Carbon Nitride–Polymer Nanocomposite Anion-Exchange Membranes

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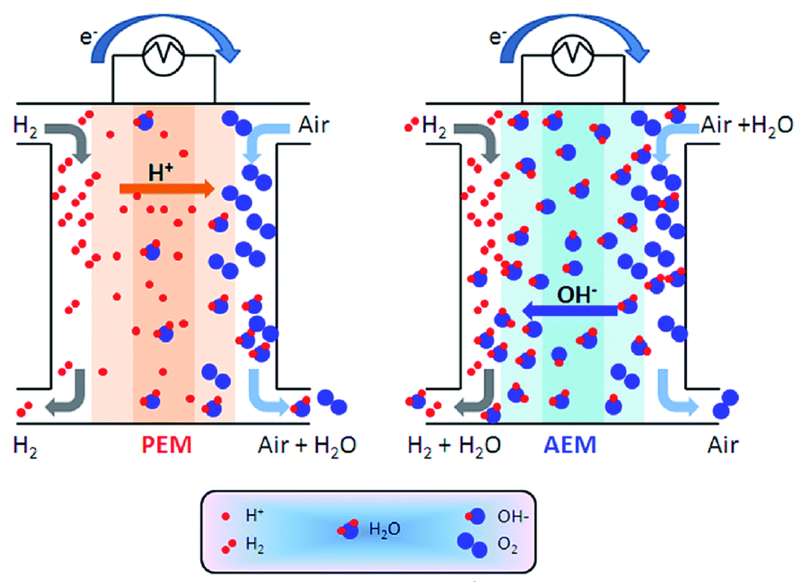
INTRODUCTION

- Fuel cells generate electricity by chemical reactions.
- Anion exchange membrane fuel cells (AEMFC's) do not require the use of precious metals.
- This work proposes the fabrication of novel polymeric membranes to overcome some limitations of the existing AEMs, such as their low OH^- conductivity and poor chemical stability in KOH.



Source: Varcoe *et.al.*

PEM: Proton-exchange membrane

AEM: Anion-exchange membrane

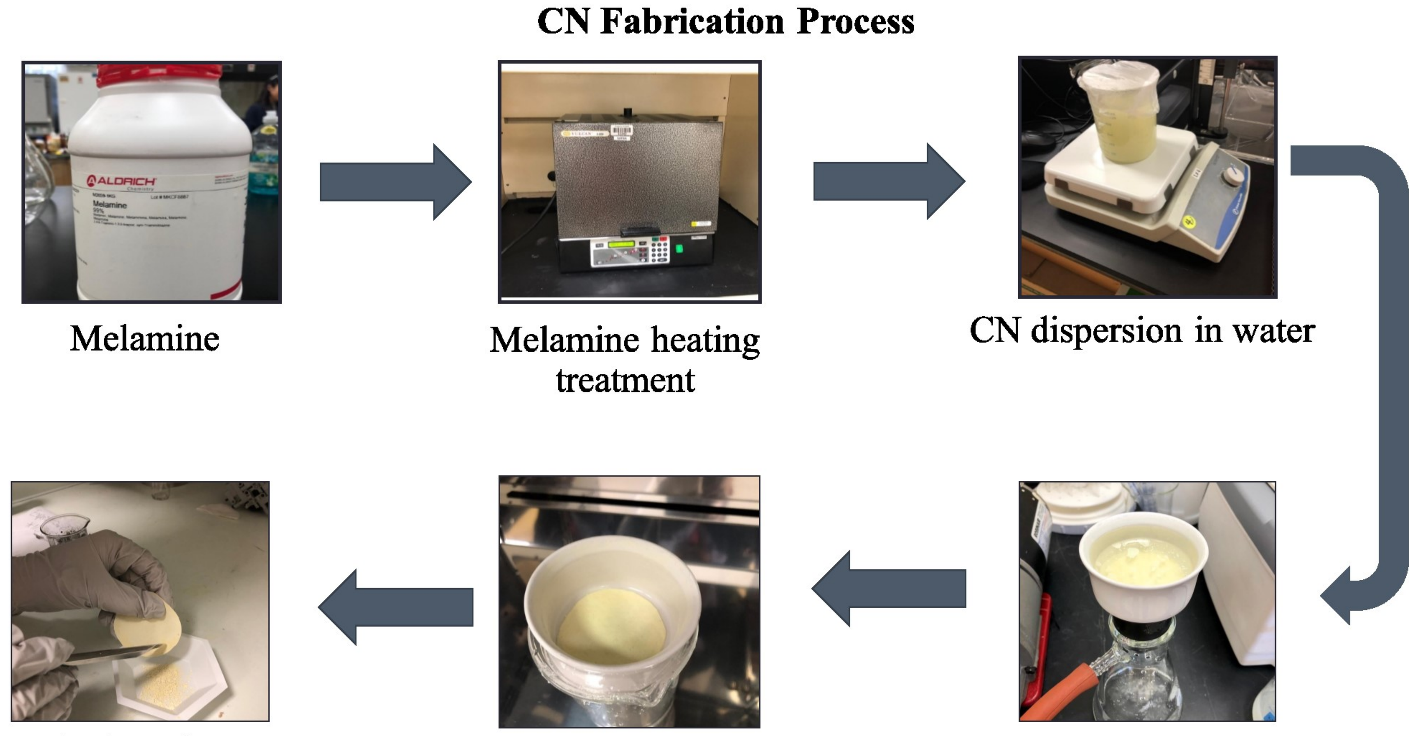
OBJECTIVES

The goal of this research project is to fabricate nanocomposite AEMs with enhanced OH^- conductivity and chemical stability. In order to accomplish this goal is it necessary to:

1. Establish the optimal conditions to fabricate the nanocomposite membranes.
2. Study the effect of carbon nitride (CN) content, temperature, relative humidity, and KOH soaking time on the OH^- conductivity of the fabricated membranes.

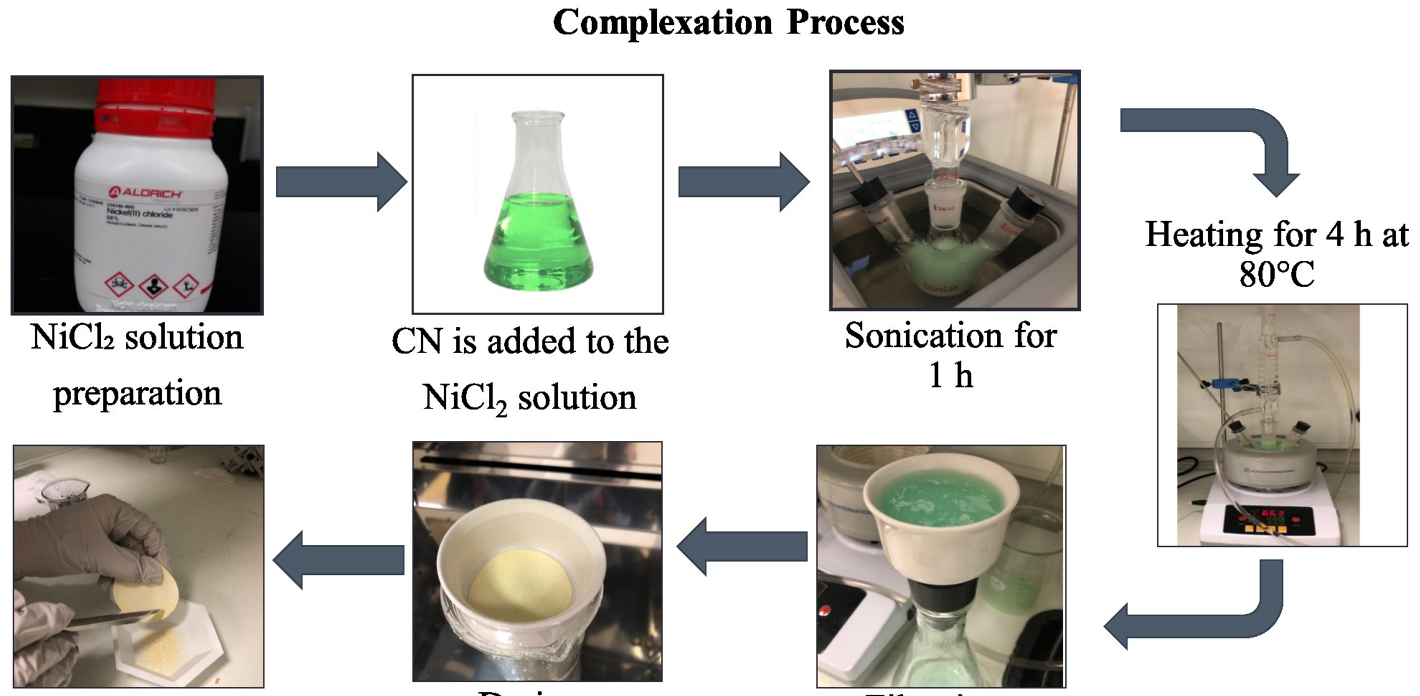
METHODOLOGY

CN Fabrication Process



Melamine → Melamine heating treatment → CN dispersion in water → Filtration → Drying at 60°C → Final product

Complexation Process

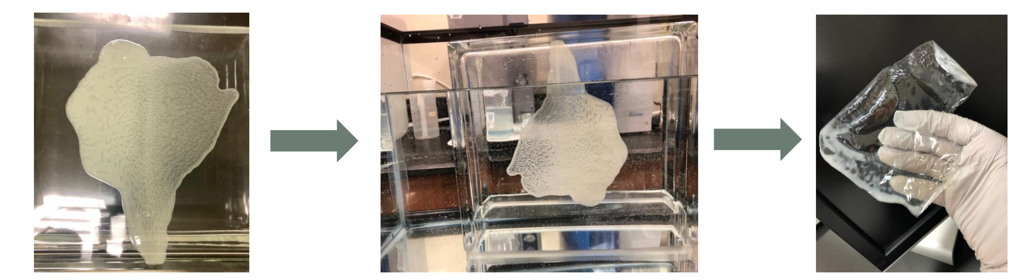


$NiCl_2$ solution preparation → CN is added to the $NiCl_2$ solution → Sonication for 1 h → Heating for 4 h at 80°C → Filtration → Drying → Final Product

CN Characterization Techniques

Technique	Analysis
Raman, FTIR, UV-vis	Chemical
Fluorescence & Tyndall Effect	Qualitative
AFM	Size & Shape

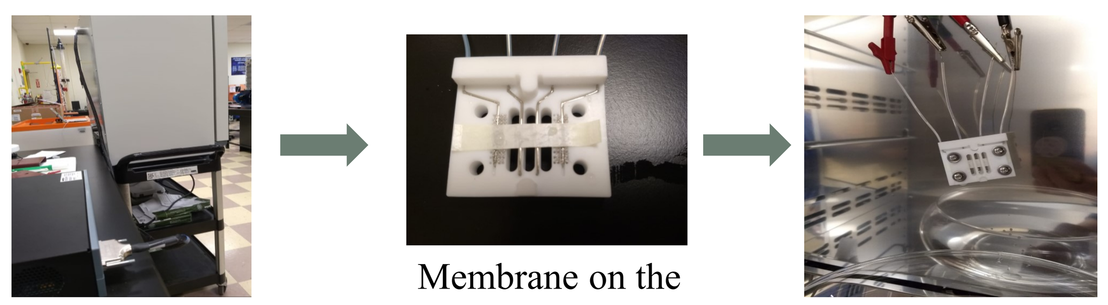
Membrane Fabrication



Solvent casting → Membrane detachment → Dry Membrane

Membrane Characterization

Electrochemical Impedance Spectroscopy (EIS)

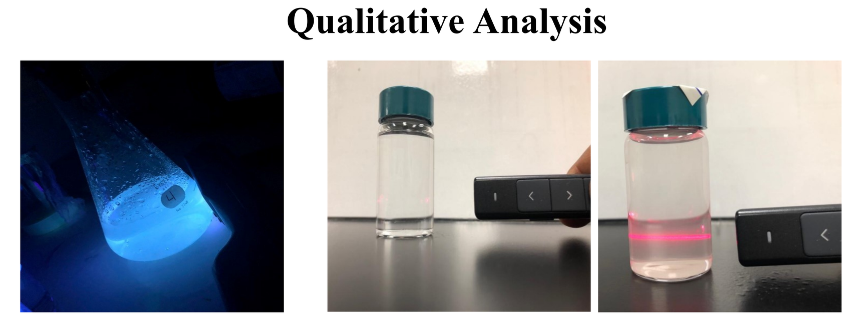


Chamber → Membrane on the cell → Potentiostat Connections

Experiments performed in a frequency range between 25,000 - 0.1 Hz at different temperatures and 100 RH%

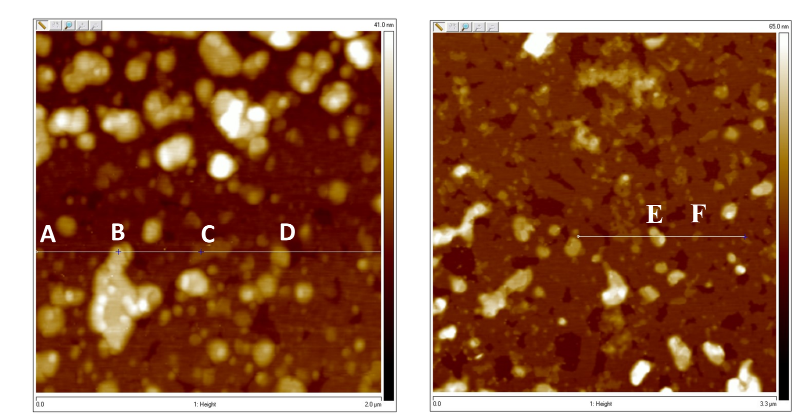
RESULTS

Physical Characterization of CN: Qualitative Analysis

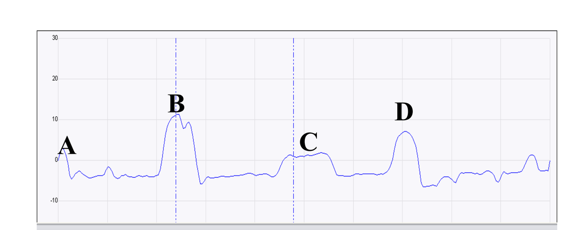


Fluorescence | Tyndall Effect

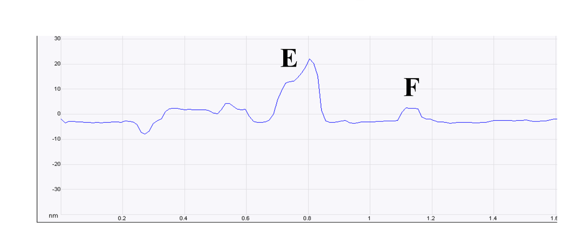
Physical Characterization of CN: AFM



CN Nanosheets Sample 1 | CN Nanosheets Sample 2

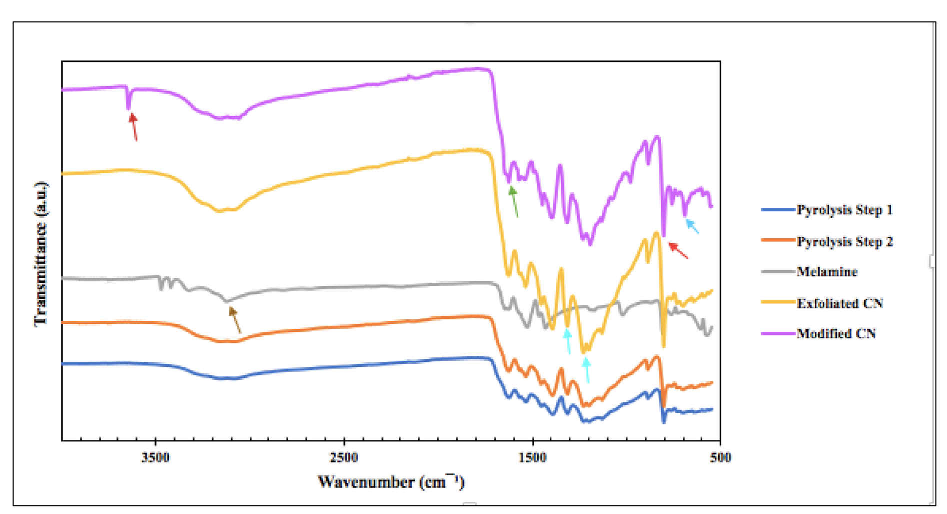


Profile: Sample 1

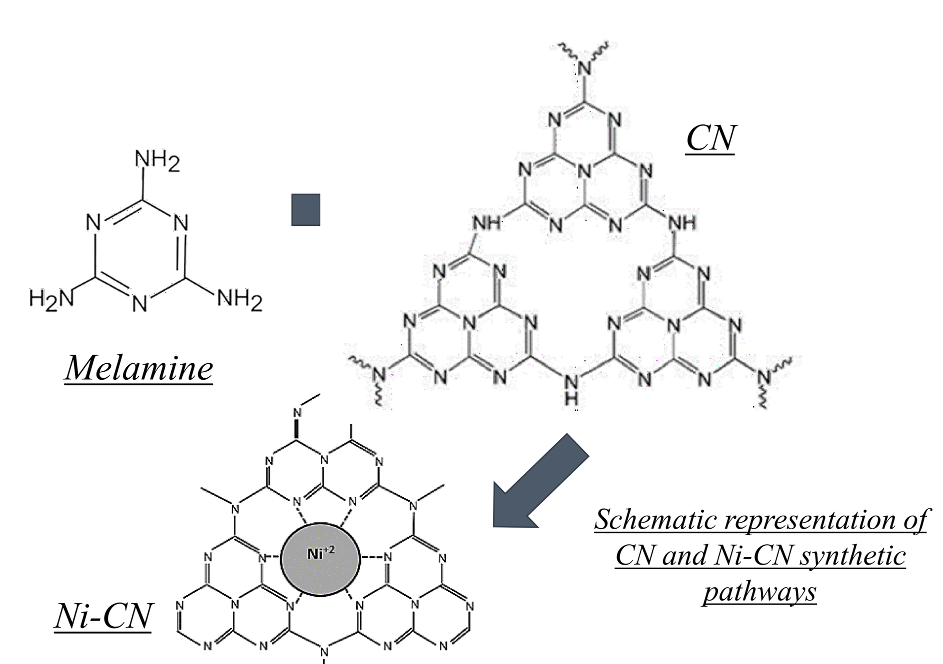


Profile: Sample 2

Chemical Characterization of CN & Ni-CN: FTIR

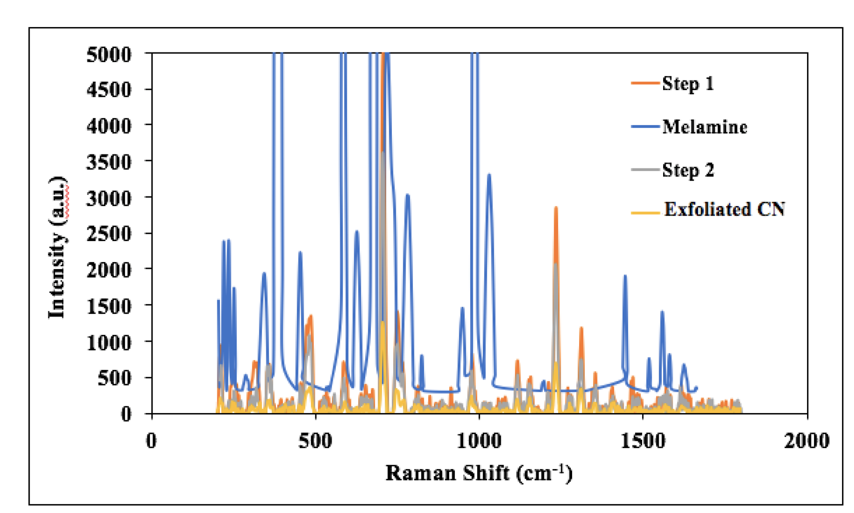


Wavenumber (cm^{-1})	Description
800	heterocycles
1228 1315	tertiary amines
1625	vibration of C=N bonds
3111	amino functional groups
3645	presence of impurities
690	Cl-C stretching
500- 600	Ni-N bond



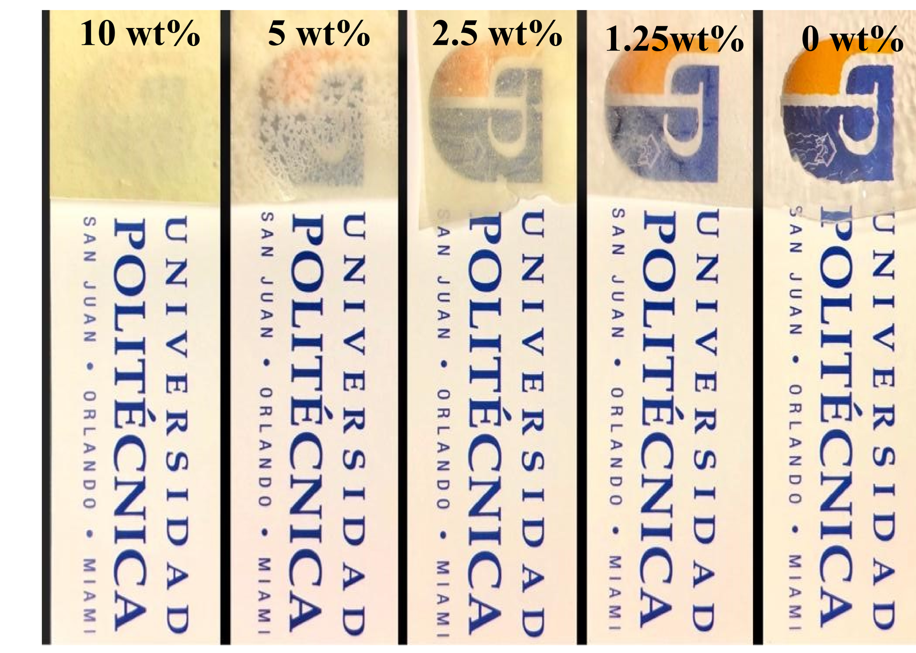
Schematic representation of CN and Ni-CN synthetic pathways

Chemical Characterization of CN: Raman

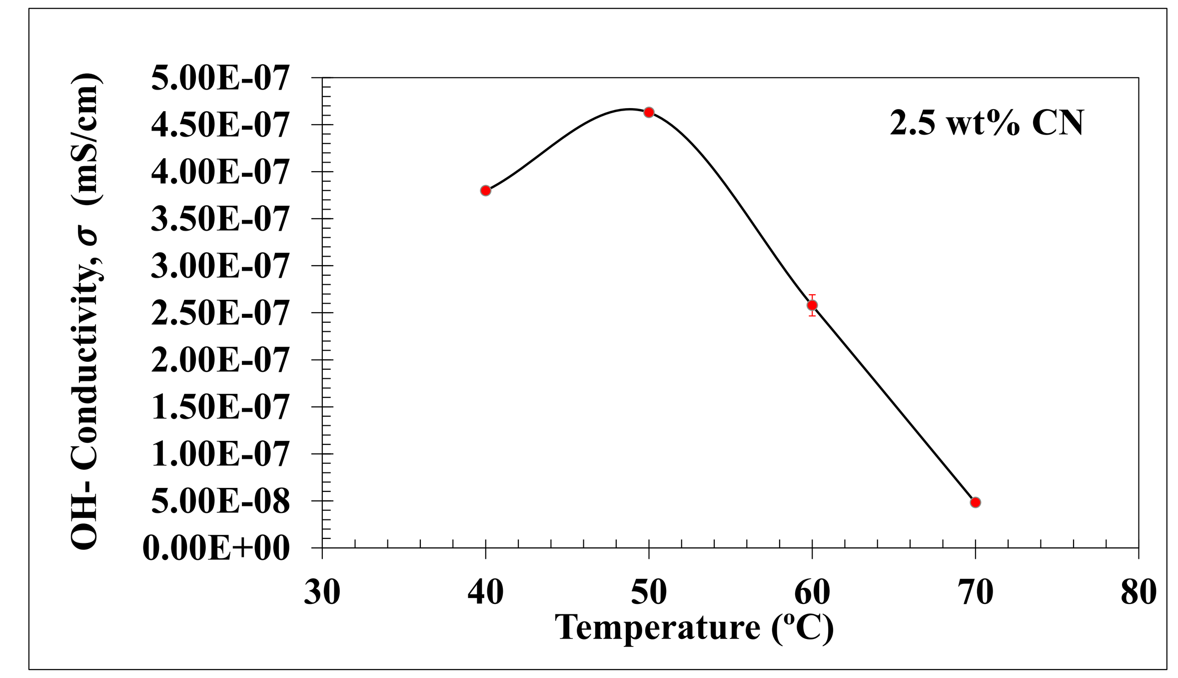


Raman Shift (cm^{-1})	Description
1200-1700	C–N stretching vibrations
980	triazine rings
690	s-triazine and melamine

Fabricated Membranes



OH^- Conductivity of the Fabricated Membranes



CONCLUSIONS

- The membranes were successfully fabricated with different CN wt%. All the membranes exhibited excellent mechanical properties at high temperatures (~ 90ºC).
- For the membrane with a CN content of 2.5 wt%, the maximum conductivity reached was 4.63x 10^{-7} mS/cm (at 50ºC). At higher temperatures, the membrane dries up and loses ionic conductivity.

FUTURE WORK

- Improve the membrane hydration system
- Characterize the rest of CN nanocomposite membranes
- Fabricate and characterize the Ni-CN nanocomposite membranes

ACKNOWLEDGMENTS

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References

Varcoe, J., Atanassov, P., Dekel, D., Herring, A., Hickner, M., Kohl, P., Kucernak, A., Mustain, W., Nijmeijer, K., Scott, K., Xuk, T., Zhuangl, L., Anion-exchange membranes in electrochemical energy systems. Energy and Environmental Science, 7, 3135-3191 (2014)

Movil, O. Frank, L., Staser, J., (2016) Graphene Oxide–Polymer Nanocomposite Anion-Exchange Membranes. Journal of The Electrochemical Society, 162 (4) F419-F426 (2015)

Xiao, K., Giusto, P., Wen, L., Jiang, L., & Antonietti, M. (2018). Nanofluidic Ion Transport and Energy Conversion through Ultrathin Free-Standing Polymeric Carbon Nitride Membranes. *Angewandte Chemie - International Edition*, *57*(32), 10123–10126.

Zhenxing , Z., Kexin, L., Liushui , Y., Yuhua , D., Huigin, G., Mignxin, H., & Yihang, G., Fabrication of carbon nirtride nanotubes by a simple water-induced morphological transformation process and their efficient visible-light photocatalytic activity. RSC Advances, 59513-59518 (2014)

Zhu, J., Xiao, P., Li, H., and Carabineiro, S. (2014) Graphitic Carbon Nitride: Synthesis, Properties, and Applications in Catalysis ACS Applied Materials & Interfaces 6 (19), 16449-16465 (2014)