

## Supporting Information

### Hydroxyl-Conductive 2D Hexagonal Boron Nitrides based Anion Exchange Membrane Water Electrolysis for Sustainable Hydrogen Production

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#### Synthesis of hBN nanofiller:

Using a probe sonicator (Sonics Vibra Cell VCX 750, Fisher Scientific, 750 W, 20 kHz), the commercially available pristine hBN bulk (Sigma-Aldrich Co. Ltd., powder 1  $\mu\text{m}$ ) was mixed in a solution of isopropyl alcohol (IPA, Sigma-Aldrich Co. Ltd. 70% in  $\text{H}_2\text{O}$ ) and Sustainion<sup>®</sup> (XA-9 Alkaline Ionomer 5% in ethanol, purchased from Dioxide Materials) was added to hBN IPA dispersion. The concentration of hBN bulk in the final solution is 5 mg/mL and the volume ratio of IPA: Sustainion<sup>®</sup> is 3:2. The hBN dispersion was exfoliated by liquid phase exfoliation using a tip sonicator for 2 h at 30% amplitude.<sup>1</sup> After 2 h of sonication, 1M KOH solution was added to the hBN dispersion and the final solution was exfoliated for another hour at 30% amplitude. After exfoliation, the functionalized hBN dispersion was centrifuged at 3 krpm for 30 mins to separate

unexfoliated thicker flakes. Eventually, the pellet which consisted of thicker flakes of hBN was separated from the supernatant.

#### **Casting of hydroxyl conductive-hBN AEMs:**

Specific volumes of BN-OH dispersion and PVA solution were used in casting hydroxyl conductive AEMs of different weight (wt.) %. We cast membranes of different wt.% which were 15wt.% and 25wt.% of hBN nanocomposite. The two solutions were homogeneously mixed in specific volume ratios by mild sonication for 30 minutes. The mixed solutions were poured out in petri dishes of 7 cm and 10 cm and placed in a gravity oven at 80 °C for 4 hours. After 4 h, the solution should be completely dried, the samples were treated at 90 °C for another hour. After that step, the oven was stopped, and the sample was cooled down to room temperature and brought out of the oven once it was at room temperature. Distilled water was added to peel the samples and once the sample was peeled, it was stored in distilled water overnight. Next morning, 1M KOH solution was prepared and the sample of BN-OH membrane was immersed in 1M KOH solution for 48 h for activation of the sample. After 48 h, the sample was taken out and rinsed using DI water to remove excess of KOH and dried using kim wipes. The BN-OH AEM was ready to be tested. Samples with low-loaded hBN nanocomposite with PVA (M1: 15 wt% of hBN nanofiller) and high-loaded BN nanocomposite with PVA (M2: 25 wt% of hBN nanofiller) were synthesized, tested, and compared with Commercial Sustainion membrane (CS-M3).

#### **AEMWE cell fabrication and testing:**

For the full cell testing, porous Ni based electrodes were produced on the surface of 4 cm<sup>2</sup> Ni mesh (NM) substrate using thermal spray technique.<sup>2</sup> Electrodes were produced by spraying globular gas-atomized Nickel-Aluminum type alloy powders with and without Mo for anode and cathode electrodes, respectively. Al acts as a pore-forming agent. Coated porous electrodes were produced on the surface of 4 cm<sup>2</sup> Ni mesh (NM) substrate using thermal spray technique. For this, Ar with secondary gases were used.

The spray powder was injected through external injection nozzles into the plasma jet, where particles were accelerated and heated due to momentum and heat transfer between plasma and particles and the quasi or fully molten particles impacted the substrate surface, flattened, solidified, and consolidated to form an electrode coating. Before the electrochemical test, the electrodes were activated in 30 wt.% KOH with suitable complex-former for removing Al as a pore-forming agent to form porosities.<sup>4</sup> Prior to testing, membranes were soaked and activated in a bath of 1M KOH for 24 h. To minimize the membrane contamination, membrane treatment was done in a closed container to avoid CO<sub>2</sub> contamination (carbonate formation that may affect conductivity). In addition, 1 M KOH solution was changed several times over this duration. Finally, the activated membranes were rinsed thoroughly with deionized water before further use. Activated membranes are placed between two coated electrodes both cathode and anode with Ni gas diffusion layers at each side and tested in 1M KOH at 60 °C by recording polarization curves up to 0.5 A cm<sup>-2</sup> with the slow scan rate of 10 mA s<sup>-1</sup>, after 30 min activation at constant current 0.2 A using biologic potentiostat. The cell durability with different membranes is evaluated by running the cell at the constant current density of 0.5 A cm<sup>-2</sup> for 250 h.

#### **Electrochemical Impedance Spectroscopy:**

For all the methods, the real impedance of samples was calculated using AC electrochemical impedance spectroscopy (EIS) in Gamry's electrochemical workstation under hydrous conditions of 80% relative humidity (RH) at various temperatures.<sup>3</sup> The frequency range was set between 1 MHz and 0.1 Hz with perturbation voltage amplitude of 5 mV. At a given temperature, the measurements were repeated at least three times with 10 min interval. The hydroxide conductivities of AEMs were then determined using the following equation.<sup>4</sup>

$$\sigma = \frac{L}{AR} \quad (S1)$$

where  $\sigma$  denotes the hydroxide conductivity, L is either the distance between the reference electrodes in the four-point cell or the thickness of powdered samples in case of two-electrode setup, R the resistance of the membrane, and A the cross-sectional area in case of the in-plane setup and the area of the electrodes in case of the two-electrode cell. The activation energies ( $E_a$ ) for the samples were tested across a range of temperatures from RT to 80 °C using the

Arrhenius equation and plots (Figures 6 (c) and (d)):  $\sigma = A \exp (E_a/RT)$ , where  $\sigma$  is the ionic conductivity,  $A$  is the pre-exponential factor,  $R$  is the gas constant (8.31 J/mol. K), and  $T$  is the temperature (K).

#### Measurement and calculation of WU, SWR and IEC:

To calculate the WU and SWR of M1, M2 and CS-M3 membranes, the samples were immersed in 1M KOH solution at room temperature for 24 h. Later, the membranes were removed and rinsed in DI water and dried, the weight and thickness of membranes were immediately measured. Later, the membranes were dried in a vacuum oven at 60 °C until a constant weight was achieved. WU and longitudinal and crosswise swelling ratios were calculated by following equations.

$$WU (\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \quad (S2)$$

$$SR (\%) = \frac{t_{wet} - t_{dry}}{t_{dry}} \times 100 \quad (S3)$$

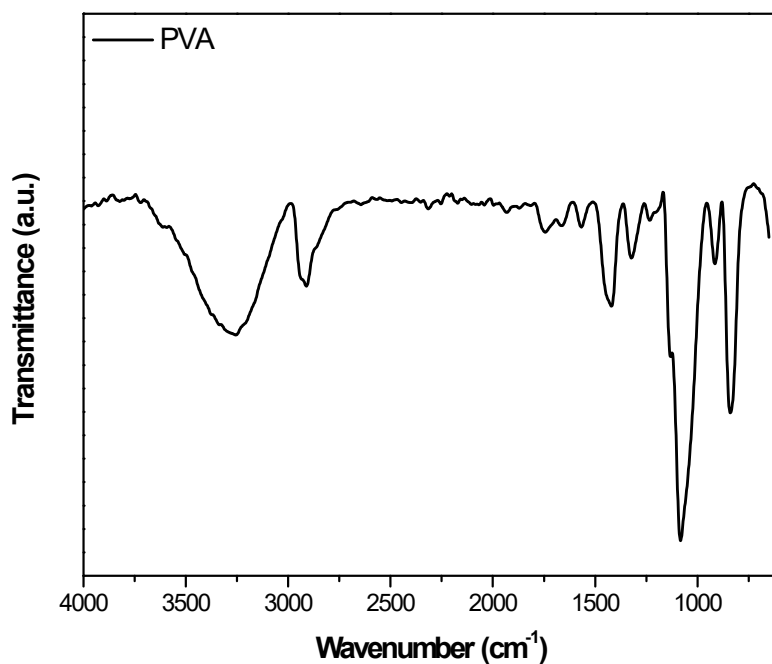
where  $W_{wet}$  and  $t_{wet}$  are the weight and thickness of hydrated AEMs and  $W_{dry}$  and  $t_{dry}$  are the weight and thickness of dried membranes.<sup>5</sup>

The ion exchange capacity (IEC) of membrane samples was determined by using the back titration method. At first, the samples were dried until the weight was constant, after which each sample was immersed in double distilled water overnight. Next, the samples were soaked in 0.01 M hydrochloric acid (HCl) for 48 hrs to exchange chloride ions with hydroxides. Back titration was then performed with 0.01 M NaOH (aqueous) standardized solution with phenolphthalein as an indicator. The IEC values were calculated using the Equation S4.

$$IEC = \frac{(M_1V_{1HCl} - M_2V_{2NaOH})}{W_{dry}} \quad (S4)$$

where IEC is the ion exchange capacity (meq·g<sup>-1</sup>),  $M_1$  (molar) and  $V_1$  (mL) are the concentration and volume of HCl solution, respectively, before the titration;  $M_2$  (molar) and  $V_2$  (mL) are the concentration and volume of NaOH solution, respectively, used in the titration;  $W_{dry}$  (g) is the dry mass of the sample.

**FTIR spectra of PVA membrane:**

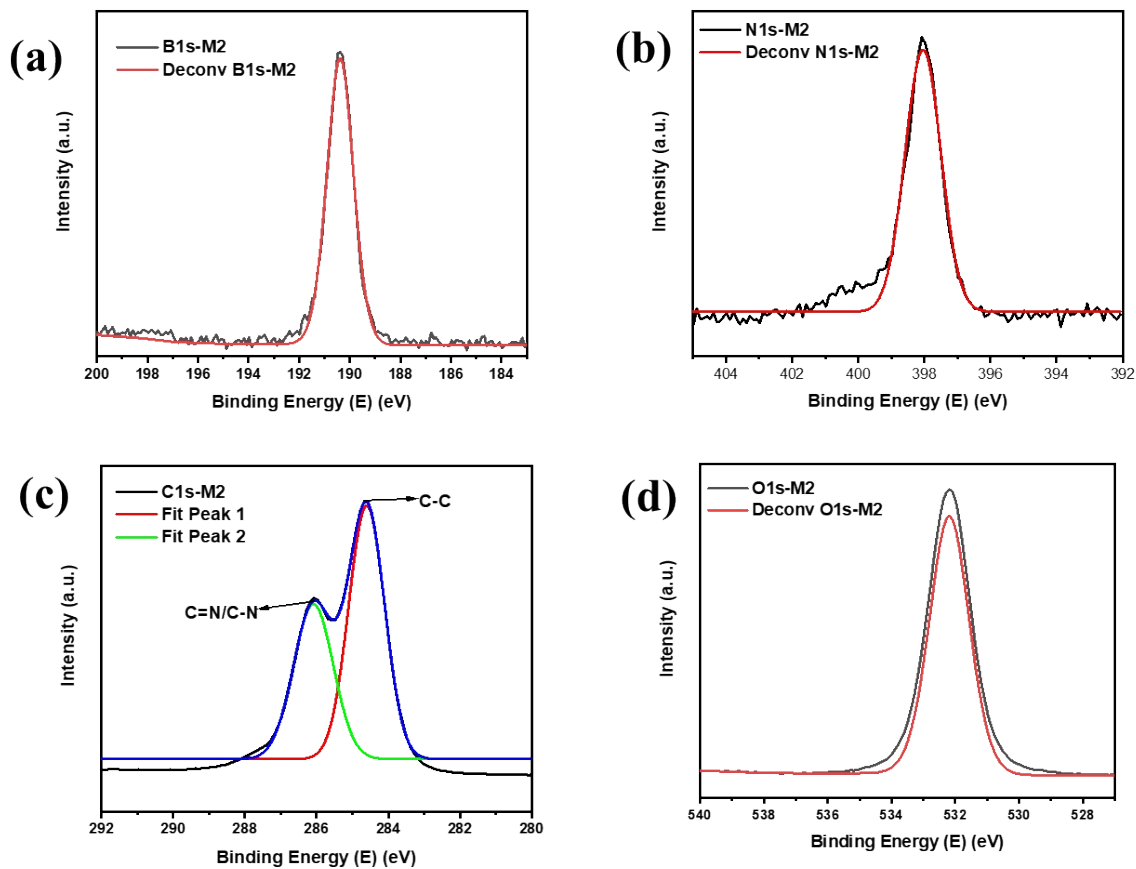


**Figure S1.** FTIR spectrum of PVA membrane.

**Table S1 – Physicochemical and mechanical properties of AEMs**

Sample	WU ratio (%)	SWR (Crosswise)	SWR (Longitudinal)	IEC (mequiv/g)	Tensile Strength (MPa)
M1	20	5	8	1.7	8.9
M2	25	5	10	2.9	9.0

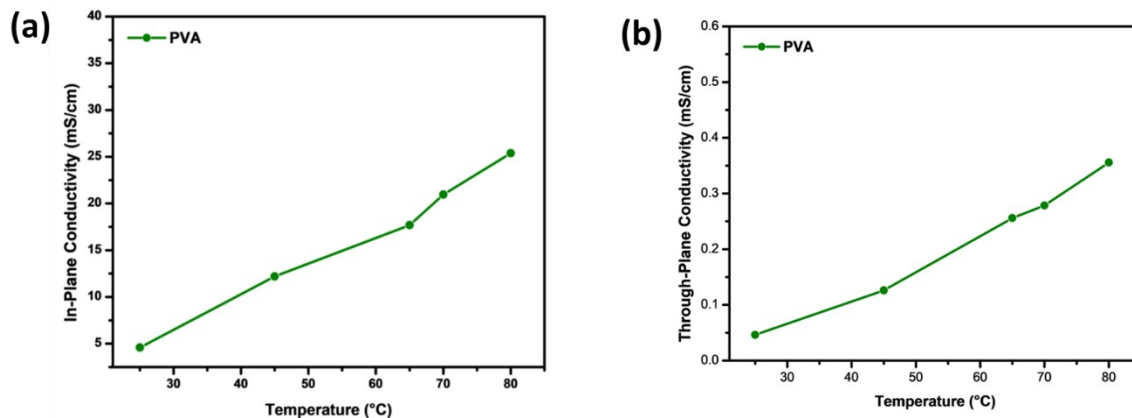
## XPS elemental analysis of M2 membrane:



**Figure S2.** XPS elemental analysis of M2 and its deconvoluted spectra for (a) B 1s, (b) N 1s, (c) C 1s, and (d) O 1s.

## Hydroxide conductivity of plain PVA membrane:

**Figure S3** shows the in-plane conductivity and through plane conductivity results of plain PVA membrane with no incorporation of 2D hBN, provided for reference. These values of in-plane and through plane conductivity are much lower than the results observed in **Figure 6 (a) and (b)**.



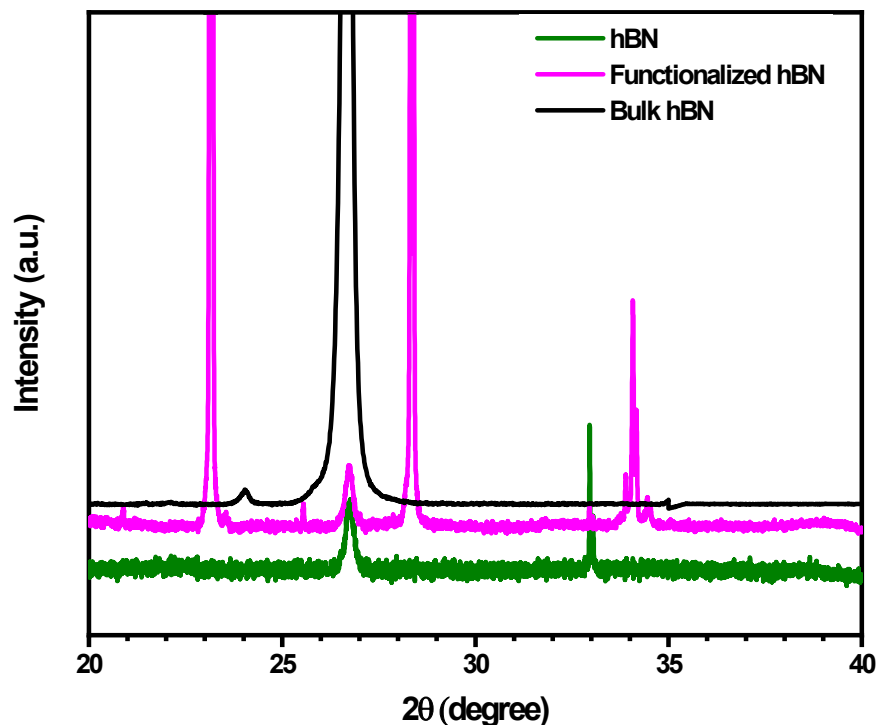
**Figure S3.** (a) In-plane conductivity and (b) through plane conductivity of PVA membrane.

**Table S2 – Overview of performance of AEM electrolyzer in the literature**

	Catalysts	Membrane	Electrolyte	Temp.	Performance mA/cm <sup>2</sup> @1.8V	Degradation	Duration	Ref.
1	Raney Ni NiFe <sub>2</sub> O <sub>4</sub>	Sustainion grade T	1M KOH	60°C	837	0.7 μV/h @1 A/cm <sup>2</sup>	12.180 h	8
2	Raney Ni NiFe <sub>2</sub> O <sub>4</sub>	Sustainion X37-50	1M KOH	60°C	744	0.7 μV/h @1 A/cm <sup>2</sup>	10.100 h	8
3	Raney Ni NiFe <sub>2</sub> O <sub>4</sub>	Fumasep FAS 50	1M KOH	60°C		655 μV/h @1 A/cm <sup>2</sup>	140 h	8
4	NiFeCo NiFe <sub>2</sub> O <sub>4</sub>	Sustainion	1M KOH	60°C	510	5 μV/h @1 A/cm <sup>2</sup>	1950 h	9
5	NiFeCo NiFe <sub>2</sub> O <sub>4</sub>	FAS-50	1M KOH	60°C	240	400 μV/h @1 A/cm <sup>2</sup>	200 h	9
6	NiFe NiMo	xQAPS	Pure Water	70°C	240	6300 μV/h @0.4 A/cm <sup>2</sup>	8 h	10
7	NiFe-LDH	Fumasep AA- 3-PK-130 a	1M KOH	60°C	700	1500 μV/h @0,5 A/cm <sup>2</sup>	110 h	11
8	Raney Ni	M1	1M KOH	60°C	228	272 μV/h @0,5 A/cm <sup>2</sup>	250 h	This work
9	Raney Ni	M2	1M KOH	60°C	500@1.78V	468 μV/h @0.5 A/cm <sup>2</sup>	250 h	This work

## XRD of hBN

XRD spectra of bulk hBN, exfoliated hBN and functionalized hBN are shown in **Figure S4**. It is observed *via* XRD that the exfoliated 2D hBN crystals are oriented in the (002) direction with a characteristic peak observed at 26.7°, in agreement with literature reports.<sup>6,7</sup> The interplanar spacing between the layers is calculated and observed that the interplanar spacing has increased in functionalized hBN as compared to exfoliated hBN and bulk samples.



**Figure S4.** XRD spectrum of bulk hBN, exfoliated hBN and functionalized hBN nanosheets

## REFERENCES:

1. J. Kaur, A. Malekhouyan, G. S. Selopal, Z. M. Wang, F. Rosei and H. Zarrin, *ACS Applied Materials and Interfaces*, 2021, **13**, 6532–6544.
2. H. A. Miller, K. Bouzek, J. Hnat, S. Loos, C. I. Bernäcker, T. Weißgärber, L. Röntzsch and J. Meier-Haack, *Sustainable Energy and Fuels*, 2020, **4**, 2114–2133.
3. J. Z. Xiaozi Yuan, Haijiang Wang, Jian Colin Sun, *International Journal of Hydrogen Energy*, 2007, **32**, 4365–4380.



4. H. Zarrin, J. Wu, M. Fowler and Z. Chen, *Journal of Membrane Science*, 2011, **394**, 193–201.
5. J. Ran, L. Wu, B. Wei, Y. Chen and T. Xu, *Scientific Reports*, 2014, **4**, 1–5.
6. A. F. Khan, D. A. C. Brownson, E. P. Randviir, G. C. Smith and C. E. Banks, *Anal Chem*, 2016, **88**, 9729–9737.
7. K. Zhang, Y. Feng, F. Wang, Z. Yang and J. Wang, *J Mater Chem C Mater*, 2017, **5**, 11992–12022.
8. B. Motealleh, Z. Liu, R. I. Masel, J. P. Sculley, Z. R. Ni and L. Meroueh, *International Journal of Hydrogen Energy*, 2021, **46**, 3379–3386.
9. Z. Liu, S. D. Sajjad, Y. Gao, H. Yang, J. J. Kaczur and R. I. Masel, *International Journal of Hydrogen Energy*, 2017, **42**, 29661–29665.
10. L. Xiao, S. Zhang, J. Pan, C. Yang, M. He, L. Zhuang and J. Lu, *Energy Environ Sci*, 2012, **5**, 7869e71.
11. M. Klingenhof, S. Selve, C. M. Günther, J. Schmidt, F. Razmjooei, P. Strasser, and S. A. Ansar, *ACS Applied Energy Materials*, 2024 **7**, 6856–6861.