## S1 Membrane characterization

Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) technique was performed with spectrum GX series 49387 spectrometer in the range of 4000–400 cm<sup>-1</sup>. FE-SEM imaging was done using Field Emission Scanning Electron Microscope (FE-SEM-Jeol JSM 7100F). Thermal stabilities of the membrane samples were evaluated by using thermogravimetric analysis (TGA) of NETZSCH TG 209F1 Libra which involves heating of vacuum dried samples at the rate 10°C within a temperature range 25°C-600°C under N<sub>2</sub> atmosphere. Stress/strain curve for membranes are measured by using Zwick Roell, Z2.5 universal testing machine (UTM). Oxidative stability of prepared membranes by immersing the membranes into Fenton's reagent (2 ppm FeSO<sub>4</sub> in 3% H<sub>2</sub>O<sub>2</sub>) at 80 °C was also measured. The loss in ionic conductivity before and after oxidative stability was recorded.

## S2 Water uptake, Ion Exchange Capacity (IEC) and Swelling ratio (SR)

Water Uptake of membranes were determined by recording the weight gain after dipping  $2 \times 2$  cm<sup>2</sup> membrane sample in water for 24h. The dry weight of membrane were noted after vacuum drying at 100°C for 2h. Water uptake ( $Ø_w$ ) for membranes was calculated by using following formula:

$$\mathcal{O}_{\rm W} = \frac{W_{wet} - W_{Dry}}{W_{Dry}} \times 100\% \qquad (1)$$

Where  $W_{wet}$  and  $W_{dry}$  are the wet and dry weight of composite membrane samples. Swelling ratio of membranes were evaluated by taking volume difference in wet and dry condition and calculated by following equation:

$$SR = \frac{S_{wet} - S_{dry}}{S_{dry}} \times 100\%$$
(2)

Where  $S_{wet}$  and  $S_{dry}$  are volume of wet and dry membrane samples respectively.

IEC of membrane samples was calculated by simple acid-base titration. Membrane samples were washed and equilibrated in 1.0 M HCl solution for 24 h, to convert remaining charge sites into H<sup>+</sup>. Thereafter, the samples were washed several times with DI water to remove excess of HCl than immersed into 1 M NaCl solution for another 24 h, exchange of sodium ion with proton in the membranes happens. The amount of H<sup>+</sup> liberated was estimated by titrating against with 0.1 M NaOH solution using phenolphthalein as an indicator. IEC for membranes were calculated by using following equation:

$$IEC = \frac{V \times C}{W dry}$$
(3)

Where V, C and  $W_{dry}$  are the titre value during titration, concentration of NaOH solution and dry weight of sample respectively.

## S3 Electrochemical characterizations

A Bio-logic VSP potentiostat controlled by EC-Lab software was used for electrochemical tests. Electrochemical impedance spectroscopy (EIS) experiments were performed in three electrode mode under continuous circulation of 1.5 M solution of VO<sup>2+</sup> in 3M H<sub>2</sub>SO<sub>4</sub> in the VRFB cell. EIS was performed at open circuit potential ( $E_{OC}$ ) (AC voltage perturbation is 10 mV in the frequency range 2000 kHz - 1000 mHz). Cell resistance ( $R_r$ ) were determined from the high-frequency intercept. Ionic conductivity of the prepared membranes was measured in water using potentiostat/galvanostat (CH-608E). Membrane sample of 2 cm<sup>2</sup> are immersed in hydrochloric acid (0.1M) for 24 h and then washed with DI water in order to remove excess of HCl. Membrane samples are placed between two circular steel electrodes (1 cm<sup>2</sup>). Membrane samples resistance was obtained by Nyquist plot and ionic conductivity ( $\sigma$ ) was calculated from the equation:

$$\sigma \left(\Omega^{-1} \operatorname{cm}^{-1}\right) = \frac{L(cm)}{R(\Omega) \times A(cm^2)} \quad \dots \qquad (4)$$

Where A is the surface area of membrane sample, R is the resistance of membrane sample and L is the distance between the electrodes used to measure the potential [35,39,41]. Selectivity is obtained through the ratio of ionic conductivity and vanadium permeability by using following equation:

$$S = \frac{\sigma}{P} \qquad (5)$$

S is selectivity,  $\sigma$  is ionic conductivity and P is vanadium permeability [42].



Fig. S1: FTIR-ATR for the prepared membranes



Fig. S2: TGA thermogram for the prepared membranes



Fig. S3: Stress- strain curves for the prepared membranes



Fig. S4: Effect on VE with number of cycles for both the membranes

Current Density/	50 mA/cm <sup>2</sup>			100 mA/cm <sup>2</sup>		
Membrane	Current Efficiency (%)	Voltage Efficiency (%)	Energy Efficiency (%)	Current Efficiency (%)	Voltage Efficiency (%)	Energy Efficiency (%)
HA-35	89	84	75	94	71	67
HA-45	93	94	87	95	84	80
Nafion 117	-	-	-	93	87	81

**Table S1:** Cell efficiencies at varied current density for HA-35 and HA-45 membranes

**Table S2:** Current density and power density for prepared membranes

Membrane	Current density at peak power (mA/cm <sup>2</sup> )	Peak Power density (mW/cm <sup>2</sup> )
HA-35 HA-45	353 470	239 336