Promoting proton conduction performance of Nafion composite membrane through doping simple and low-cost hydrated calcium terephthalate

Na Wang, Li Ding, Huiqi Zou, Zhipeng Huan, Jing Lu*, Houting Liu*, Suna Wang*, Yunwu Li

Table S1 Crystal and refinement data for Ca-MOF.

formula	$C_8H_{10}O_7Ca$
formula weight	258.24
Crystal system	monoclinic
space group	$P2_1/c$
a/Å	7.1121(2)
b/Å	21.6576(7)
c/Å	6.5900(2)
α/°	90
β/°	92.236(3)
γ/°	90
V/Å^3, Z	1014.30(6), 4
D_{calc}(Mg/m^3), μ(mm^{-1})	1.691, 5.582
F(000)	536
θ range(°)	4.082-67.206
Limiting indices	-8≤h≤7, -25≤k≤16, -7≤l≤7
Reflections collected/unique	7967/ 1816 [R(int)=0.0421]
Data/restraints/parameters	1816/0/146
Completeness	100%
Goodness-of-fit on F^2	1.057
Final Rindices[I>2sigma(I)]	R_1=0.0413, wR_2=0.1114
R indices(all data)	R_1=0.0427, wR_2=0.1126
Largest diff. peak，hole	1.065，-0.343e·Å^{-3}

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

O(1)-Ca(1)#1	2.3624(16)	O(1)-Ca(1)	2.4901(16)
O(2)-Ca(1)#2	2.3497(17)	O(2)-Ca(1)	2.5278(16)
Ca(1)-O(5)	2.392(2)	Ca(1)-O(7)	2.5267(18)
Ca(1)-O(6)	2.3746(17)	Ca(1)-O(7)#1	2.6394(18)
O(5)-Ca(1)-O(2)	93.59(7)	O(2)#1-Ca(1)-O(6)	83.63(6)
O(1)-Ca(1)-O(2)	51.73(5)	O(1)#2-Ca(1)-O(6)	85.56(6)
O(7)-Ca(1)-O(2)	68.19(6)	O(2)#1-Ca(1)-O(5)	72.54(7)

O(2)#1-Ca(1)-O(7)#1	68.93(6)	O(1)#2-Ca(1)-O(5)	72.77(7)
O(1)#2-Ca(1)-O(7)#1	145.90(6)	O(6)-Ca(1)-O(5)	106.64(8)
O(6)-Ca(1)-O(7)#1	77.71(6)	O(2)#1-Ca(1)-O(1)	78.64(6)
O(5)-Ca(1)-O(7)#1	140.48(7)	O(1)#2-Ca(1)-O(1)	128.55(6)
O(1)-Ca(1)-O(7)#1	65.23(5)	O(6)-Ca(1)-O(1)	142.58(6)
O(7)-Ca(1)-O(7)#1	79.23(5)	O(5)-Ca(1)-O(1)	99.08(8)
O(2)-Ca(1)-O(7)#1	101.87(5)	O(2)#1-Ca(1)-O(7)	146.94(6)
O(2)#1-Ca(1)-O(1)#2	138.77(6)	O(1)#2-Ca(1)-O(7)	68.86(6)
O(6)-Ca(1)-O(7)	81.08(6)	O(5)-Ca(1)-O(7)	140.13(7)
O(2)#1-Ca(1)-O(2)	126.06(6)	O(1)-Ca(1)-O(7)	96.32(6)
O(1)#2-Ca(1)-O(2)	77.64(5)	O(6)-Ca(1)-O(2)	148.59(6)

Symmetry codes: #1 x, -y+1/2, z-1/2; #2 x, -y+1/2, z+1/2.

Table S3 The water uptakes and area swelling ratios of pure nafion membrane and Ca-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%
Ca-MOF/Nafion-3	0.0151	0.0176	0.2211	0.2289	16.56%	3.53%
Ca-MOF/Nafion-5	0.0169	0.0198	0.2261	0.2333	17.16%	3.18%
Ca-MOF/Nafion-7	0.0170	0.0201	0.2122	0.2187	18.24%	3.06%
Ca-MOF/Nafion-9	0.0321	0.0380	0.3801	0.3907	18.38%	2.79%

Table S4 Proton conductivities of pure nafion membrane and Ca-MOF/Nafion composite membranes at different temperatures.

T (K)	pure Nafion ($S\cdot cm^{-1}$)	Ca-MOF/Nafion-3 ($S\cdot cm^{-1}$)	Ca-MOF/Nafion-5 ($S\cdot cm^{-1}$)	Ca-MOF/Nafion-7 ($S\cdot cm^{-1}$)	Ca-MOF/Nafion-9 ($S\cdot cm^{-1}$)
308	2.55×10^{-3}	3.56×10^{-3}	3.01×10^{-3}	4.40×10^{-3}	3.16×10^{-3}
313	2.95×10^{-3}	3.90×10^{-3}	3.93×10^{-3}	5.32×10^{-3}	4.22×10^{-3}
318	3.48×10^{-3}	4.69×10^{-3}	4.99×10^{-3}	6.39×10^{-3}	5.28×10^{-3}
323	4.19×10^{-3}	4.93×10^{-3}	5.31×10^{-3}	7.98×10^{-3}	6.21×10^{-3}
328	4.76×10^{-3}	6.45×10^{-3}	6.46×10^{-3}	9.99×10^{-3}	7.11×10^{-3}
60	5.43×10^{-3}	7.39×10^{-3}	7.20×10^{-3}	1.14×10^{-2}	7.67×10^{-3}
65	6.26×10^{-3}	8.41×10^{-3}	7.35×10^{-3}	1.29×10^{-2}	9.57×10^{-3}
70	7.00×10^{-3}	9.25×10^{-3}	8.49×10^{-3}	1.39×10^{-2}	1.08×10^{-2}
75	7.45×10^{-3}	1.03×10^{-2}	9.25×10^{-3}	1.51×10^{-2}	1.19×10^{-2}

80	8.48×10^{-3}	1.08×10^{-2}	1.04×10^{-2}	1.65×10^{-2}	1.31×10^{-2}

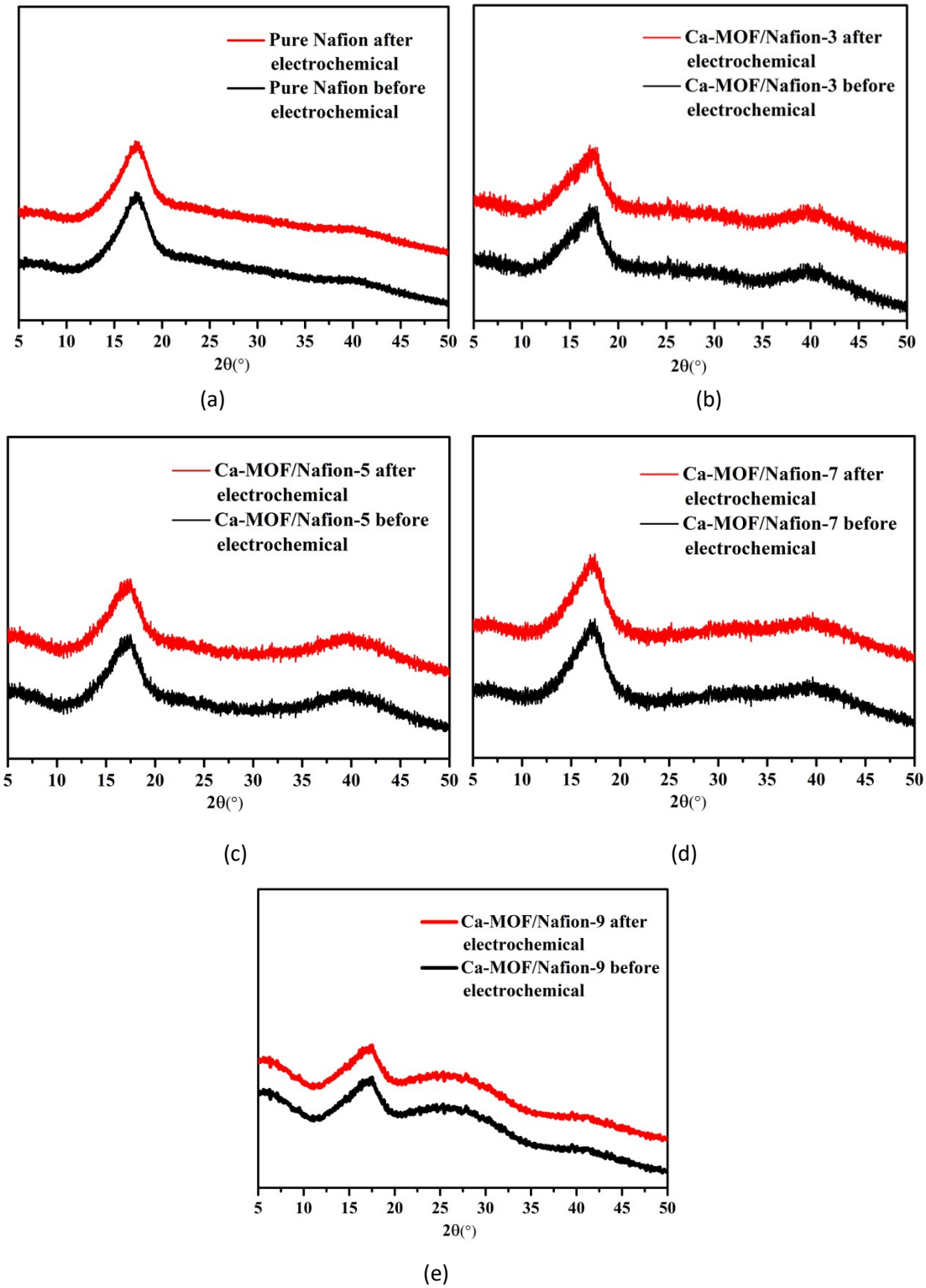

Fig. S1 (a) The PXRD patterns of pure nafion membrane before and after the electrochemical experiment; (b, c, d and e) The PXRD patterns of Ca-MOF/Nafion composite membranes before and after the electrochemical experiment.

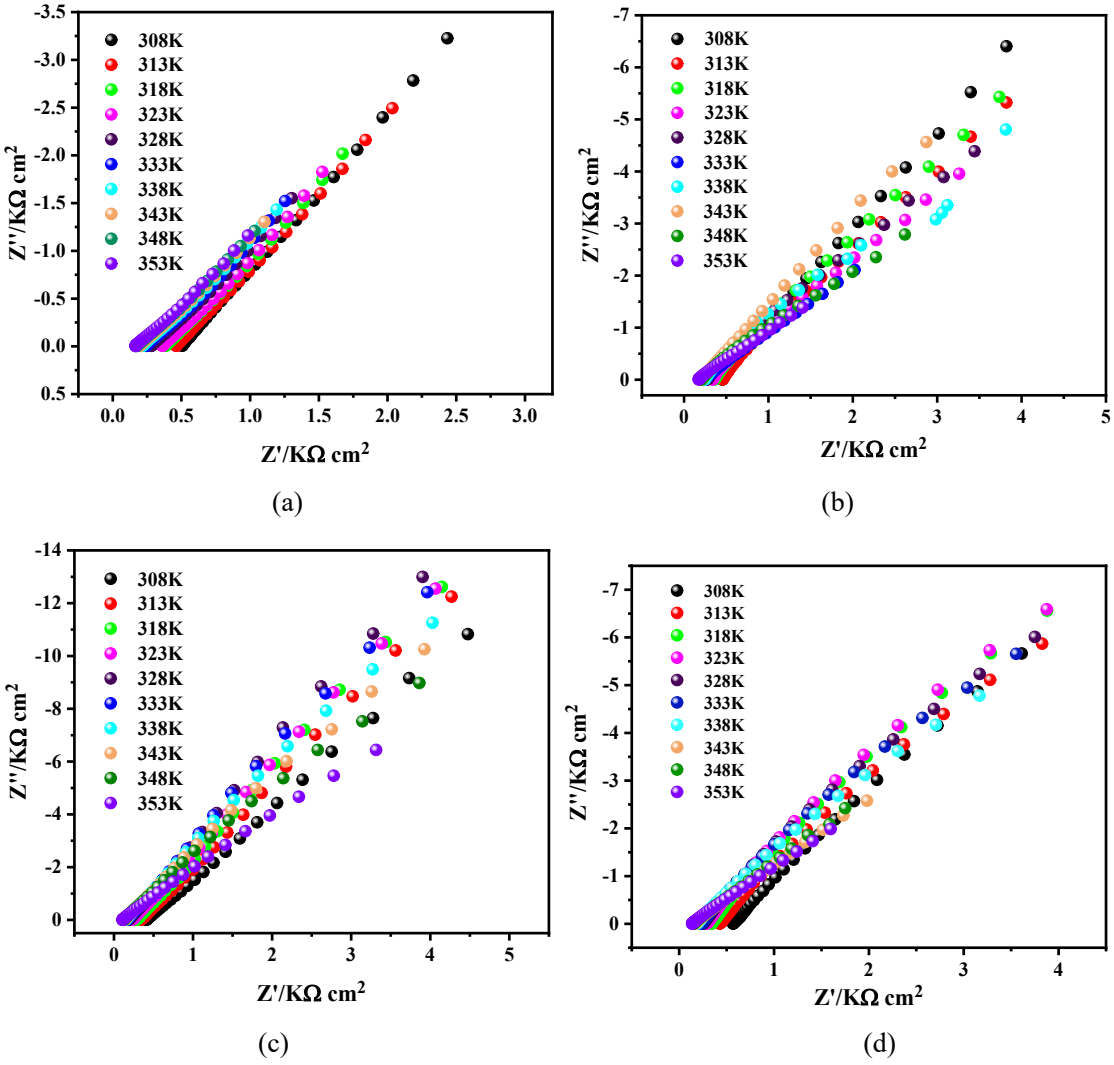

Fig. S2 Nyquist curves of (a) Ca-MOF/Nafion-3 (b) Ca-MOF/Nafion-5; (c) Ca-MOF/Nafion-7; (d) Ca-MOF/Nafion-9 composite membranes at different temperatures.

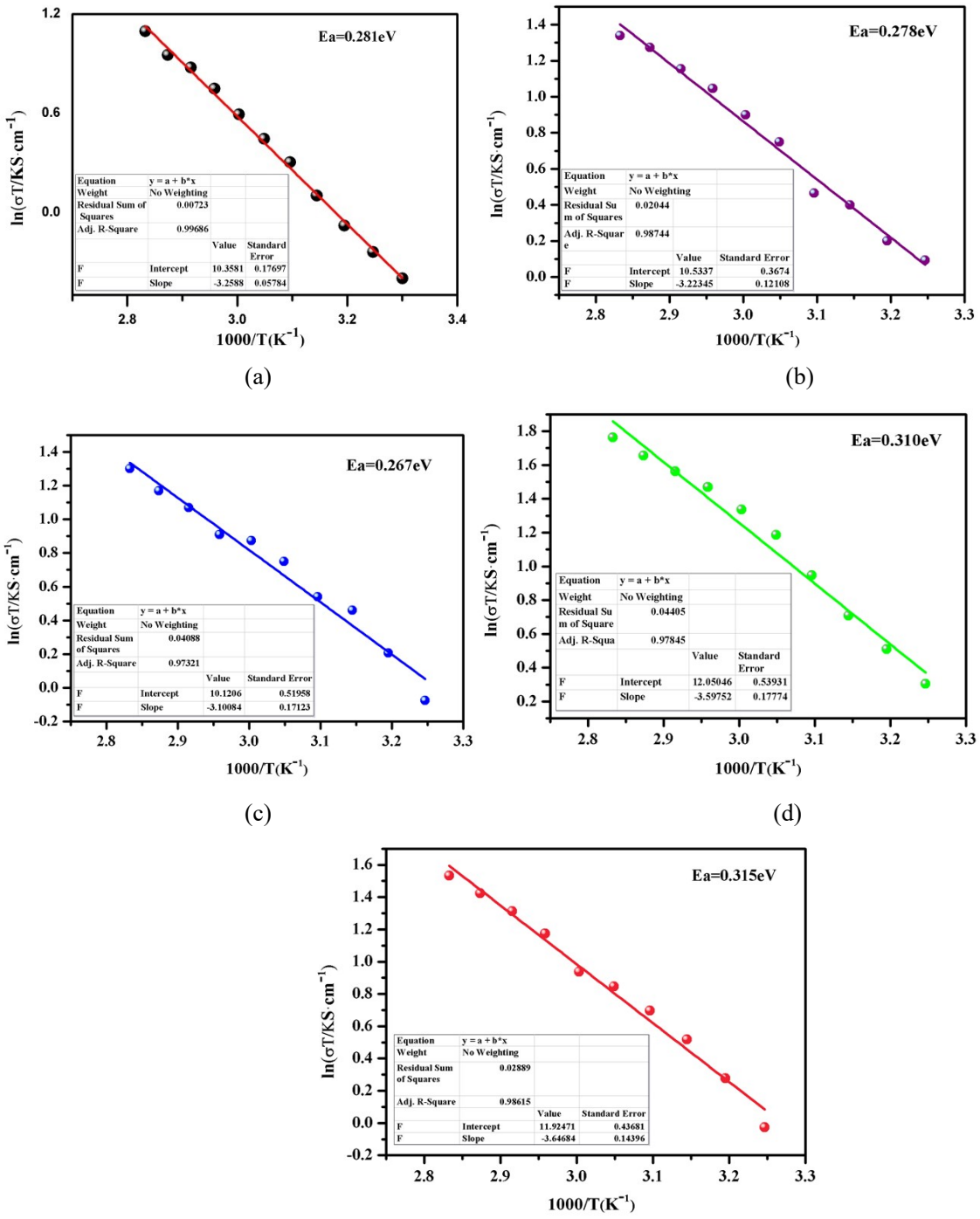

Fig. S3 Plot of $\ln(\sigma_{H^+}T)$ *vs.* 1/T with fitted activivity energy and R^2 values of (a) pure nafion membrane and (b) Ca-MOF/Nafion-3; (c) Ca-MOF/Nafion-5; (d) Ca-MOF/Nafion-7; (e) Ca-MOF/Nafion-9 composite membranes.