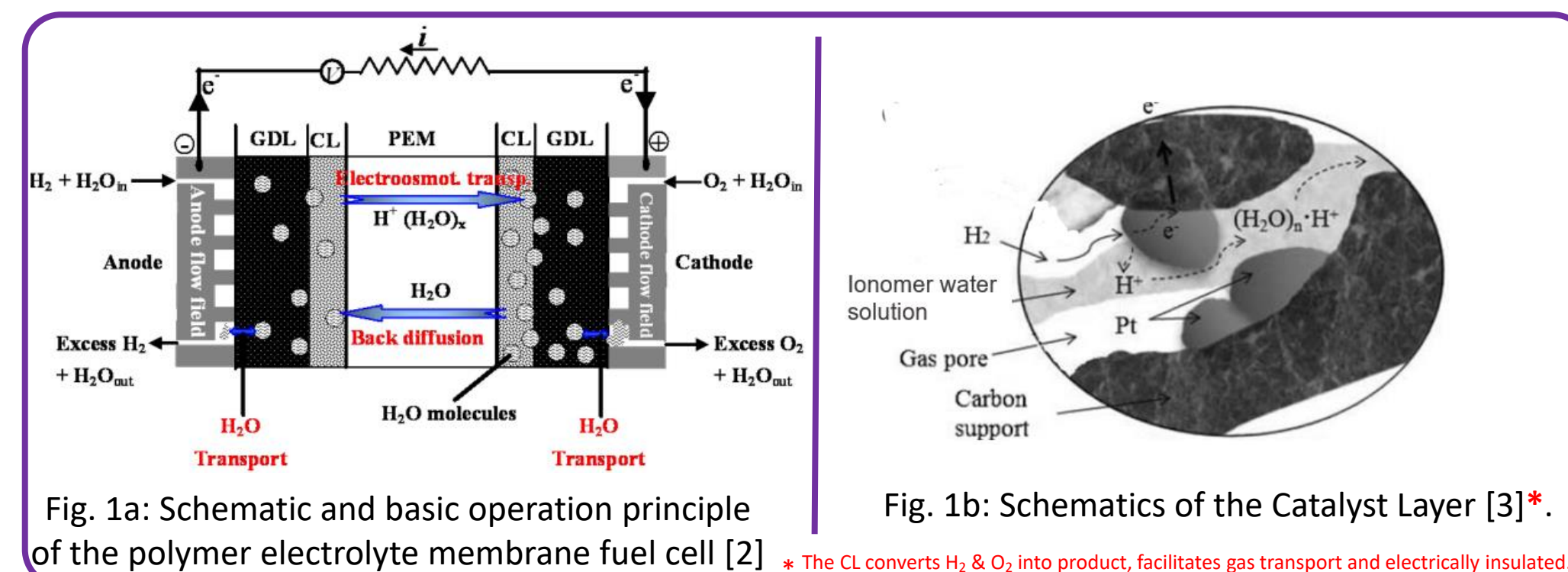


Abstract

Today, we are at an age of unprecedented change, one where the need to protect our environment is a global societal concern. Sustainability is now a key factor in the long-term viability of the global energy infrastructure. We envision a future where industry can meet growing energy demands in an environmentally sustainable way. And we are already seeing this take place. Hydrogen fuel cells have a real potential to be an important part of the solution. However, to ensure their wide scale adoption, there is a need to reduce the high cost associated with these fuel cells without compromising on performance. In this study, we introduce a highly performing, fluorine-free hydrocarbon-based proton-conducting sulfo-phenylated poly(phenylene) sPPB-H⁺ as a complete substitute for incumbent high cost perfluorosulfonic acid-based materials, both as an electrode catalyst binder, and membrane in polymer electrolyte membrane fuel cells. Power densities of 1.1 W cm⁻² are achieved using H₂/O₂ when 15 wt% ionomer content is present in the catalyst layer. This represents a 25% increase in performance over previously reported values (up to 0.8 W cm⁻²) for fully low-cost non-fluorous, hydrocarbon solid polymer electrolytes, and the first to demonstrate power densities > 1 W cm⁻². This shows that hydrocarbon-based polymers may truly represent a cheaper and efficient alternative to the expensive perfluorosulfonic acid-based PEM fuel cell polymers.

Introduction

Currently, there is a high drive towards a decarbonized and sustainable energy systems other than fossil fuels which are economically feasible and efficient in their energy conversion. In this regard, polymer electrolyte membrane fuel cells (PEMFC) Fig 1(a) over the decade have continuously gained attention as one of the most viable energy converters, due to their high-energy efficiency and low emissions [1].



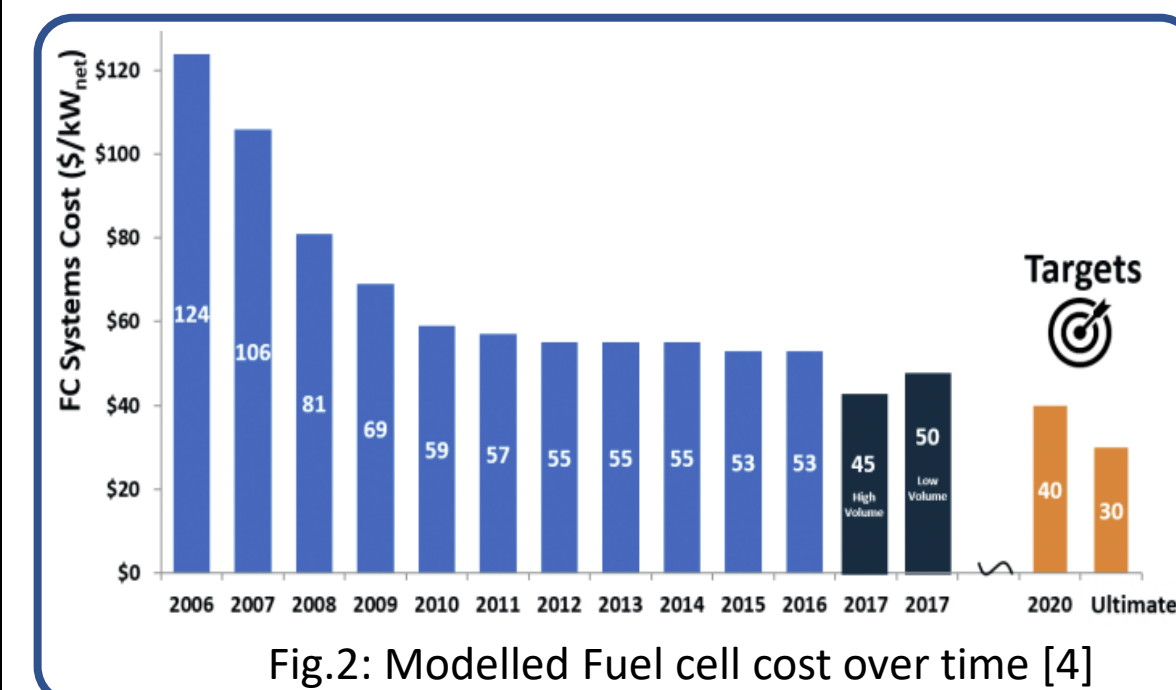
Basic operating principle of PEMFC.

- At the heart of the PEMFC is the membrane electrode assembly (MEA).
 - The MEA is made up of the PEM and the Catalyst Layer (CL) and is sandwiched between two gas diffusion layers (GDL) and two current collectors.
 - The PEMFC during operation follows the basic redox chemistry:
- Anode:** $2H_2 \rightarrow 4H^+ + 4e^-$
- Cathode:** $O_2 + 4e^- + 4H^+ \rightarrow 2H_2O$
- Reaction:** $O_2 + 2H_2 \rightarrow 2H_2O$

Introduction –cont'd

The efficient design and implementation of fuel cell technology have proven in recent times to be of great advantage in the portable, transportation, and stationary sectors.

While incremental advancements have been realized in improving the overall PEM fuel cell performance, there is still a need to:



- Increase the design efficiency.

- Reduce cost to meet up with the US department of energy (DOE) target of \$30/kW by 2035 [4].

Context: The state-of-the-art proton-conducting membranes and ionomers used in PEMFCs are currently based on **perfluorosulfonic acid** polymers such as **Nafion**® Fig 3 [5,6].

Pros

- Very good:
- Proton Conductivity.
- Mechanical stability.
- Chemical stability.

Cons

- Fluorinated feedstock which leads to:
- Complex synthesis
- High gas permeability
- Hazardous synthesis
- High manufacturing cost

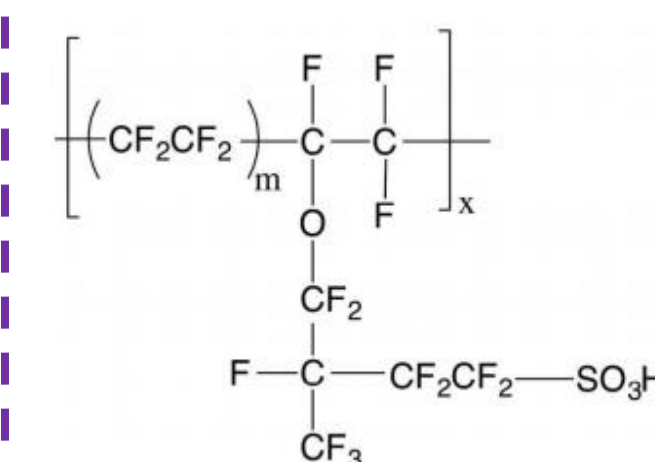


Fig. 3: Structure of perfluorinated (Nafion®) polymer [5].

Hydrocarbon (HC) membranes and ionomers:

Due to the technical difficulties associated with perfluorosulfonic acid polymers, fluorine-free hydrocarbon-based polymers are being considered as substitutes [7-8].

Pros

- Many types of starting materials / monomers.
- Easily finetuned
- Recyclable
- Cheap.
- Environmentally friendly

Cons

- Compared to PFSA polymers
- Lower ionic conductivities
- High oxidative degradation
- Low mechanical stability
- Insoluble in low B.P alcohols
- Low proton conductivity

Objective:

Show a Novel non-fluorous sulfo-phenylated poly(phenylene) sPPB-H⁺ (Fig. 4) HC polymer that is [9,10]:

- Soluble in low B.P alcohols (MeOH).
- Possess all the traditional advantages of hydrocarbon PEMFC.
- Exhibits the excellent conductivity and stability of Perfluorinated PEMFC.

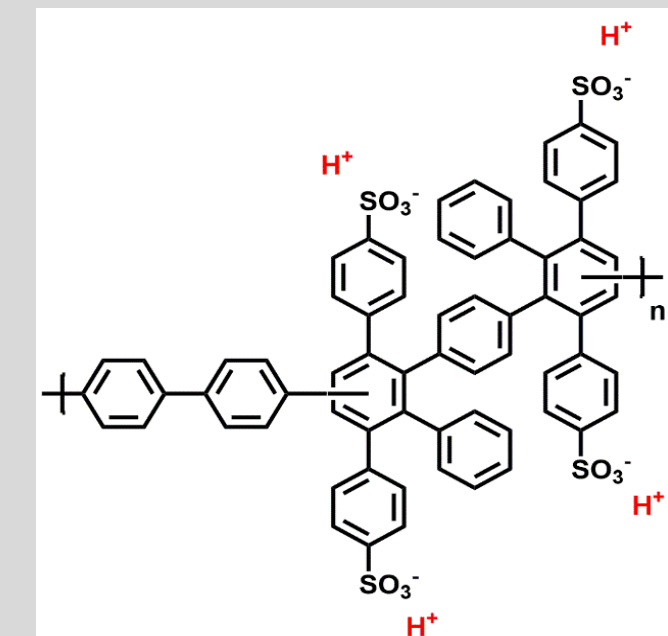


Fig. 4: Structure of sulfo-phenylated poly(phenylene) sPPB-H⁺ polymer [10]

Methodology

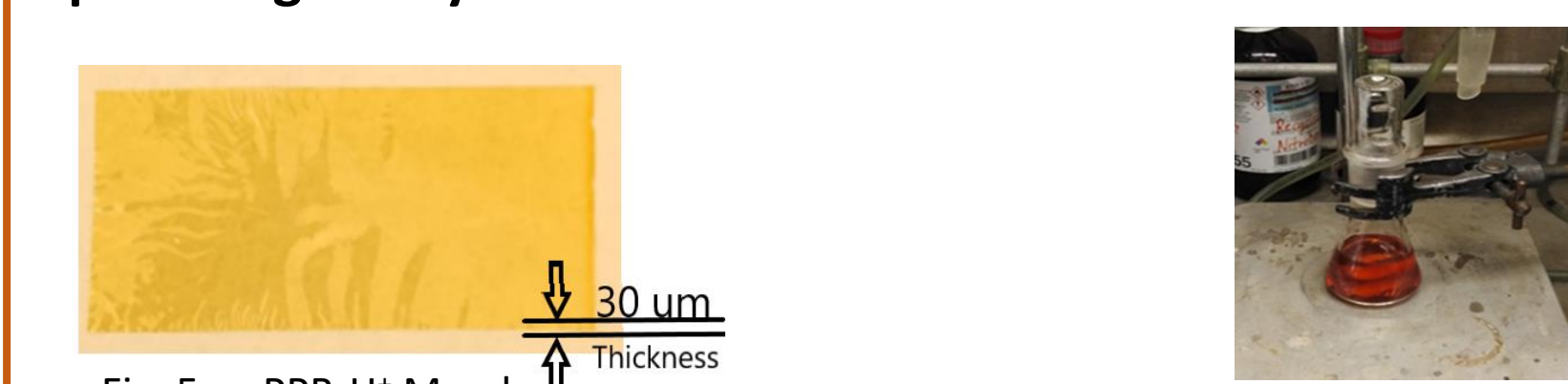
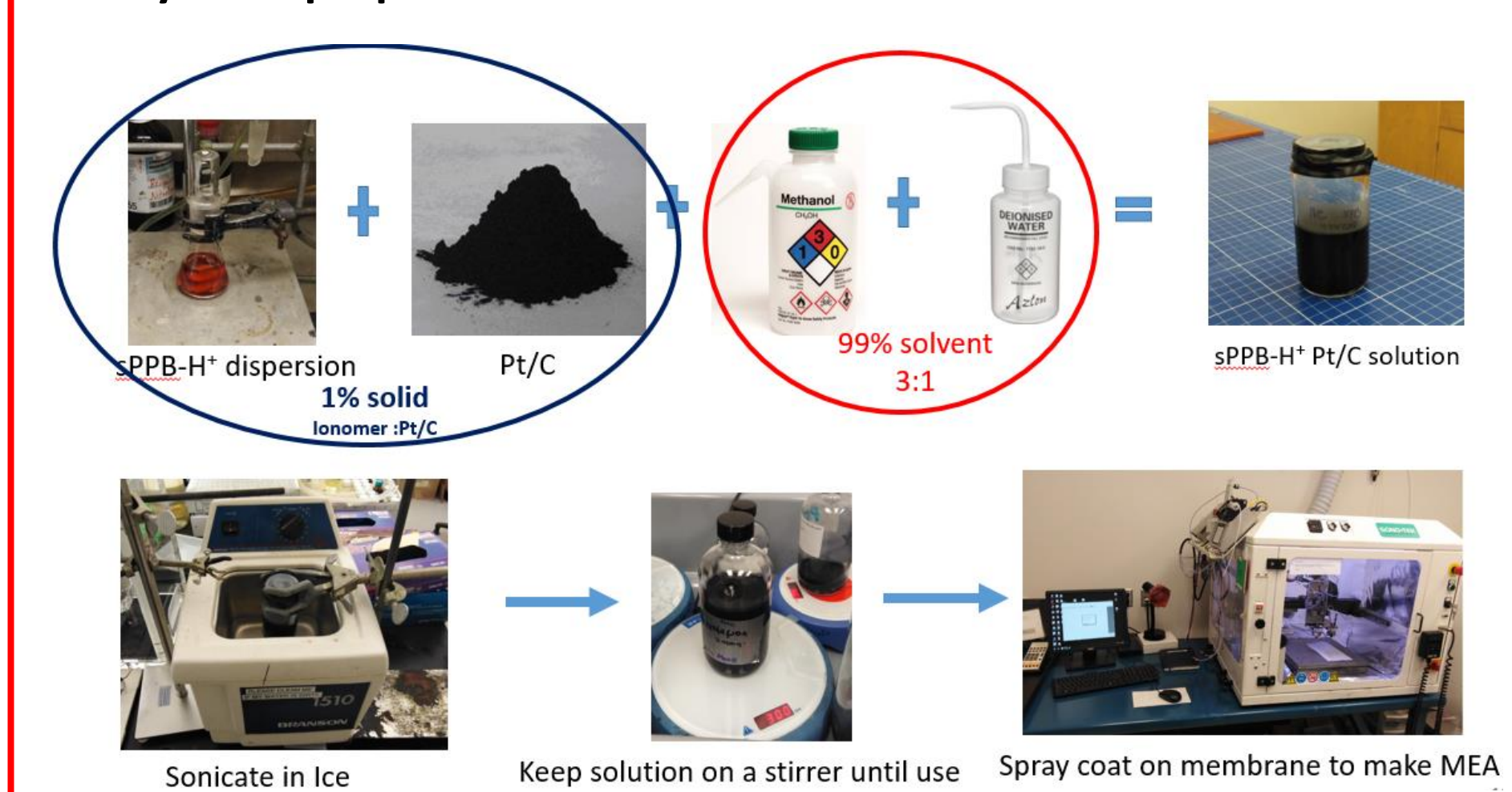
Optimizing a fully sPPB-H⁺ based MEA for PEMFC

Fig. 5a: sPPB-H⁺ Membrane

Fig. 5b: Dissolved sPPB-H⁺ Ionomer in MeOH

- The PEM used is the sPPB-H⁺ with thickness of 30 μm, as shown in Fig. 5a.
- sPPB-H⁺ ionomer is then dissolved in MeOH (5 wt% ionomer) as shown in Fig. 5b and used as binder in the catalyst layer.

Catalyst Ink preparation:



- 99% Solvent (consists of 25% water and 75% MeOH)

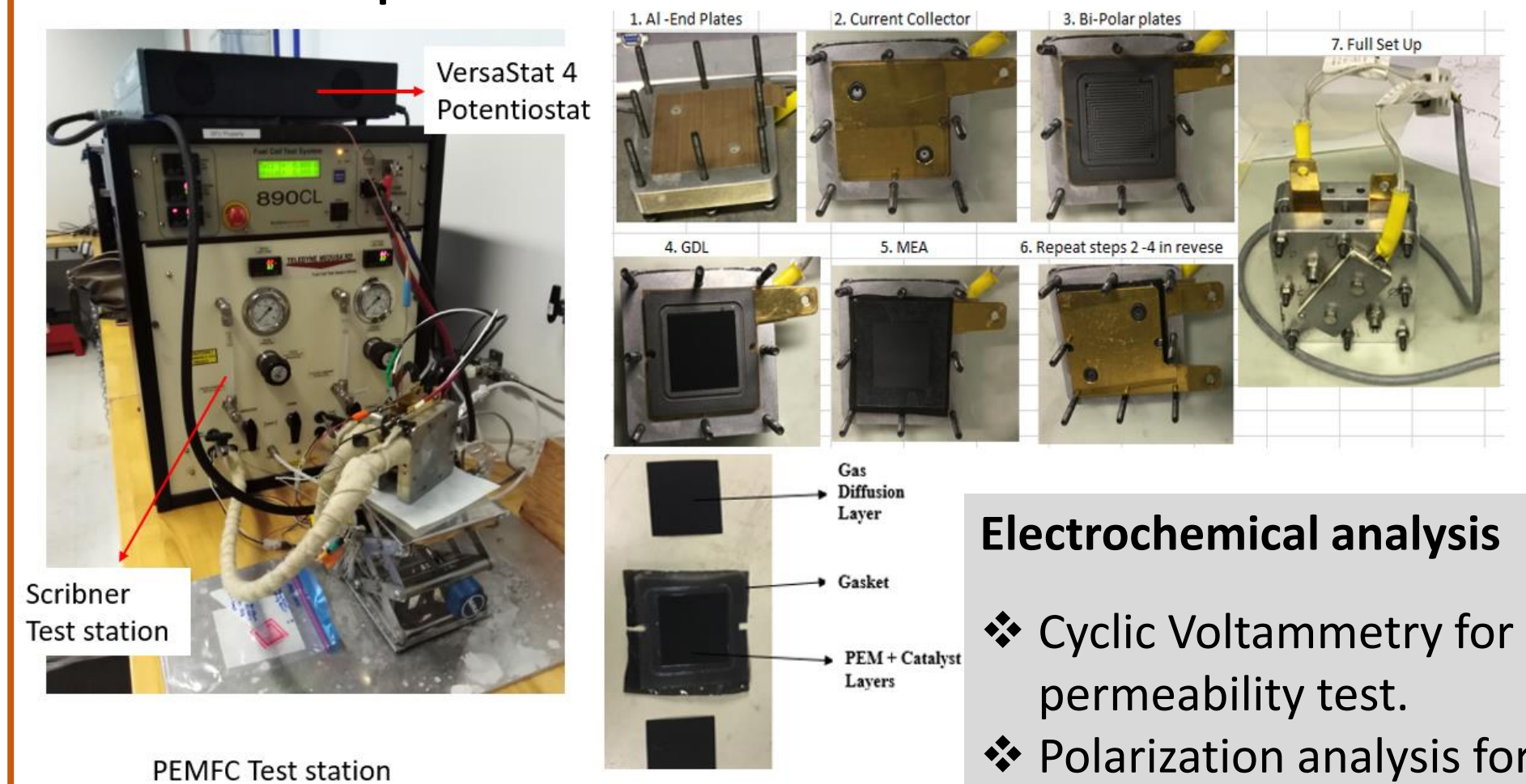
- 1% Solute (Pt/C catalyst + sPPB-H⁺ ionomer**).

**The Pt/C : sPPB-H⁺ ratio is varied to get optimal sPPB-H⁺ content to give peak performance.

Ionomer content within the catalyst layer:

- 30wt.% (Benchmark for PFSA Nafion)¹²
- 20wt.% (Benchmark for HC)¹¹
- 10wt.%
- 15wt.%
- 25wt.%

Hardware set-up

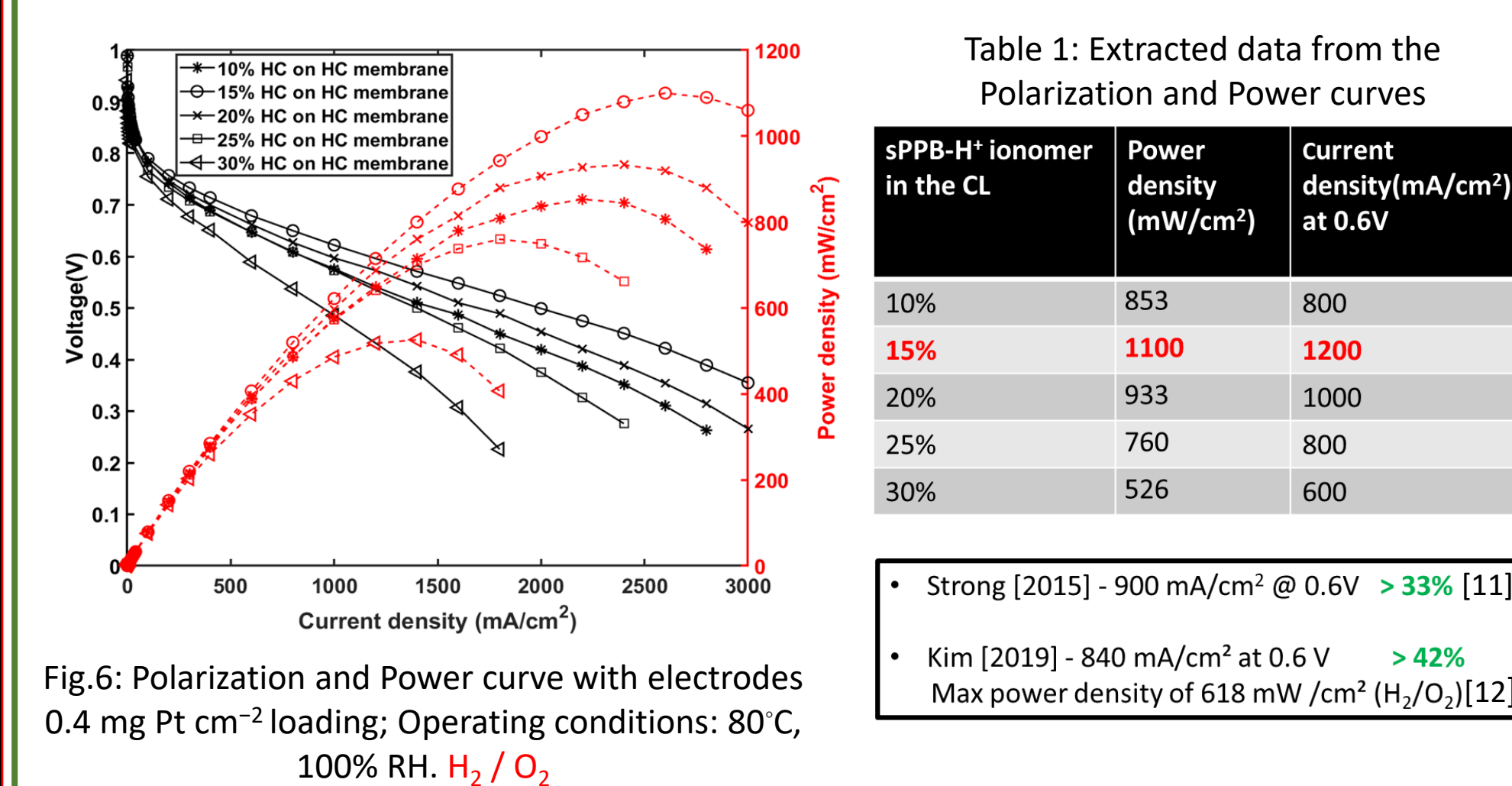


Electrochemical analysis

- Cyclic Voltammetry for gas permeability test.
- Polarization analysis for performance test.
- Electrochemical Impedance spectroscopy (EIS) to quantify losses.
- Cyclic voltammetry to determine the catalyst active surface area.

Results

Performance Analysis.



Electrochemical Impedance Spectroscopy (EIS) Analysis

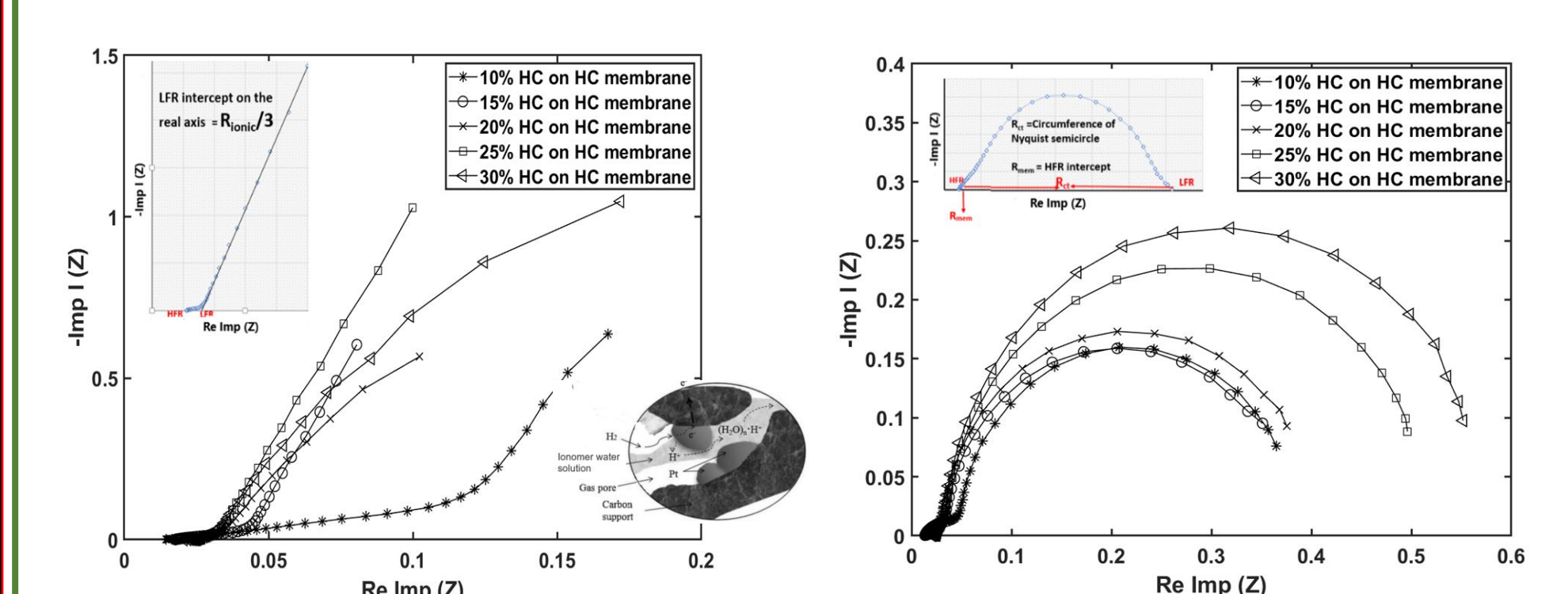


Fig. 7a: Nyquist plot to determine CL ionic resistance. H₂ anode & N₂ cathode, 100% RH, 1 atm.

Fig. 7b: Nyquist plots at 0.8 V to determine charge transfer resistance at 80°C, H₂ anode and O₂ cathode, 100% RH, 1 atm

Table 2: Extracted data from the Polarization and Power curves.

% of ionomer in the CL	Protonic Resistance in the CL, R _{protonic} (Ω)	Charge transfer resistance, R _t (Ω)	ECSA Avg. (m ² /g Pt)
10%	0.3240	0.3640	44.5
15%	0.1248	0.3798	51.8
20%	0.1005	0.4057	49.2
25%	0.0933	0.5027	41.4
30%	0.0608	0.5653	35.2

Fig. 7c: CV scans, electrodes 0.4 mg Pt cm⁻² loading, 50 mV/s

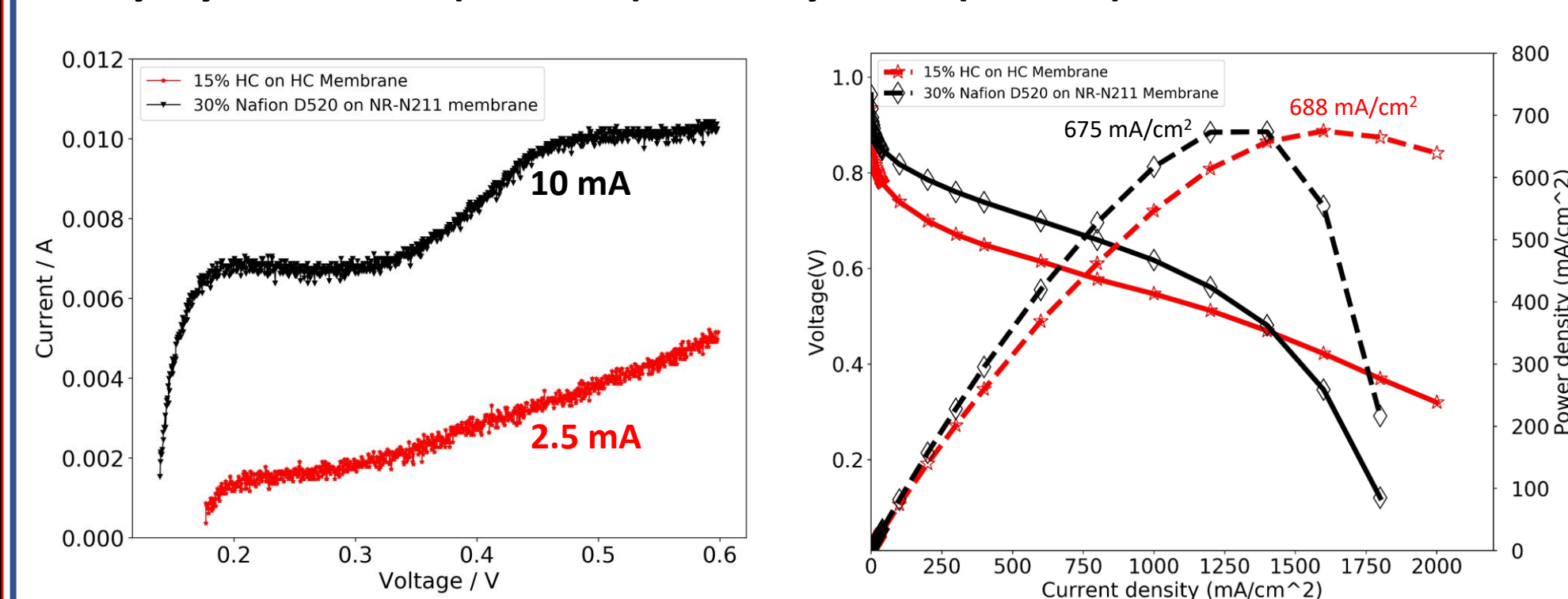
Fully Hydrocarbon (sPPB-H⁺) vs. Fully PFSA (Nafion)

Fig. 8a: LSV scan to determine rate of gas cross-over.

Fig. 8b: Polarization and Power curve with electrodes 0.4 mg Pt cm⁻² loading; Operating conditions: 80°C/100% RH. H₂ / Air

Conclusion

- Cell performance was found to depend significantly on the ionomer loading used in the catalyst layer.
- Peak performance is observed at 15 wt% ionomers in the CL.
- This work describes the first report of fully-HC PEMFC yielding a maximum power density in excess of 1 W cm⁻².
- Compared to earlier reported fully HC based PEMFC, the sPPB-H⁺ HC PEMFC shows a 25% increase in peak power density.
- It is believed that a way to improve the sPPB-H⁺ FC performance is by improving the ionic transfer resistance at the catalyst layers.
- The sPPB-H⁺ FC shows slightly higher peak performance compared to state-of-the-art Nafion under air operation.

Future Work

- Reducing CL ionic resistance of the sPPB-H⁺ HC based PEMFC.
- Determine the effect of phenyl adsorption of the sPPB-H⁺ HC polymers have on platinum catalysts, and by extension on the PEMFC performance and durability.
- Durability study of the sPPB-H⁺ based PEMFC.

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Acknowledgement

