A simple MOF constructed by Pb(II) with strong polarizing force: a filler of Nafion membrane to increase proton conductivity

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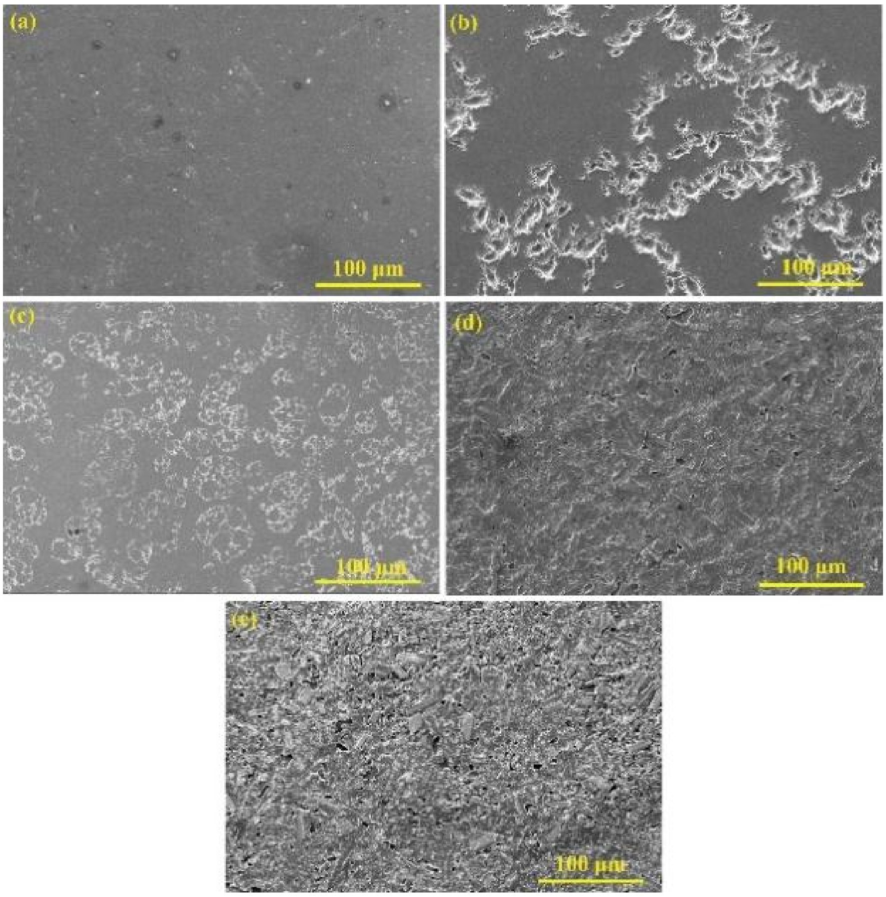


Fig. S1 The surface SEM images of (a) pure Nafion, (b) Pb-MOF/Nafion-3, (c) Pb-MOF/Nafion-5, (d) Pb-MOF/Nafion-7 and (e) Pb -MOF/Nafion-9.

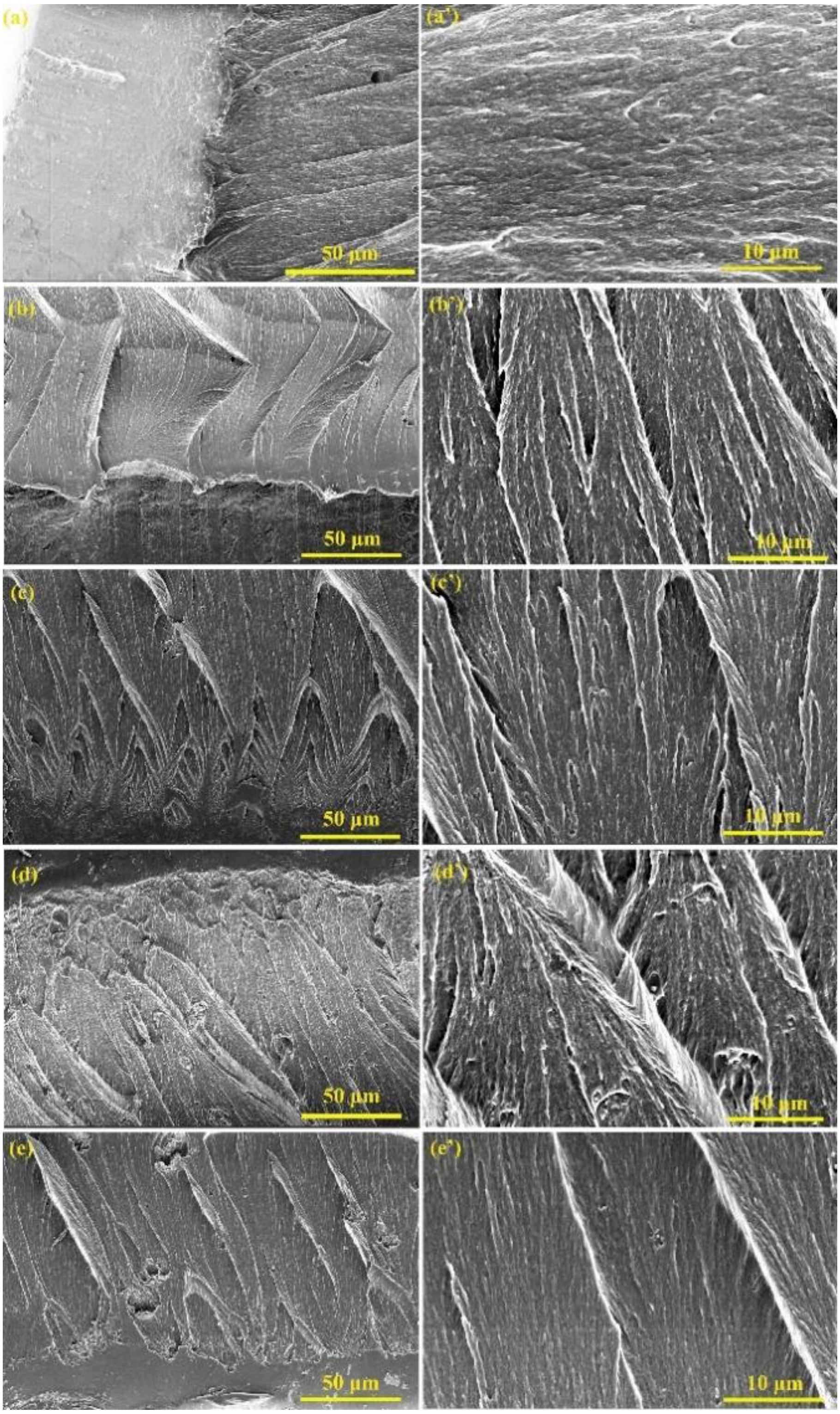
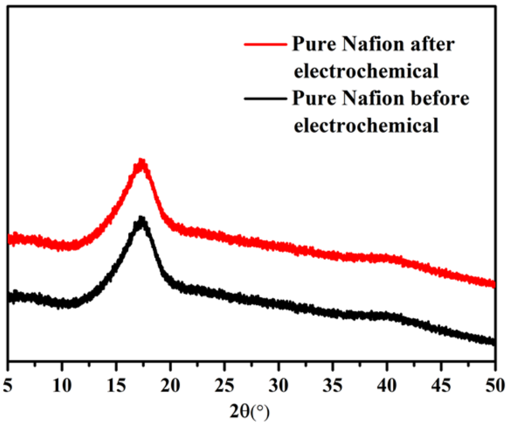
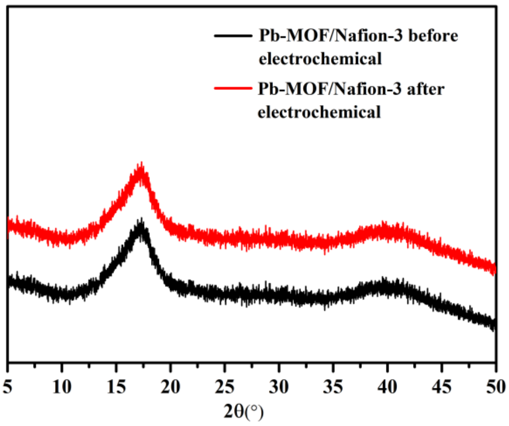


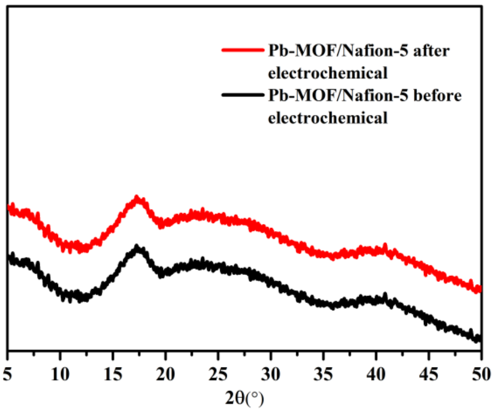
Fig. S2 The cross-sectional SEM images of pure Nafion (a and a'), Pb-MOF/Nafion-3 (b and b'), Pb-MOF/Nafion-5 (c and c'), Pb-MOF/Nafion-7 (d and d'), Pb-MOF/Nafion-9 (e and e').



(a)



(b)



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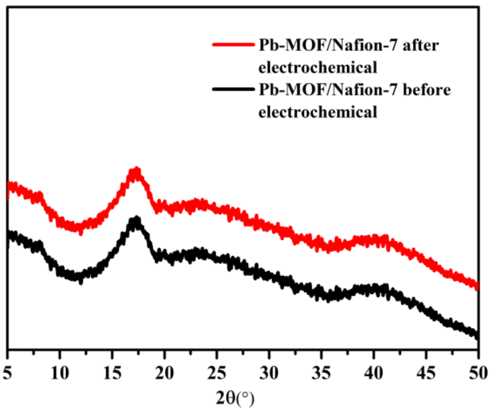
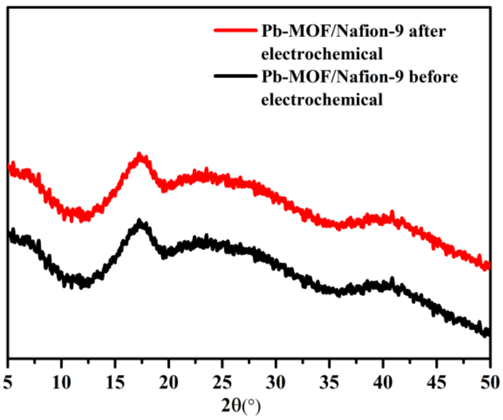


(d)



(e)

Fig. S3 (a) The PXRD patterns of pure Nafion membrane before and after the electrochemical experiment; (b, c, d and e) The PXRD patterns of Pb-MOF/Nafion composite membranes before and after the electrochemical experiment.

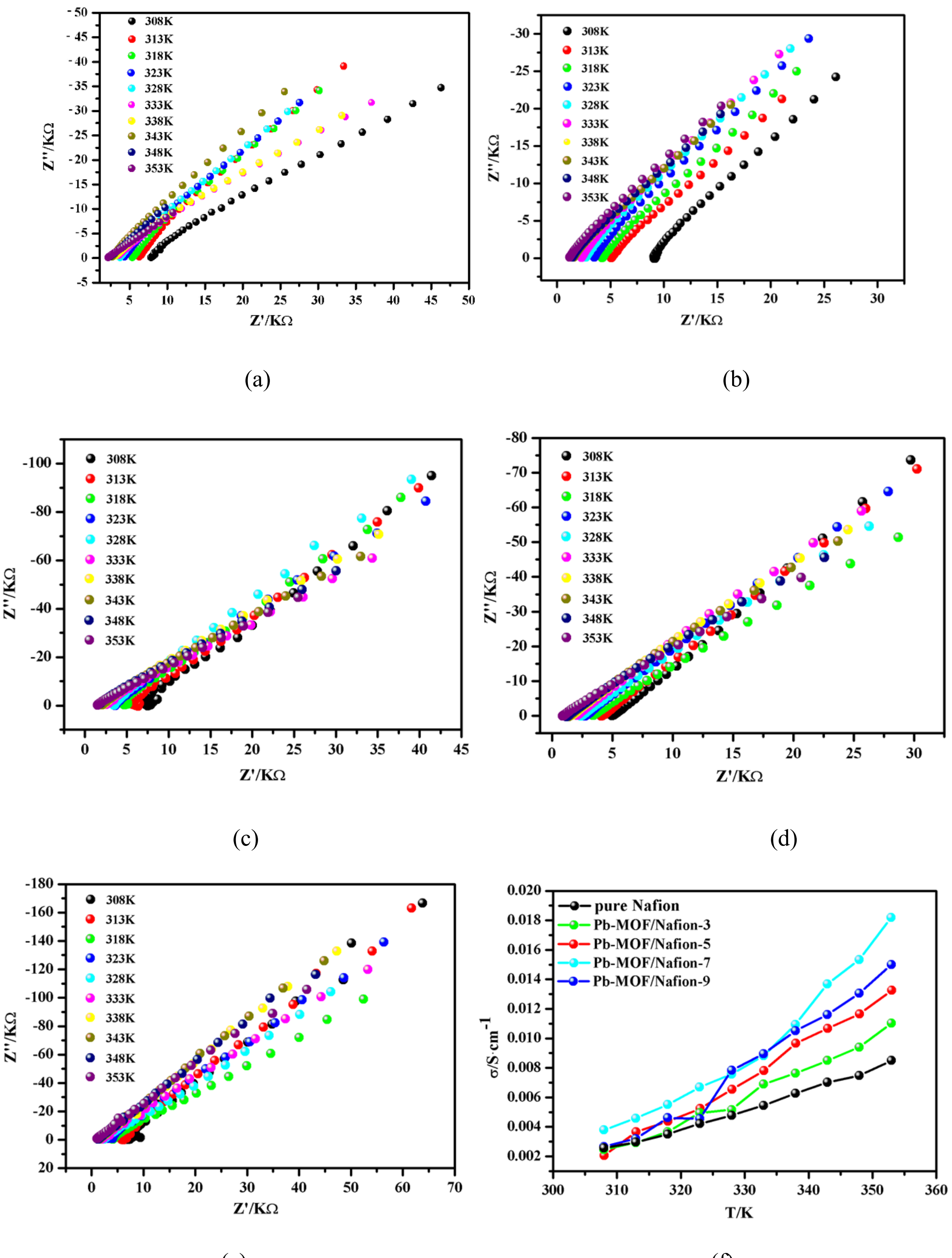
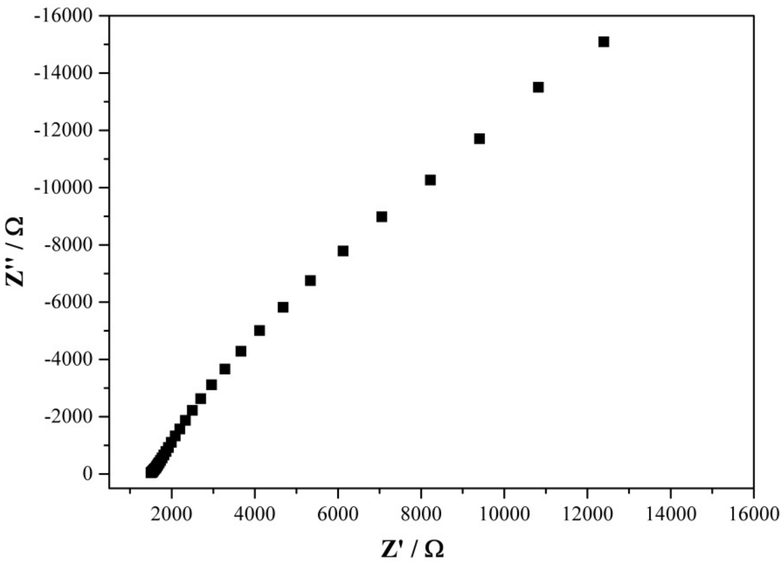
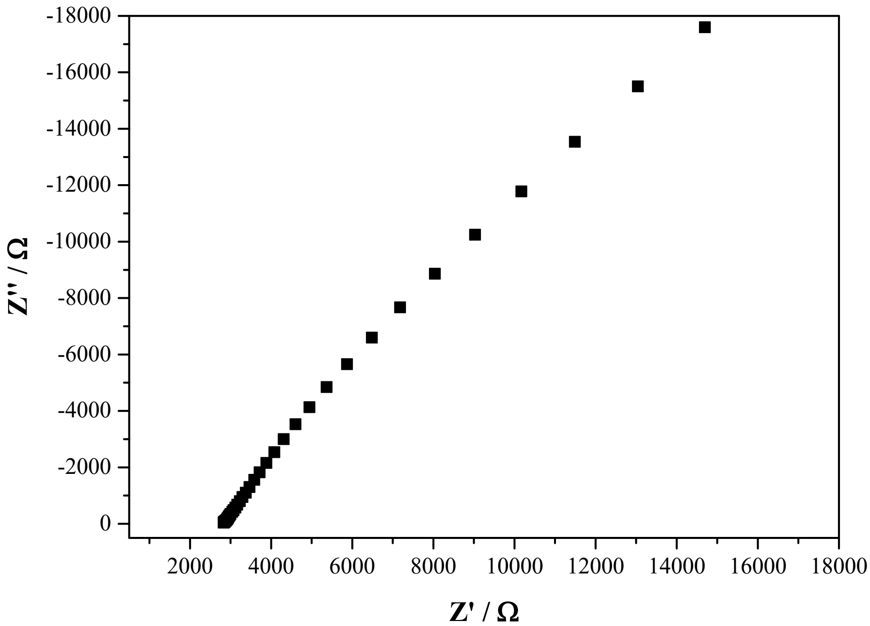


Fig. S4 Nyquist curves of (a) pure Nafion membrane; (b) Pb-MOF/Nafion-3 (c) Pb-MOF/Nafion-5; (d) Pb-MOF/Nafion-7; (e) Pb-MOF/Nafion-9 composite membranes at different temperatures.



(a)



(b)

Fig. S5 Nyquist curves of (a) $PbAc_2$/Nafion and (b) Na_3L/Nafion composite membranes at 353K.

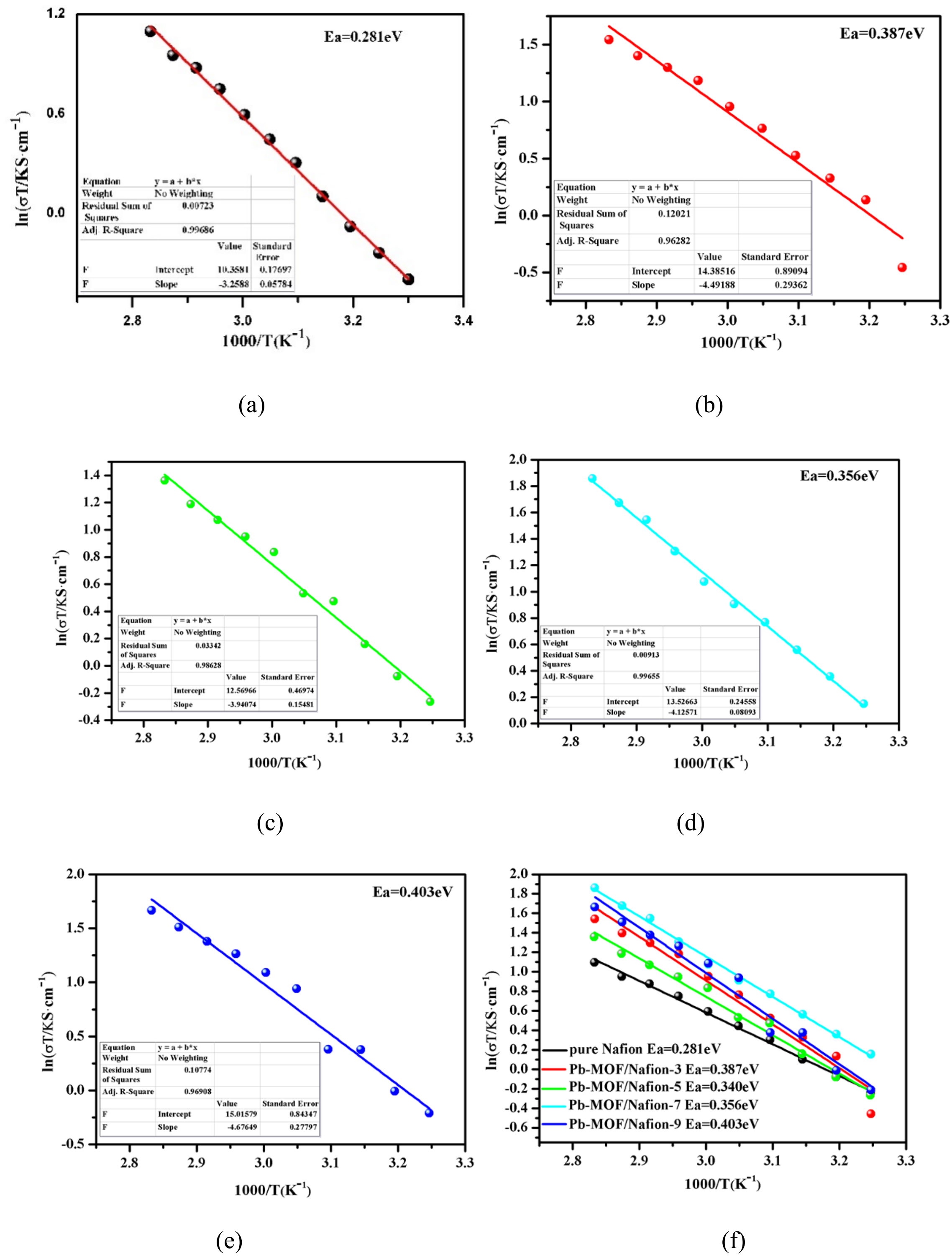


Fig. S6 Plot of $\ln(\sigma_{H^+}T)$ *vs.* 1/T with fitted activity energy and R^2 values of (a) pure Nafion membrane and (b) Pb-MOF/Nafion-3; (c) Pb-MOF/Nafion-5; (d) Pb-MOF/Nafion-7; (e) Pb-MOF/Nafion-9 composite membranes.

Table S1 Crystal and refinement data for Pb-MOF.

Empirical formula	$C_8H_4O_8Pb_2S$	Absorption coefficient/mm^{-1}	58.256
Formula weight	674.55	θ range(º)	3.953 - 67.197
Crystal system	Monoclinic	Reflections collected, unique	6983, 2048
space group	*P2₁/c*	R(int)	0.0442
a/Å	7.31490(13)	Limiting indices	-8≤h≤8, -26≤k≤17, -8≤l≤9
b/Å	22.3592(3)	Data/restraints/parameters	2048 / 0 / 173
c/Å	22.3592(3)	Completeness to θ= 67.02º/%	100.0%
β/º	22.3592(3)	Refinement method	Full-matrix least-squares on F^2
Volume/Å^3	22.3592(3)	Goodness-of-fit on F^2	1.113
Z	4	Final R indices [I>2σ(I)]	R1 = 0.0467, wR2 = 0.1189
D_{calc}(Mg/m$_3$)	3.891	R indices (all data)	R1 = 0.0485, wR2 = 0.1204
F(000)	1184	Largest diff. peak, hole	3.153, -2.010 e·Å^{-3}

Table S2 Selected bond lengths and angels of Pb-MOF.

Pb(1)-O(1)#1	2.490(8)	Pb(1)-O(3)#2	2.724(8)
Pb(1)-O(8)	2.317(8)	Pb(1)-O(8)#1	2.349(8)
Pb(2)-O(1)	2.484(8)	Pb(2)-O(3)#2	2.589(9)
Pb(2)-O(4)#2	2.413(11)	Pb(2)-O(7)	2.601(9)
Pb(2)-O(8)	2.581(8)		
O(8)-Pb(1)-O(8)#1	70.6(3)	O(8)-Pb(1)-O(1)#1	83.3(3)
O(8)#1-Pb(1)-O(1)#1	69.8(3)	O(8)-Pb(1)-O(3)#2	78.4(3)
O(8)#1-Pb(1)-O(3)#2	97.7(3)	O(1)#1-Pb(1)-O(3)#2	160.6(3)
O(4)#2-Pb(2)-O(1)	94.2(3)	O(4)#2-Pb(2)-O(8)	127.9(3)
O(1)-Pb(2)-O(8)	66.3(3)	O(4)#2-Pb(2)-O(3)#2	51.3(3)
O(8)-Pb(2)-O(3)#2	76.5(3)	O(1)-Pb(2)-O(3)#2	73.1(3)
O(1)-Pb(2)-O(7)	68.2(3)	O(4)#2-Pb(2)-O(7)	81.2(3)
O(3)#2-Pb(2)-O(7)	114.6(3)	O(8)-Pb(2)-O(7)	126.7(3)

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

Table S3. The results of bond-valence calculations of O8 .

Bond	Pb1-O8	$Pb1^{ii}$-O8	Pb2-O8
Bond length (Å)	2.317	2.349	2.581
Valence	0.49	0.45	0.28
Total valence	1.22		

Table S4 The water uptakes and area swelling ratios of pure Nafion membrane and Pb-MOF/Nafion composite membranes.

Membrane	Wdry /g	Wwet /g	Adry /cm^2	Awet /cm^2	water uptake	Area swelling
Pure Nafion	0.0217	0.0247	0.2500	0.2729	13.82%	9.16%
Pb-MOF/Nafion-3	0.0148	0.0173	0.2086	0.2164	16.89%	3.74%
Pb-MOF/Nafion-5	0.0149	0.0175	0.2088	0.2156	17.45%	3.26%
Pb-MOF/Nafion-7	0.0217	0.0257	0.2517	0.2597	18.43%	3.18%
Pb-MOF/Nafion-9	0.0226	0.0271	0.2333	0.2384	19.91%	2.19%

Table S5 Proton conductivities of pure nafion membrane and Pb-MOF/Nafion composite membranes at different temperatures.

T (°C)	pure Nafion ($S \cdot cm^{-1}$)	Pb-MOF/Nafion-3 ($S \cdot cm^{-1}$)	Pb-MOF/Nafion-5 ($S \cdot cm^{-1}$)	Pb-MOF/Nafion-7 ($S \cdot cm^{-1}$)	Pb-MOF/Nafion-9 ($S \cdot cm^{-1}$)
35	2.55×10^{-3}	2.49×10^{-3}	2.06×10^{-3}	3.77×10^{-3}	2.63×10^{-3}
40	2.95×10^{-3}	2.96×10^{-3}	3.67×10^{-3}	4.56×10^{-3}	3.17×10^{-3}
45	3.48×10^{-3}	3.69×10^{-3}	4.37×10^{-3}	5.50×10^{-3}	4.59×10^{-3}
50	4.19×10^{-3}	4.98×10^{-3}	5.24×10^{-3}	6.67×10^{-3}	4.52×10^{-3}
55	4.76×10^{-3}	5.19×10^{-3}	6.55×10^{-3}	7.55×10^{-3}	7.81×10^{-3}
60	5.43×10^{-3}	6.92×10^{-3}	7.81×10^{-3}	8.79×10^{-3}	8.93×10^{-3}
65	6.26×10^{-3}	7.65×10^{-3}	9.67×10^{-3}	1.09×10^{-2}	1.05×10^{-2}
70	7.00×10^{-3}	8.52×10^{-3}	1.07×10^{-2}	1.37×10^{-2}	1.16×10^{-2}
75	7.45×10^{-3}	9.43×10^{-3}	1.17×10^{-2}	1.53×10^{-2}	1.30×10^{-2}
80	8.48×10^{-3}	1.11×10^{-2}	1.33×10^{-2}	1.82×10^{-2}	1.50×10^{-2}