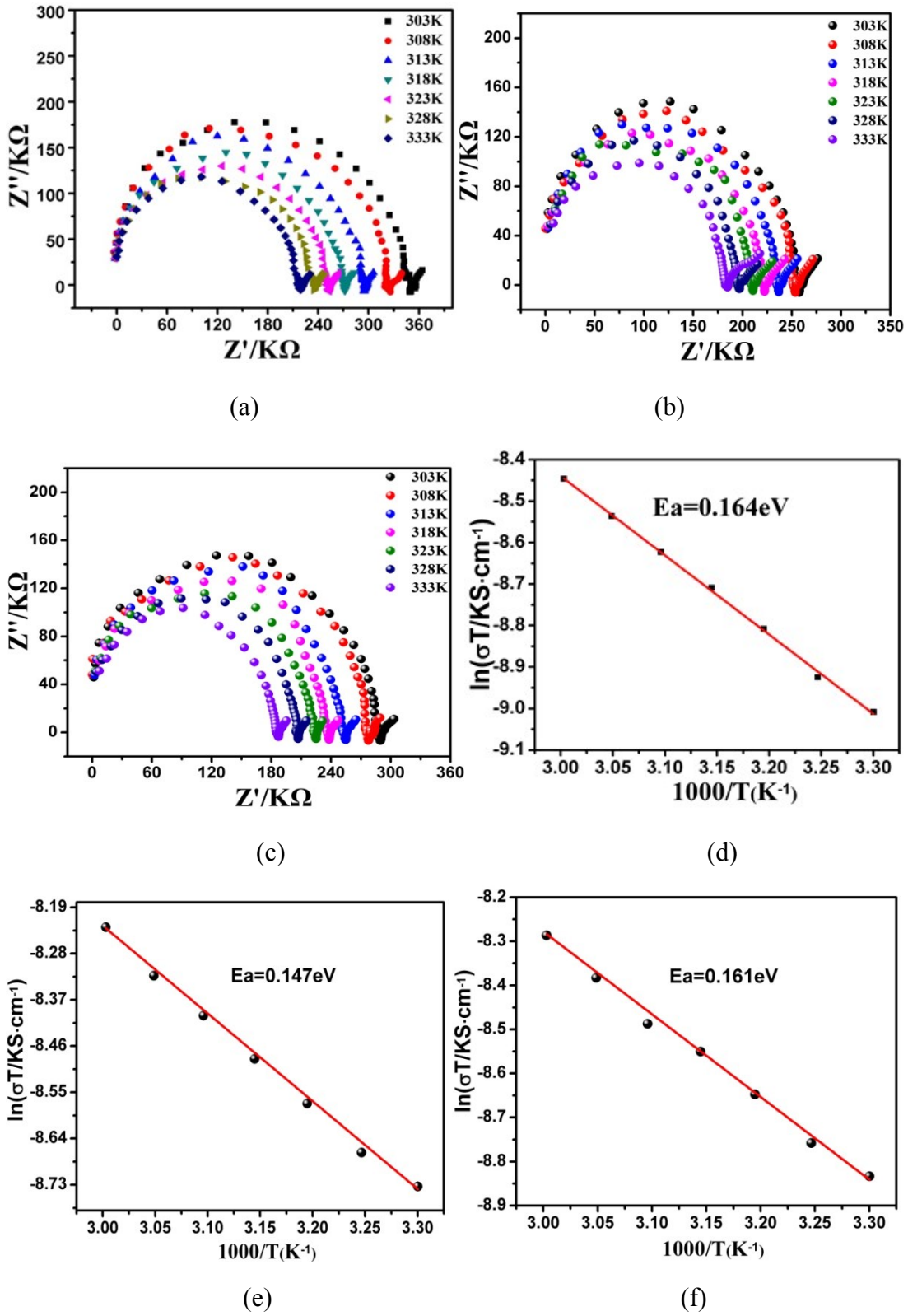

Fig. S4 The typical Nyquist plots of pure Nafion (a), **2**/Nafion (b) and **3**/Nafion (c) at different temperature; the Arrhenius plots of proton conduction for pure Nafion (d), **2**/Nafion (e) and **3**/Nafion (f).

Table S6 The proton conductivities of **1**-**3**/Nafion and pure Nafion membrane at 303k-333K temperature.

Temperature	Proton conductivity ($\mu S \cdot cm^{-1}$)			
	Nafion	1/Nafion	2/Nafion	3/Nafion
303K	0.404	0.597	0.553	0.490
308K	0.432	0.626	0.587	0.510
313K	0.478	0.677	0.604	0.560
318K	0.519	0.716	0.643	0.608
323K	0.557	0.744	0.688	0.637
328K	0.598	0.767	0.740	0.697
333K	0.645	0.838	0.801	0.787