

## Supporting Information

### **Significantly Lowered Activation Energy in Proton Conductor by Mg Substitution in a Layered Ni Metal– Organic Framework**

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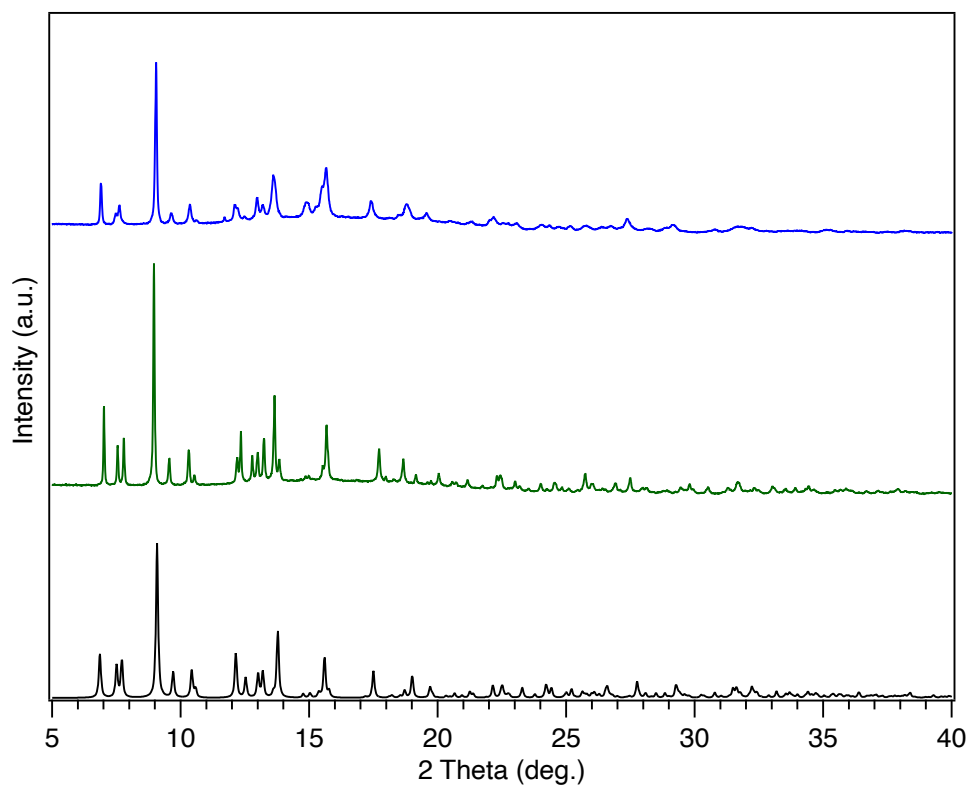
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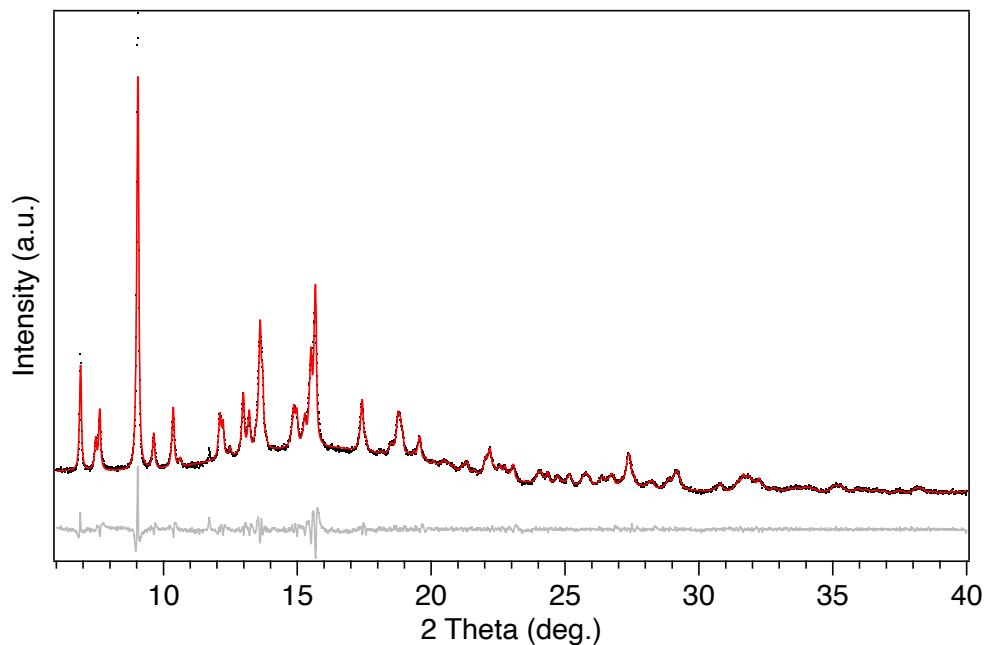
B. Huang (email: bohuang@xjtu.edu.cn).

**Table S1** Elemental analysis results of H<sub>2</sub>DAB-Mg<sub>2</sub>(ox)<sub>3</sub>, H<sub>2</sub>DAB-Ni<sub>2</sub>(ox)<sub>3</sub> and H<sub>2</sub>DAB-MgNi(ox)<sub>3</sub>.

Elem. Anal.		C %	H %	N %	C / N
H <sub>2</sub> DAB MgNi(ox) <sub>3</sub>	Calc (2H <sub>2</sub> O)	25.02	3.77	5.83	4.29
	Found	24.86	3.84	5.78	4.30
H <sub>2</sub> DAB Ni <sub>2</sub> (ox) <sub>3</sub>	Calc (2H <sub>2</sub> O)	23.66	3.57	5.52	4.29
	Found	23.56	3.38	5.56	4.23
H <sub>2</sub> DAB Mg <sub>2</sub> (ox) <sub>3</sub>	Calc (0H <sub>2</sub> O)	29.82	3.50	6.95	4.29
	Found	30.08	3.53	6.98	4.31



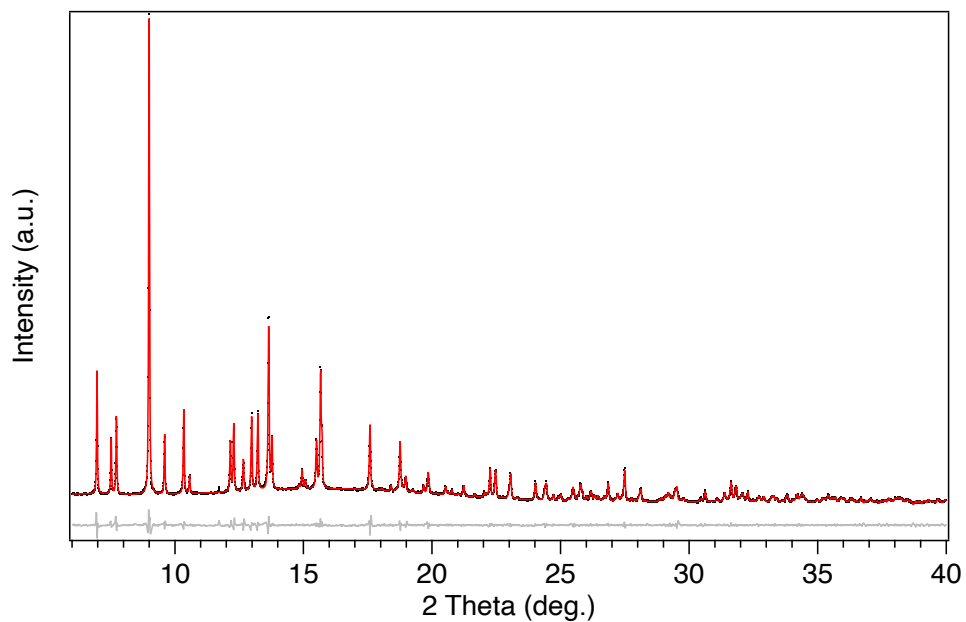
**Figure S1** H<sub>2</sub>DAB-Mg<sub>2</sub>(ox)<sub>3</sub> (blue) H<sub>2</sub>DAB-Ni<sub>2</sub>(ox)<sub>3</sub> (green) and the simulated H<sub>2</sub>DAB-Zn<sub>2</sub>(ox)<sub>3</sub> (black) at 298 K.



**Figure S2** Le Bail fitting (red curve) on XRPD pattern of H<sub>2</sub>DAB-Mg<sub>2</sub>(ox)<sub>3</sub> (black dots). The grey curve shows the difference between fitting curve and raw pattern. The wavelength was 1.000 Å.

**Table S2** Le Bail fitting results of H<sub>2</sub>DAB-Mg<sub>2</sub>(ox)<sub>3</sub>.

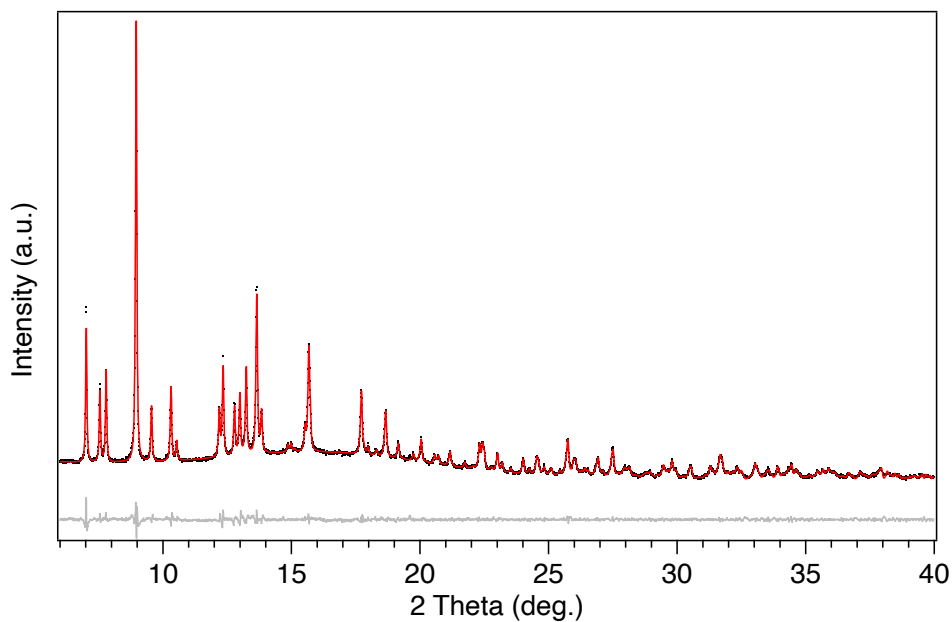
<b>Space group</b>	P-1		
<i>a</i>	6.735 Å	<i>α</i>	62.60°
<i>b</i>	8.996 Å	<i>β</i>	88.08°
<i>c</i>	9.417 Å	<i>γ</i>	71.44°
<b>Crystal size</b>	93(1) nm		
<i>R</i> <sub>wp</sub>	3.69%		



**Figure S3** Le Bail fitting (red curve) on XRPD pattern of  $\text{H}_2\text{DAB-MgNi(ox)}_3$  (black dots). The grey curve shows the difference between fitting curve and raw pattern. The wavelength was 1.000 Å.

**Table S3** Le Bail fitting results of  $\text{H}_2\text{DAB-MgNi(ox)}_3$ .

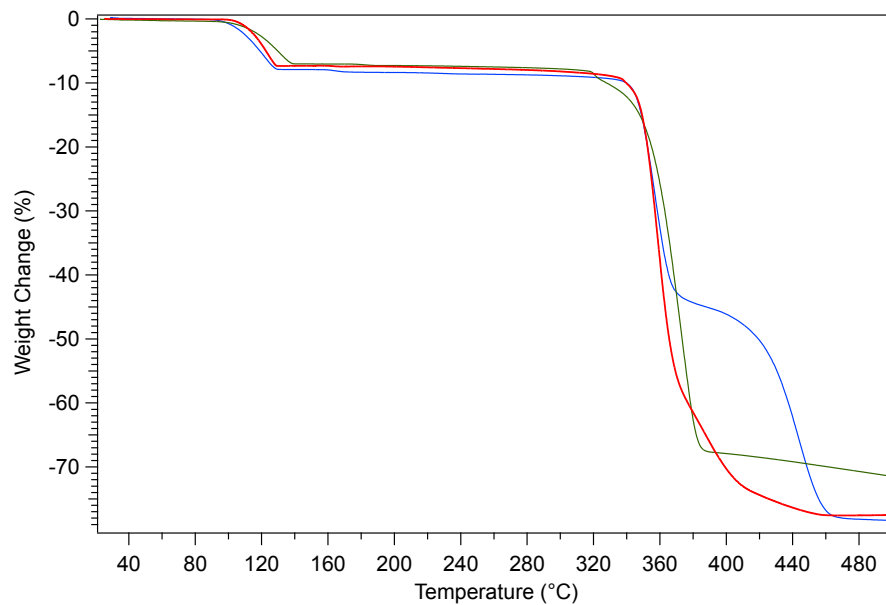
<b>Space group</b>	P-1		
<i>a</i>	6.801 Å	<i>α</i>	62.37°
<i>b</i>	8.936 Å	<i>β</i>	88.27°
<i>c</i>	9.375 Å	<i>γ</i>	71.14°
<b>Crystal size</b>	234(2) nm		
<i>R</i> <sub>wp</sub>	2.90%		



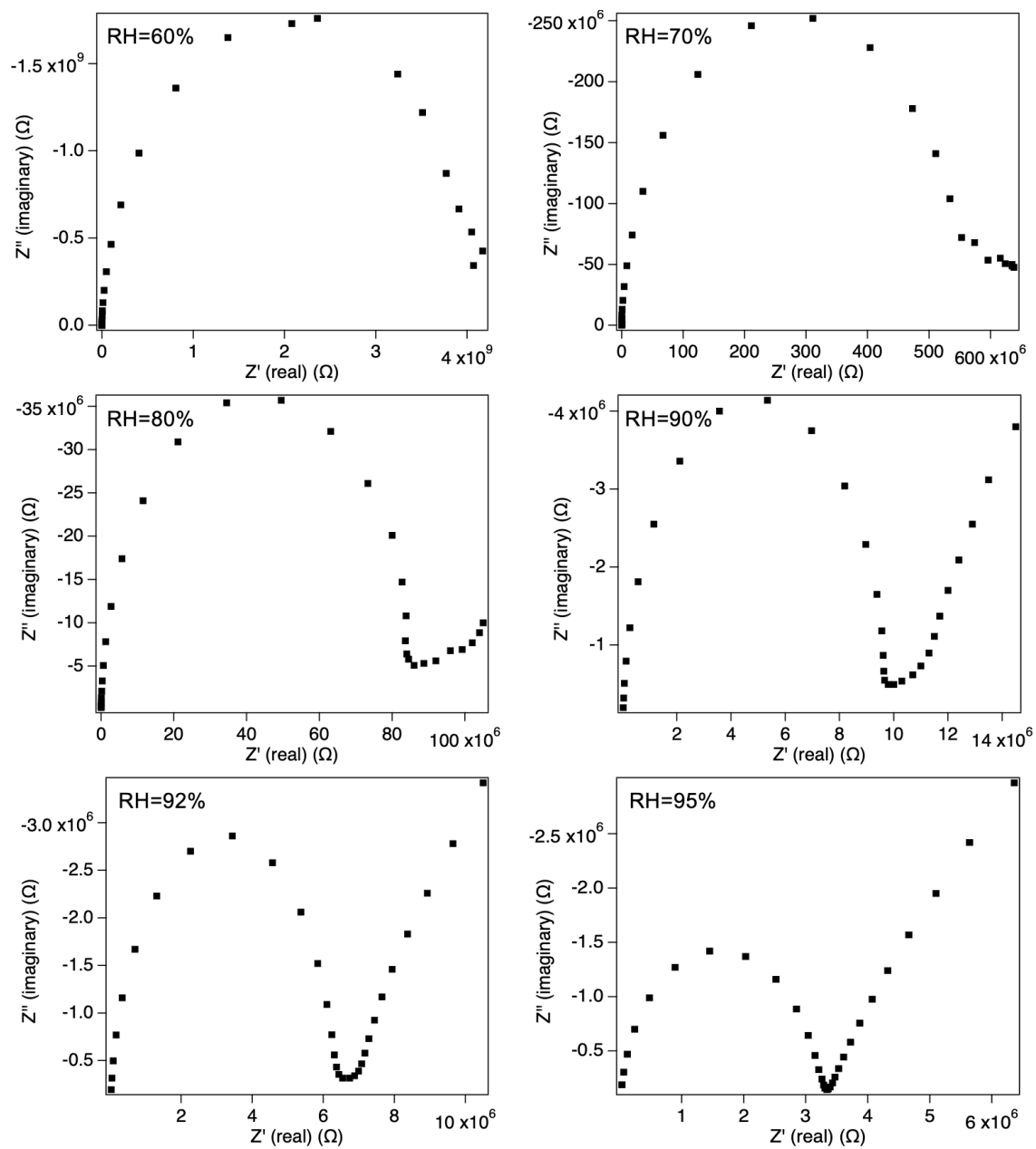
**Figure S4** Le Bail fitting (red curve) on XRPD pattern of H<sub>2</sub>DAB-Ni<sub>2</sub>(ox)<sub>3</sub> (black dots). The grey curve shows the difference between fitting curve and raw pattern. The wavelength was 1.000 Å.

**Table S4** Le Bail fitting results of H<sub>2</sub>DAB-Ni<sub>2</sub>(ox)<sub>3</sub>.

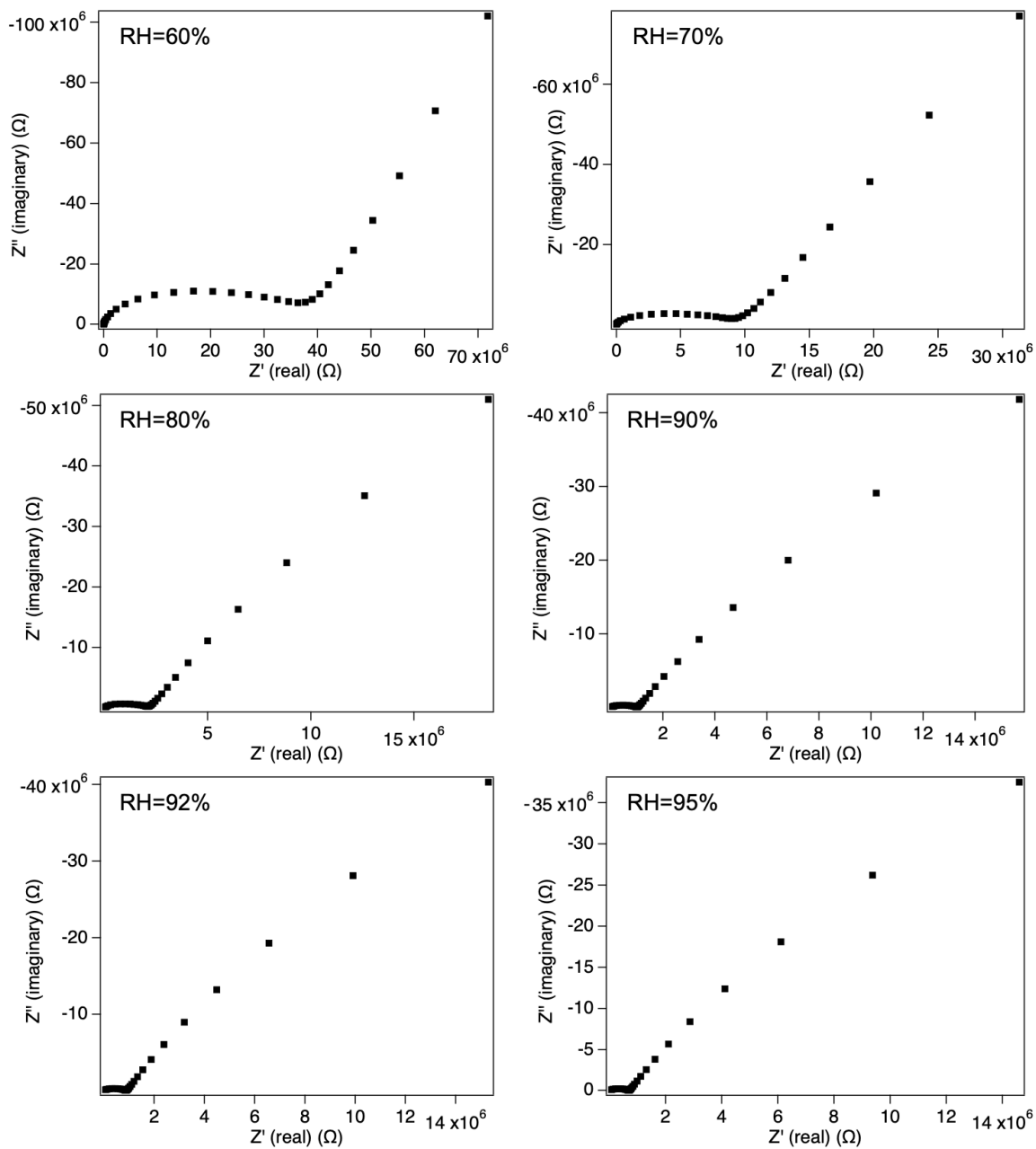
<b>Space group</b>	P-1		
<i>a</i>	6.844 Å	<i>α</i>	62.17°
<i>b</i>	8.895 Å	<i>β</i>	88.34°
<i>c</i>	9.327 Å	<i>γ</i>	70.81°
<b>Crystal size</b>	133(1) nm		
<b><i>R</i><sub>wp</sub></b>	2.27%		



**Figure S5** Thermogravimetric analysis plots of the dried H<sub>2</sub>DAB-Mg<sub>2</sub>(ox)<sub>3</sub> (blue) H<sub>2</sub>DAB-Ni<sub>2</sub>(ox)<sub>3</sub> (green) and H<sub>2</sub>DAB-MgNi(ox)<sub>3</sub> (red). The heating rate was 5 °C / min.

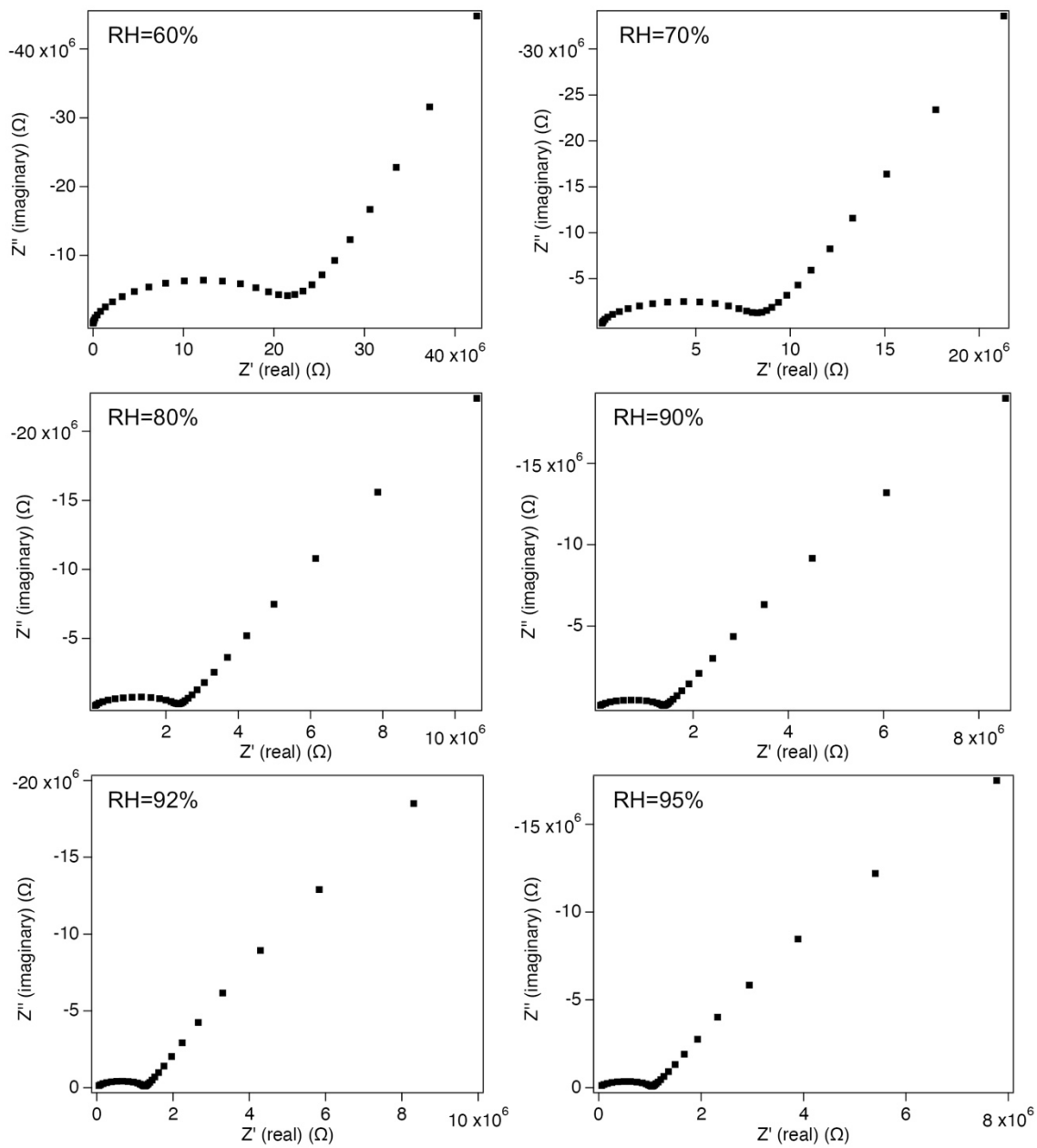


**Figure S6** Nyquist plots for  $\text{H}_2\text{DAB-Mg}_2(\text{ox})_3$  at 298 K.

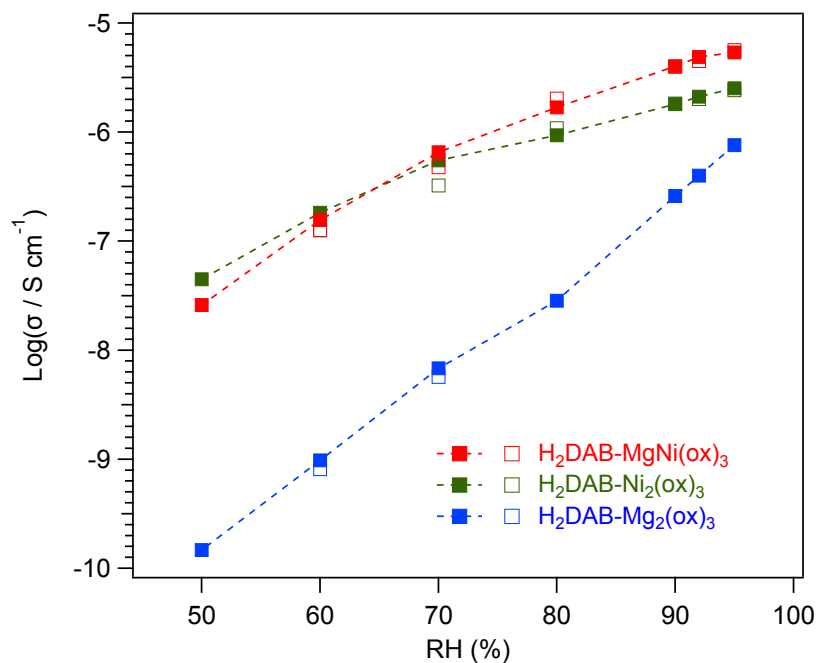


**Figure S7** Nyquist plots for  $\text{H}_2\text{DAB-MgNi(ox)}_3$  at 298 K.





**Figure S8** Nyquist plots for  $\text{H}_2\text{DAB-Ni}_2(\text{ox})_3$  at 298 K.



**Figure S9** Humidity dependence at RH increasing (solid) and RH decreasing (hollow) processes of proton conductivities for H<sub>2</sub>DAB-Mg<sub>2</sub>(ox)<sub>3</sub>, H<sub>2</sub>DAB-Ni<sub>2</sub>(ox)<sub>3</sub> and H<sub>2</sub>DAB-MgNi(ox)<sub>3</sub>. The measurement temperature was 298 K.