

Grafted Materials as Membranes and Adsorbents

“Effects of gamma radiation absorbed dose on VBC grafting onto LDPE films and on anion exchange membrane fuel cells performance”

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2nd International Conference on
Applications of Radiation
Science and Technology

#ICARST2022

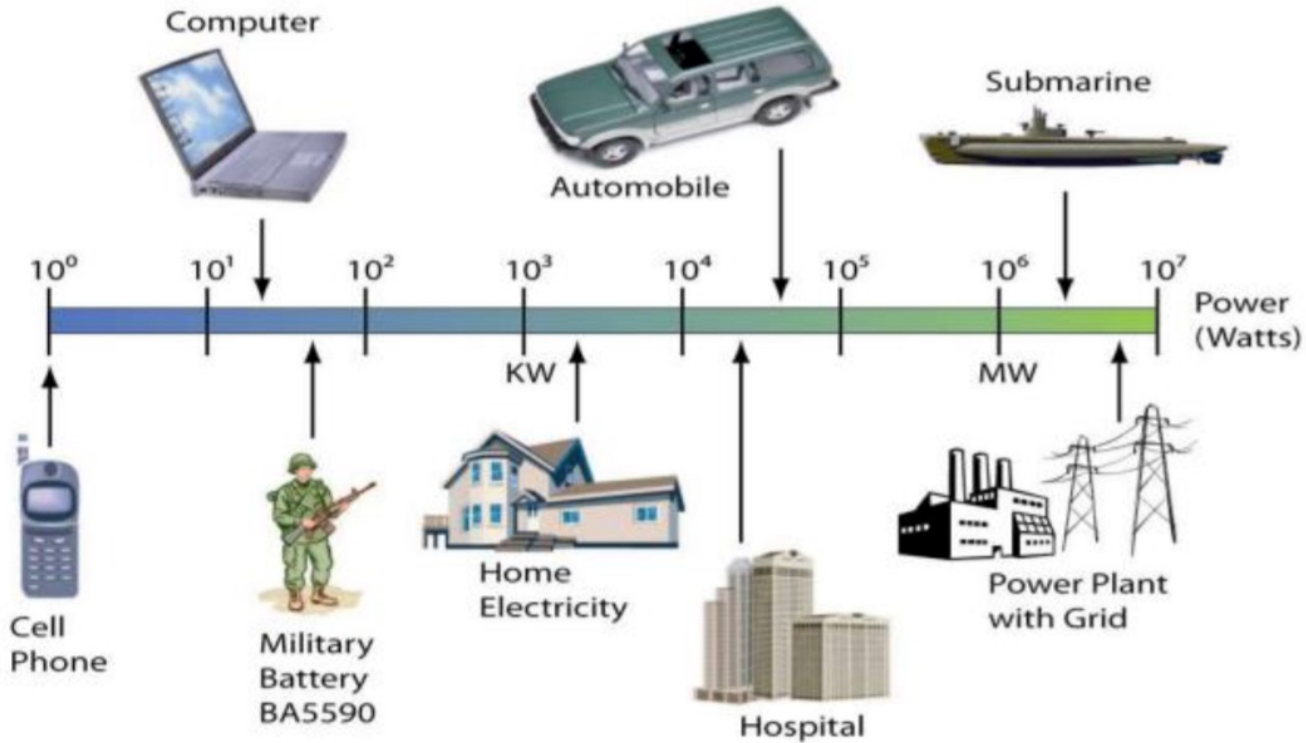
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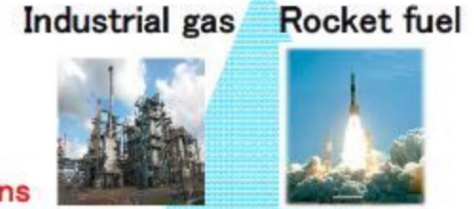
Introduction

Fuel Cell Power Spectrum



Previously

Industrial gas and specialty applications



Currently

Full-scale energy usage



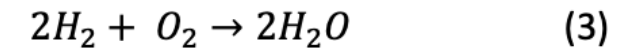
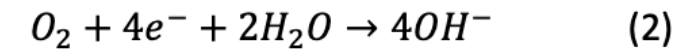
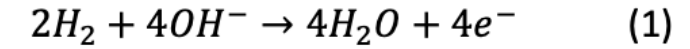
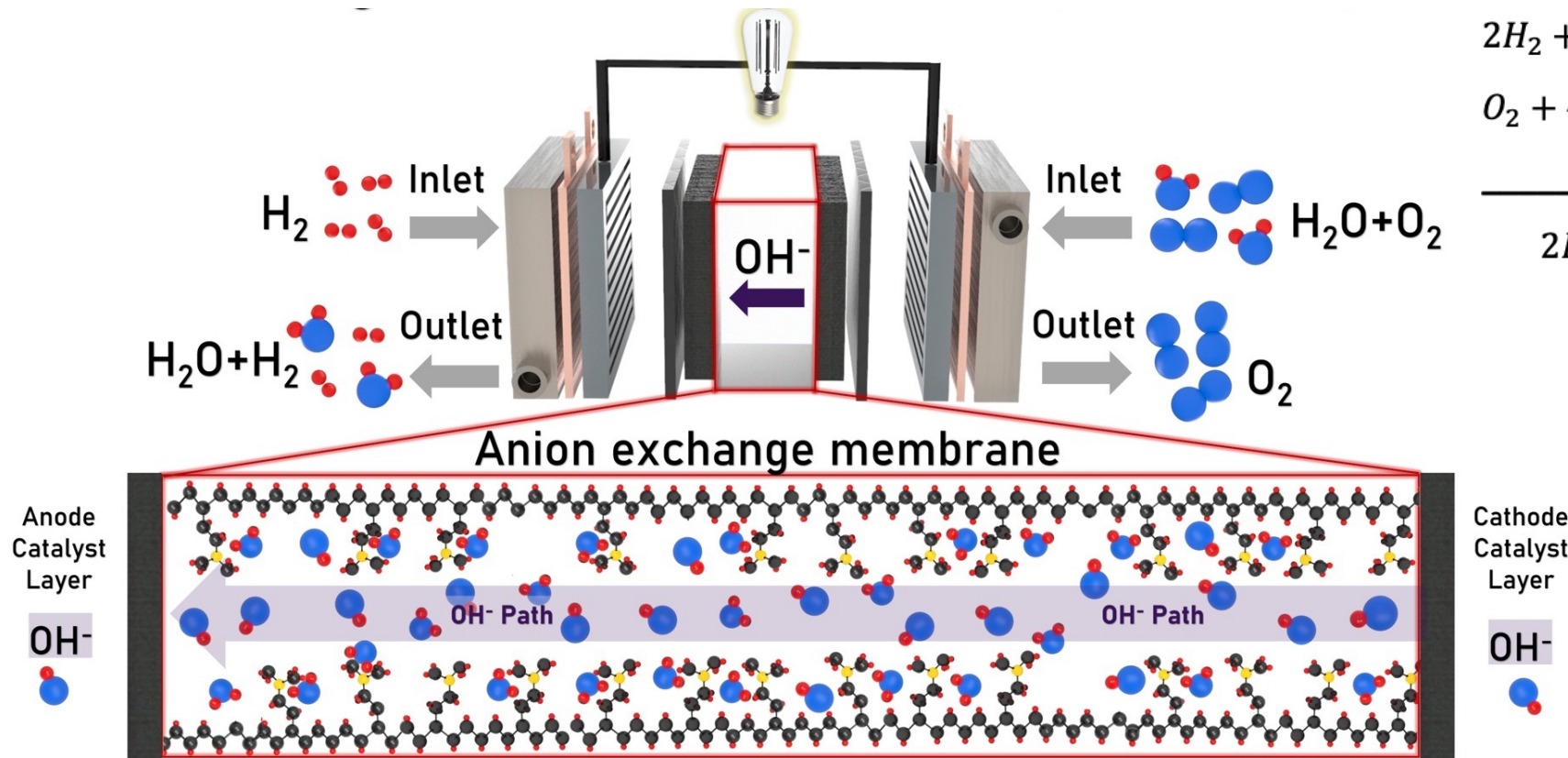
Future

Diverse applications



Source: Agency for Natural Resources and Energy

Anion Exchange Membrane Fuel Cell (AEMFCs)



PtRu/C 40 wt% Pt and 20 wt% Ru

Pt/C, 40 wt% Pt

<https://www.mdpi.com/2073-4360/14/6/1197>

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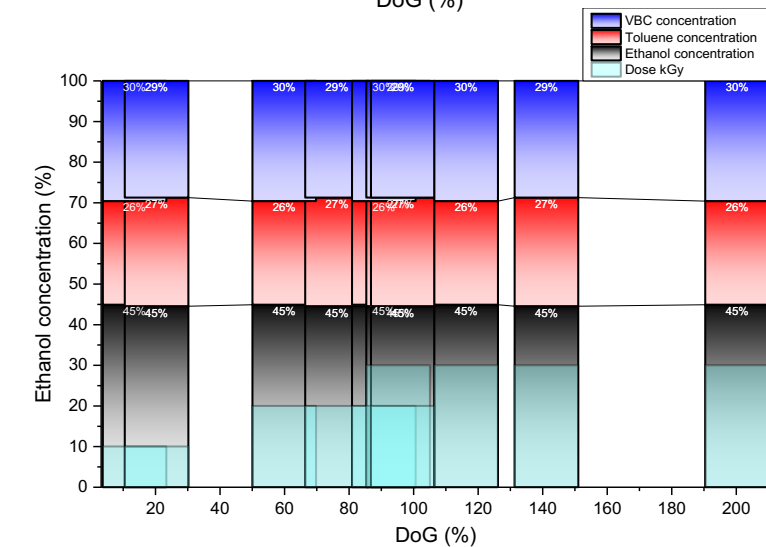
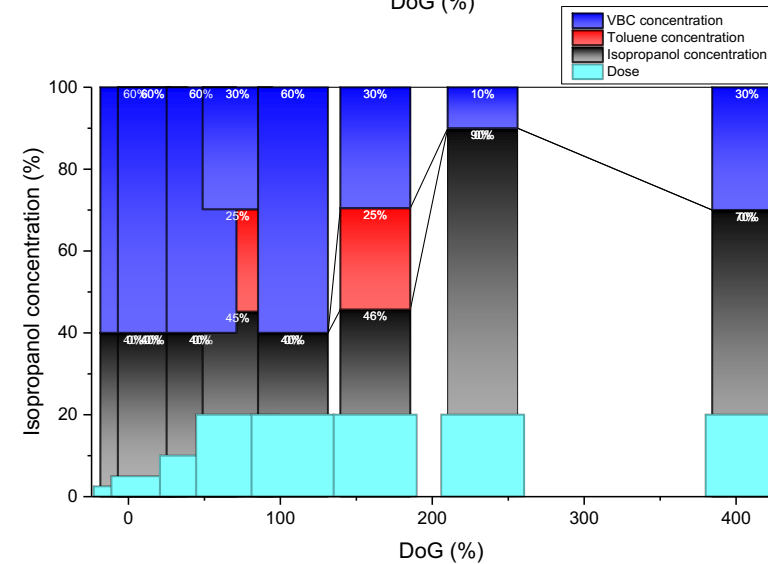
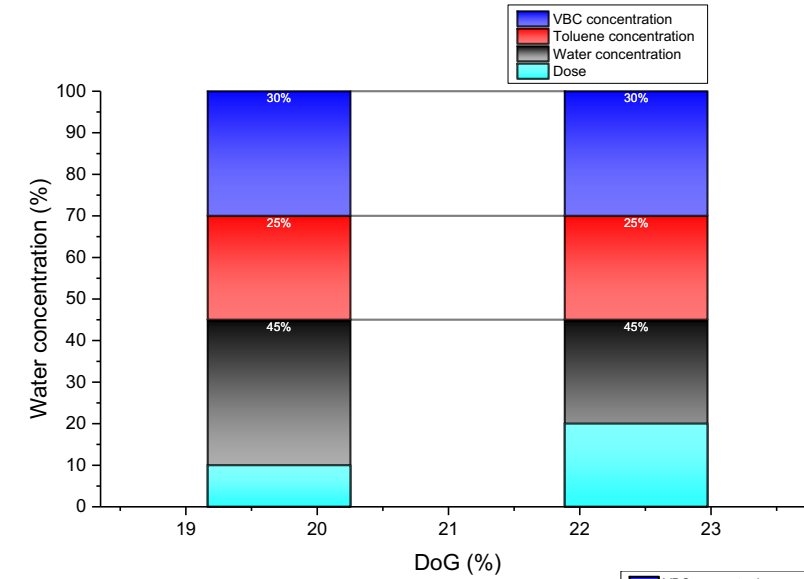
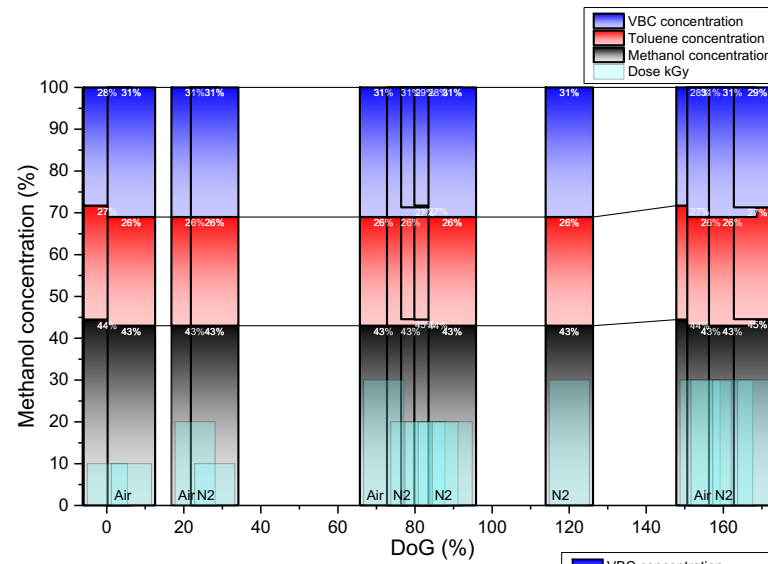
Radiation Induced Grafting - RIG



Radiation absorbed doses (0-30kGy)

Dose rate $\sim 0.5 \text{ kGy}^{-1}\text{h}^{-1}$

LDPE-g-poly VBC

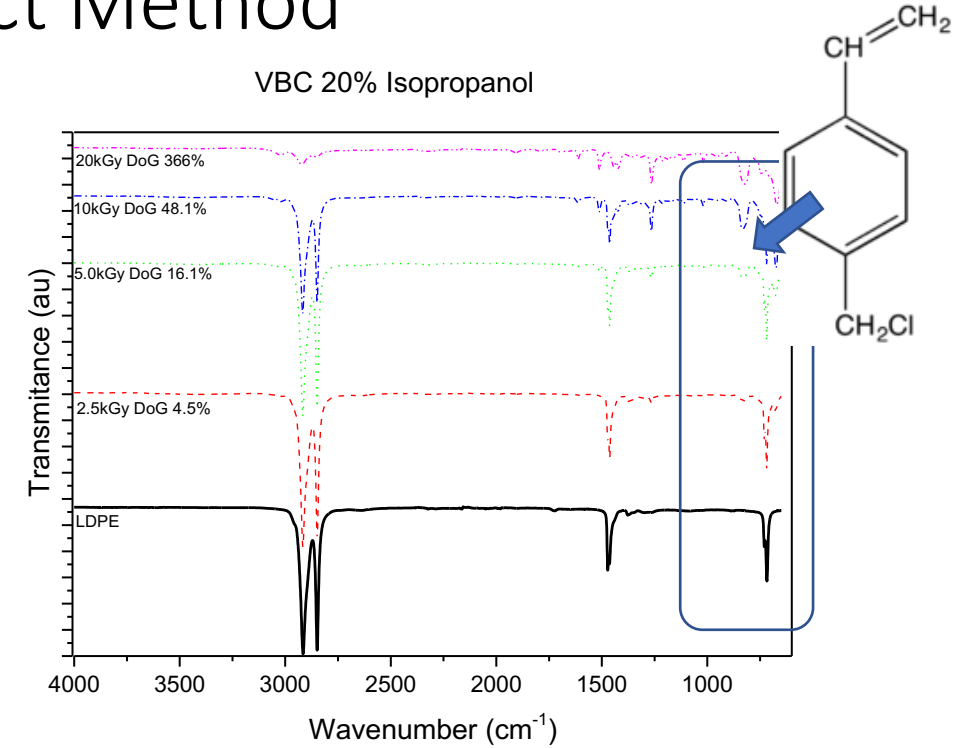
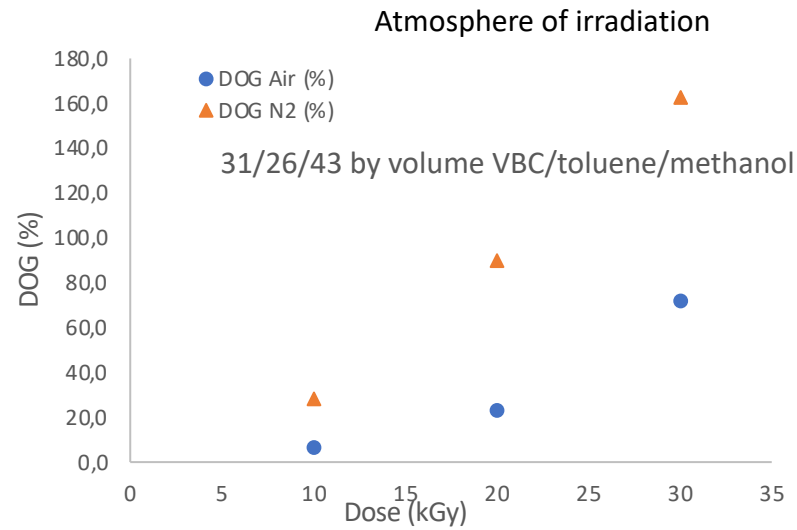


LDPE Radiation Induced Grafting by Direct Method

Gammacell 220



previously



RIG membranes by direct method in ternary mixture: 4-VBC, toluene and alcohol at 20kGy radiation absorbed dose, dos rate $\sim 0.5 \text{ kGy h}^{-1}$.

Solvent	DoG (%)	WU (%)	IEC
Isopropanol	94	53	2,45
Ethanol	76	42	2,26
Methanol	83	36	2,14

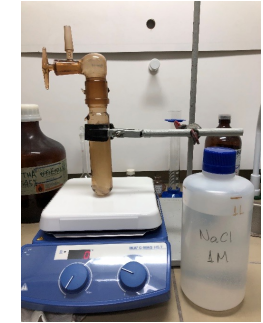
Radiation Induced Grafting - RIG



Radiation absorbed doses (10-30kGy)
Dose rate $\sim 0.5 \text{ kGy}^{-1}\text{h}^{-1}$

4-VBC. N₂ purge
VBC:Toluene:Methanol v:v:v
(31:26:43)

R. Espiritu, M. Mamlouk, K. Scott, Int. J. Hydrogen Energy
41 (2) (2016) 1120–1133, <https://doi.org/10.1016/j.ijhydene.2015.10.108>.

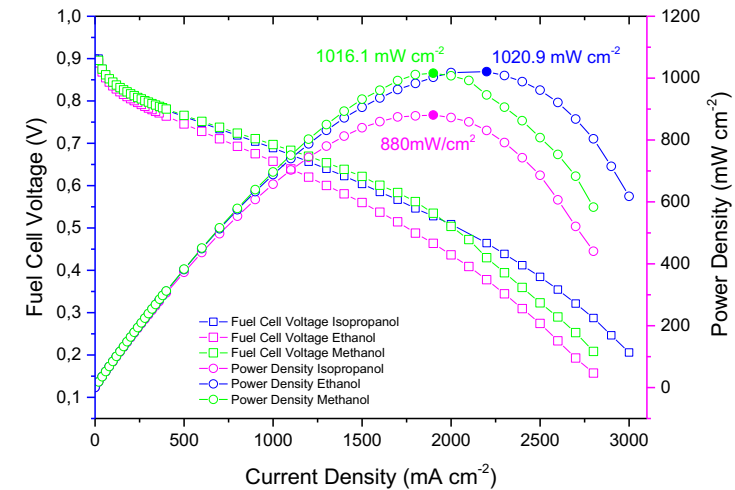
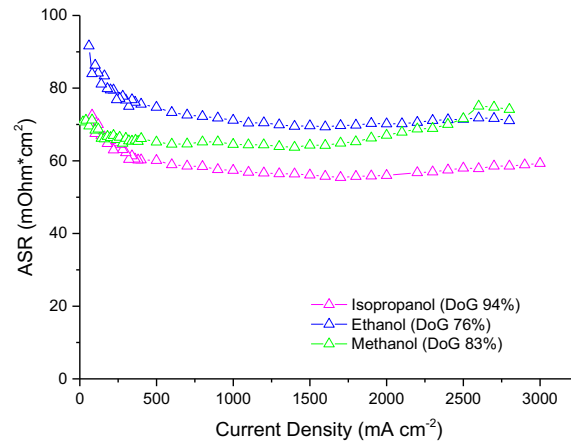
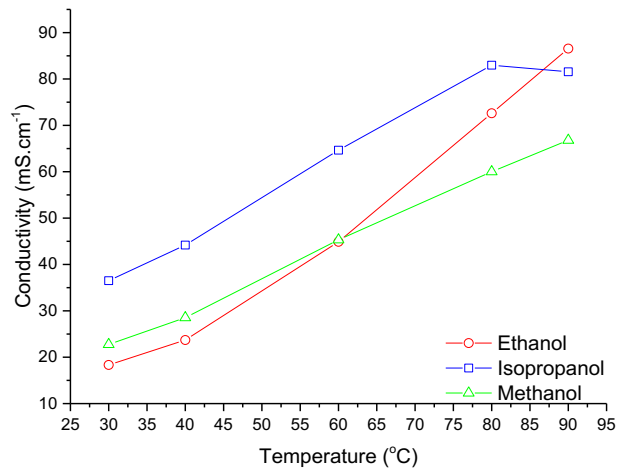
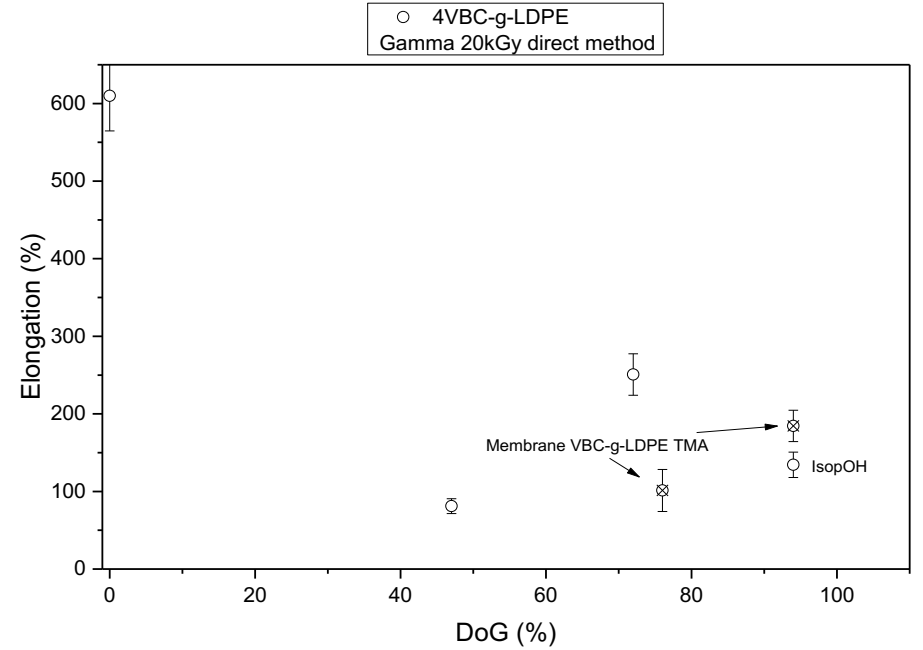
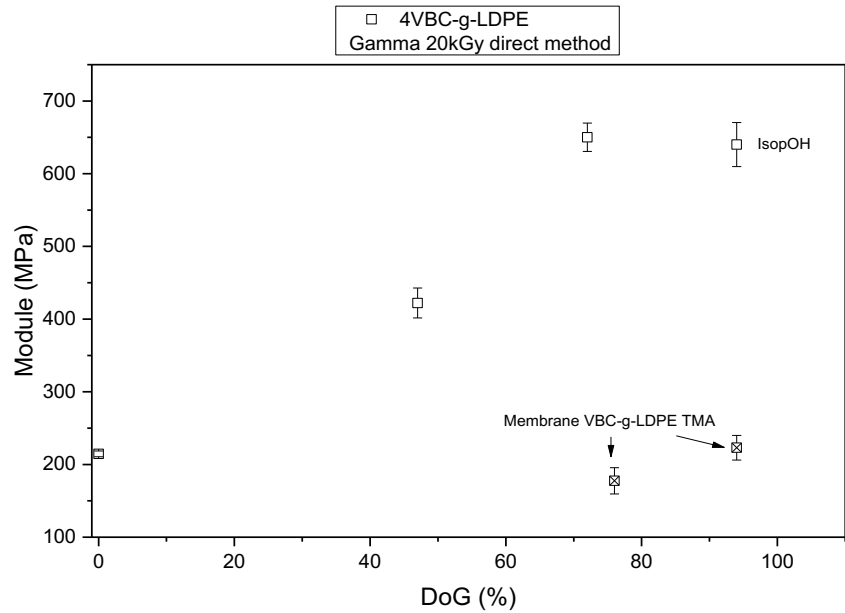


Treatment with NaCl for Cl-groups addition was performed, responsible for ionic exchange and ionic groups stabilization.

The optimization of parameters and conditions of irradiation have been evaluated by degree of grafting. Functionalization with quaternary ammonium groups was made in water by using trimethylamine (TMA).

LDPE Radiation Induced Grafting by Direct Method

Gammacell 220



ELECTROCHEMICAL PROPERTIES



Catalytic Electrodes

hydration number

$$\lambda = \frac{WU}{IEC (mol\ g^{-1}) \cdot M_{H_2O} (g\ mol^{-1})}$$

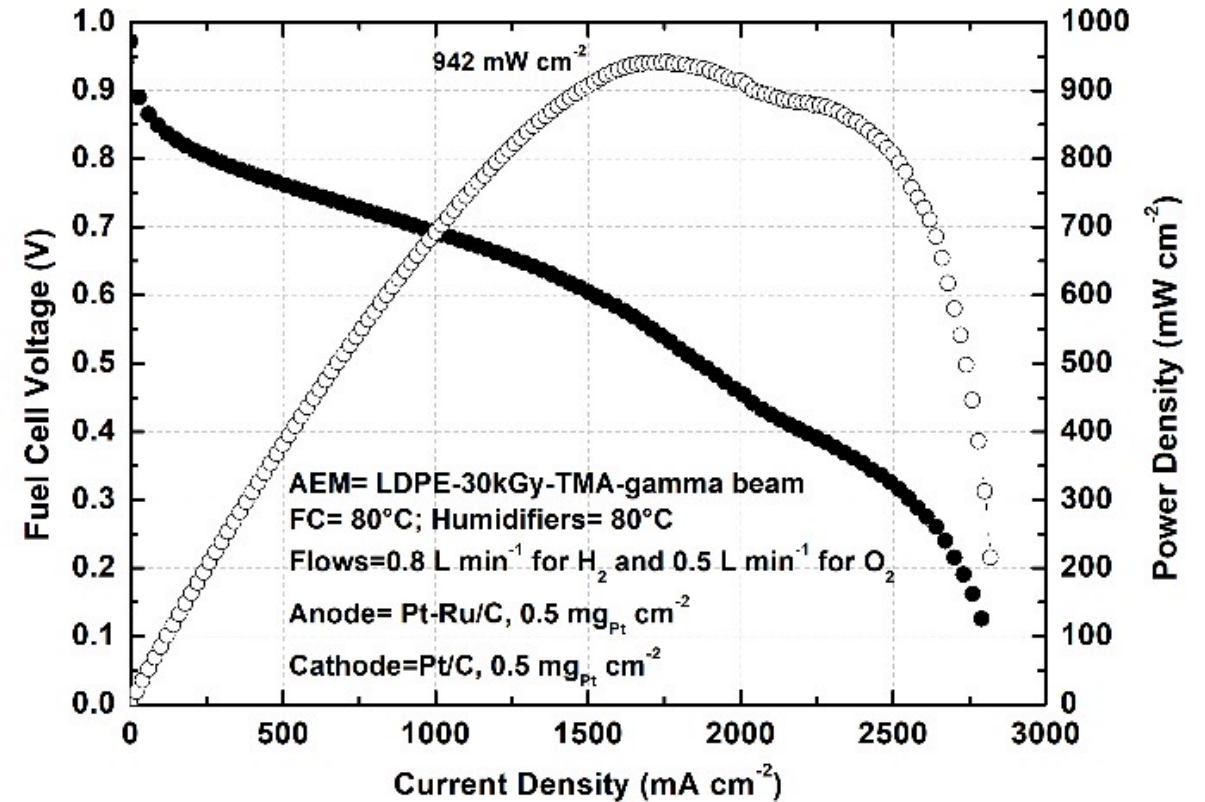
Scribner Assoc. 850C fuel cell test station
 - anode was fed with pure H₂ (99.999%), flow of 0.8 L min⁻¹
 - cathode with pure O₂ (99.998%), flow of 0.5 L min⁻¹
 - 80 °C during all experiments
 - optimal temperatures for humidifiers for this AEM (range of 77–80 °C) at ambient pressure.

Ionic conductivity (σ) of AEMs in Cl⁻ form by a frequency response analyzer (Solartron 1260)
 - frequency range of 0.1 Hz–10 MHz
 - a.c. amplitude of 100 mV.
 - Samples with 1 × 4 cm² area in a 4-probe commercial sample holder (FuelCon[®] TrueXessory-PCM) with an external temperature controller

$$\sigma = \frac{d}{R \times w \times t}$$

Fuel Cell dynamic test preliminary

AEM synthesized by RIG of VBC onto LDPE with 30 kGy radiation absorbed was tested in a fuel cell and reached a maximum power density of 942 mW cm^{-2} at 80°C with gases flow of 0.8 L min^{-1} and 0.5 L min^{-1} for H_2 and O_2 , respectively.



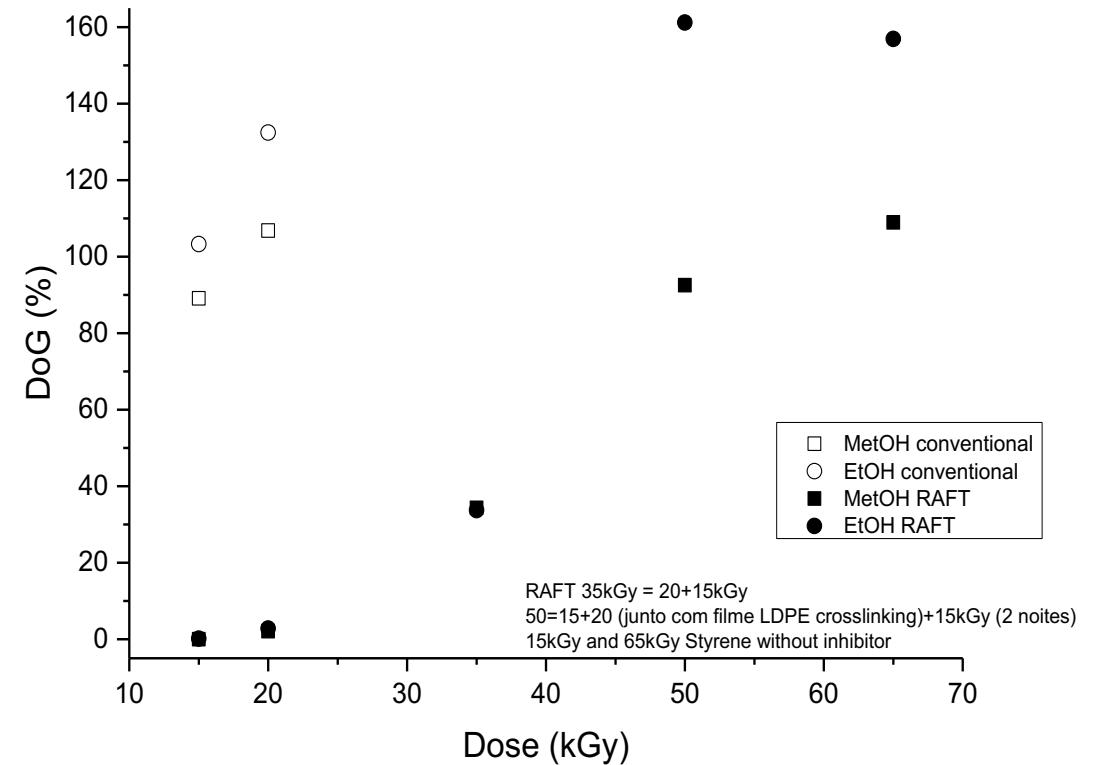
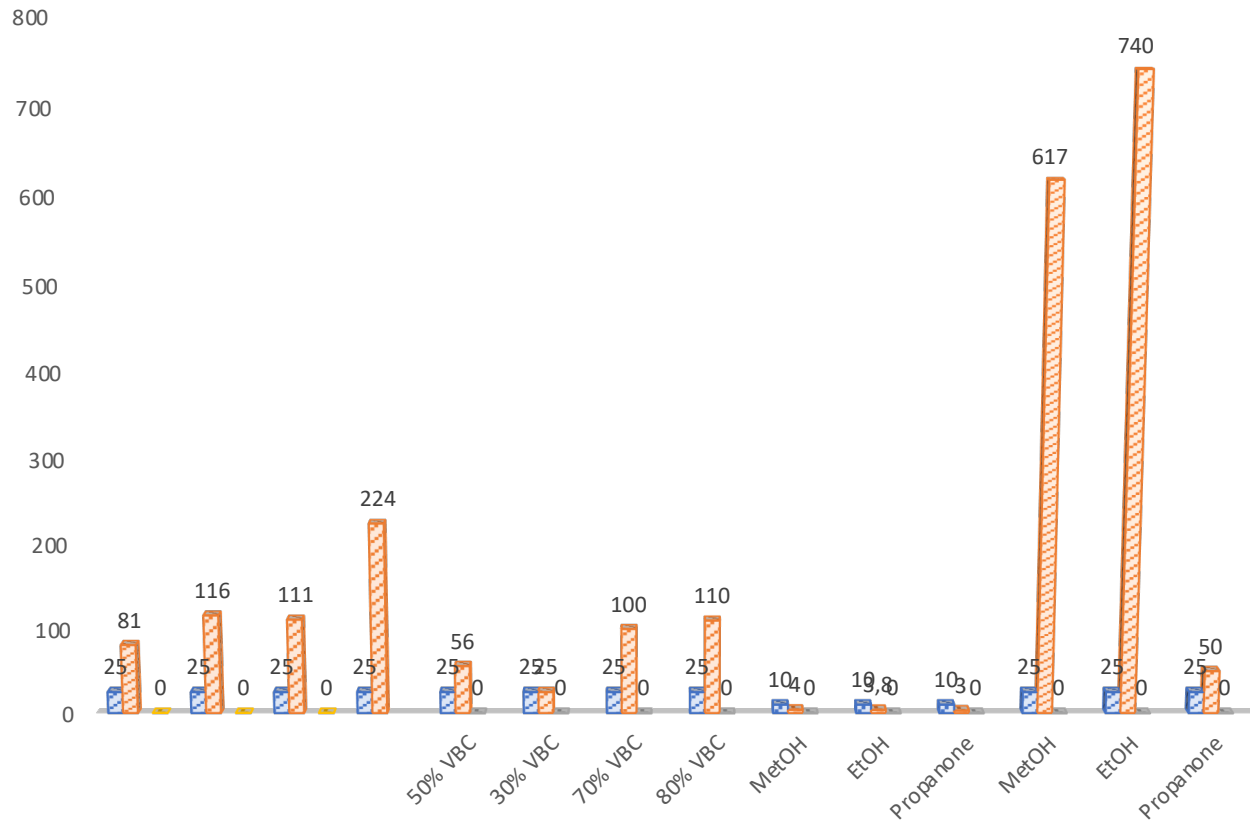
Conclusion for conventional RIG

Degree of Grafting (DoG) increased with radiation absorbed dose increase, homopolymerization affected some grafted membranes at high radiation absorbed doses. Also, atmosphere of irradiation affected the DoG. The resulting AEM synthesized by RIG of VBC onto LDPE with 30 kGy radiation absorbed was tested in a fuel cell and reached a maximum power density of 942 mW cm^{-2} at $80 \text{ }^\circ\text{C}$ with gases flow of 0.8 L min^{-1} and 0.5 L min^{-1} for H_2 and O_2 , respectively.

RIG RAFT polymerization

(Dr Murat and Prof Dr Guven, Hacettepe University – IAEA)

■ Dose (kGy) ■ DoG (%) ■ Condition ■ MwT g/mol



LDPE Radiation Induced Grafting by Direct Method

RAFT or **R**eversible **A**ddition-**F**ragmentation chain **T**ransfer is a form of living radical polymerization

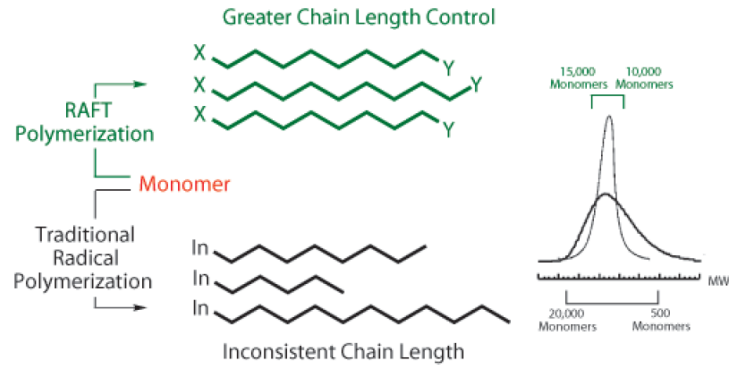


Figure 1. General comparison of polymers made with traditional radical polymerization against those made using RAFT process.

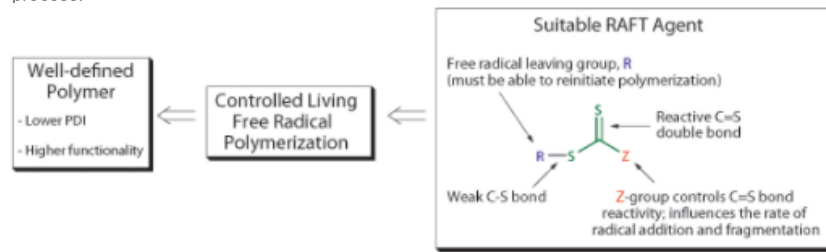
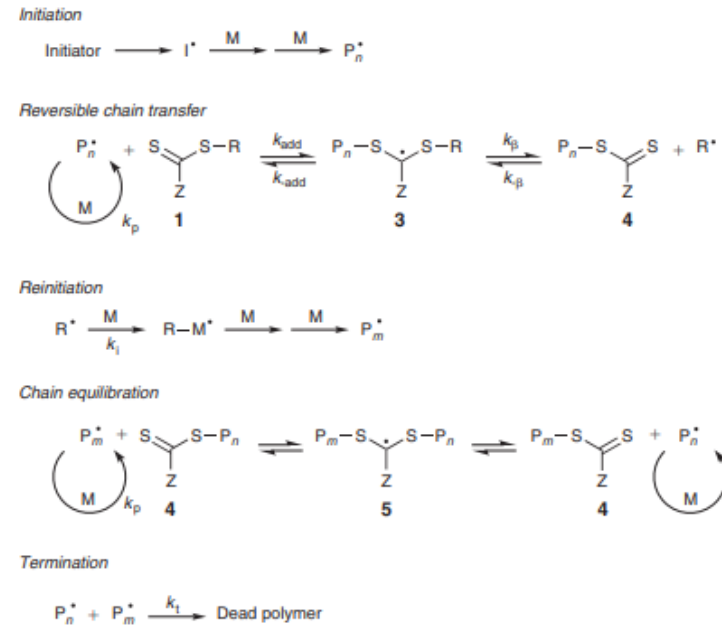
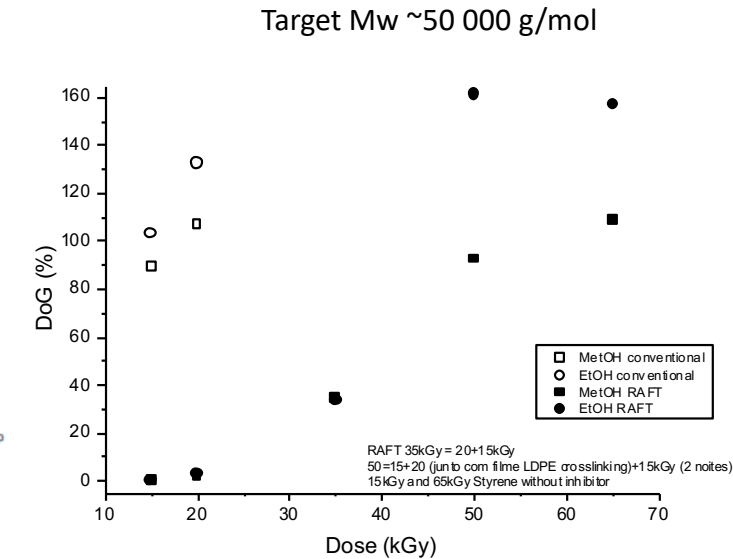


Figure 2. General structure of a RAFT agent; choice of the RAFT agent is critical to obtain polymers with low PDI and controlled architecture.

<https://www.sigmaaldrich.com/technical-documents/articles/materials-science/polymer-science/raft-polymerization.f>

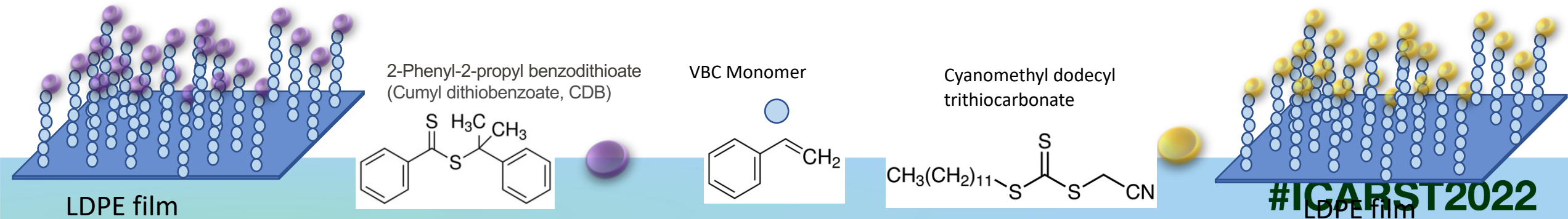


Scheme 6. Mechanism of RAFT polymerization.



Grafting From - gamma radiation as initiator

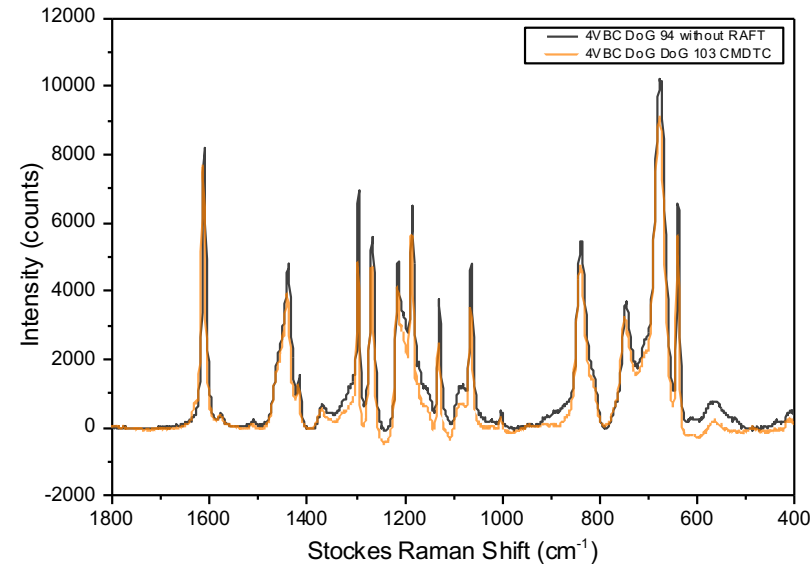
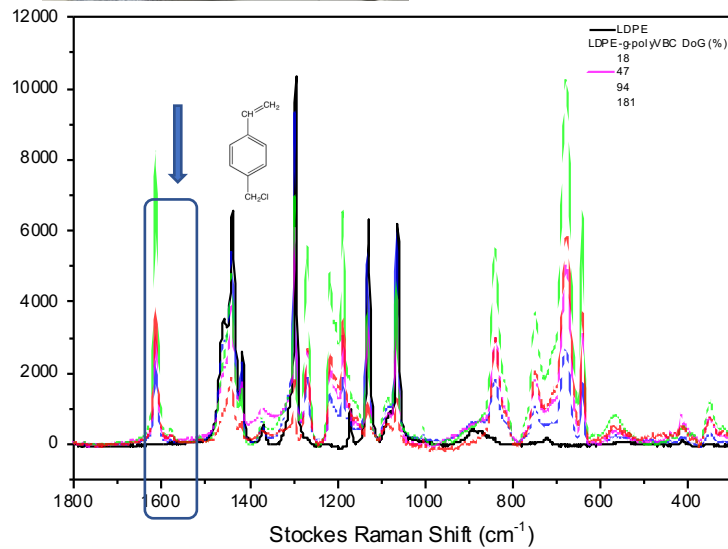
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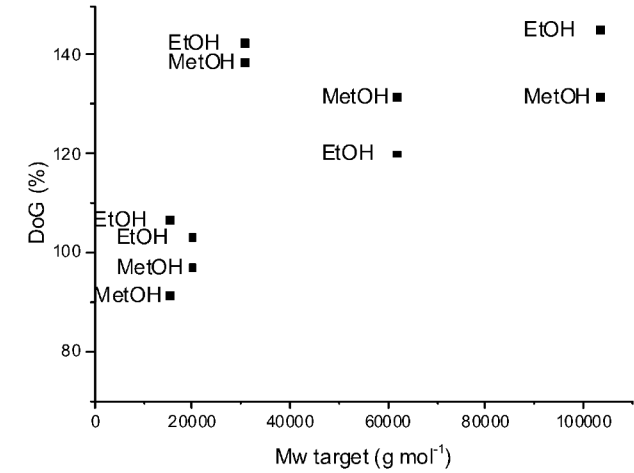
LDPE and HDPE Radiation Induced Grafting by Direct Method



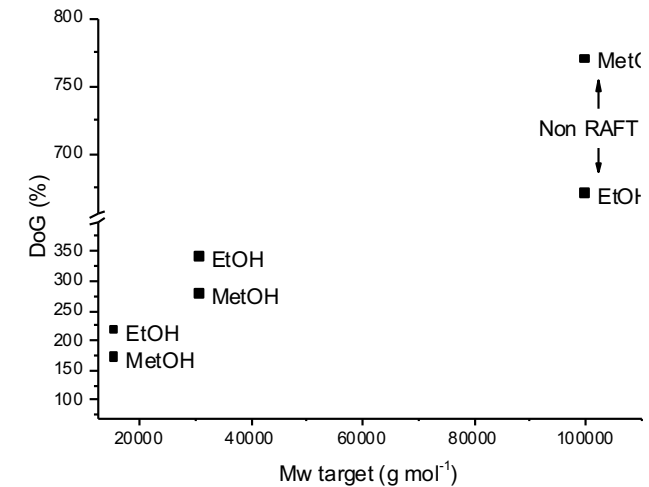
Gammacell 220 model



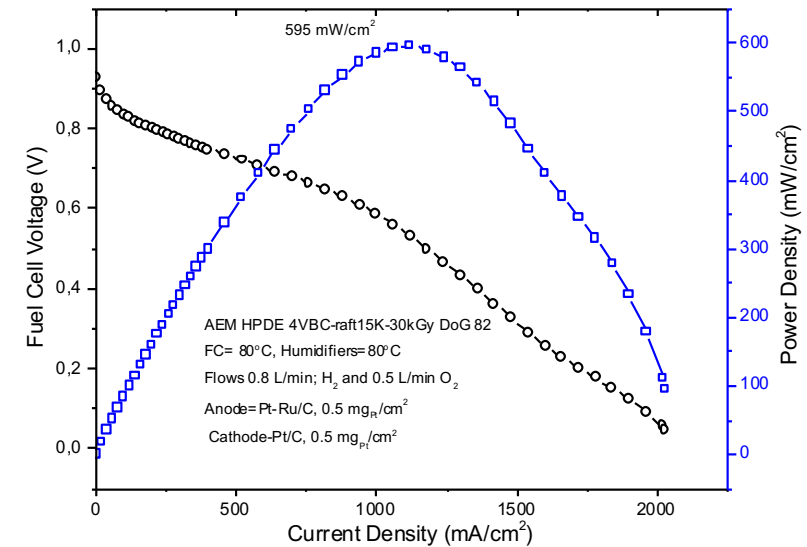
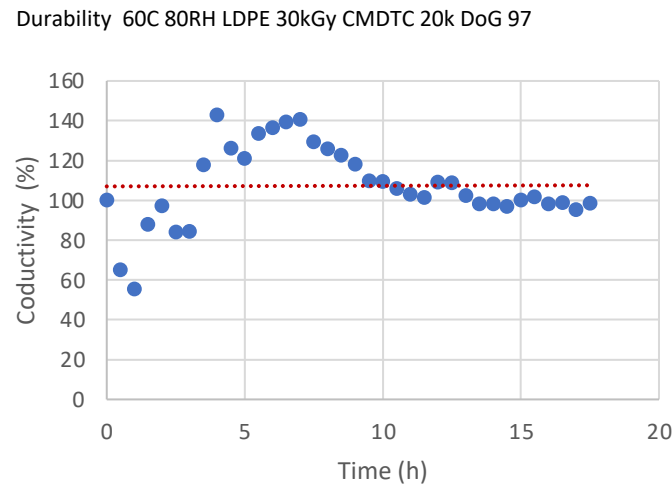
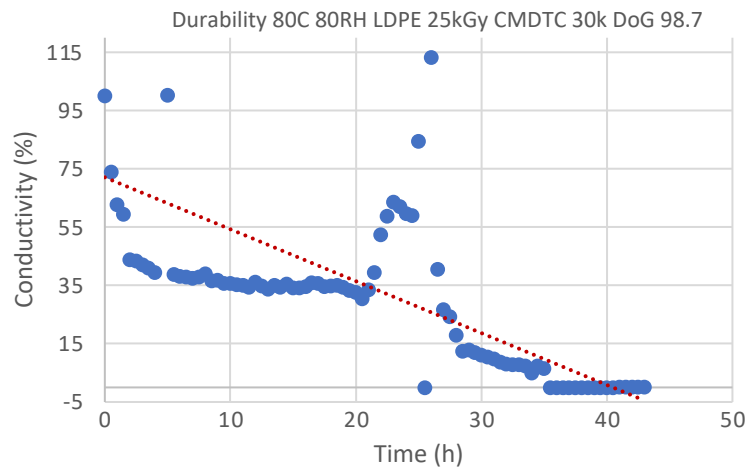
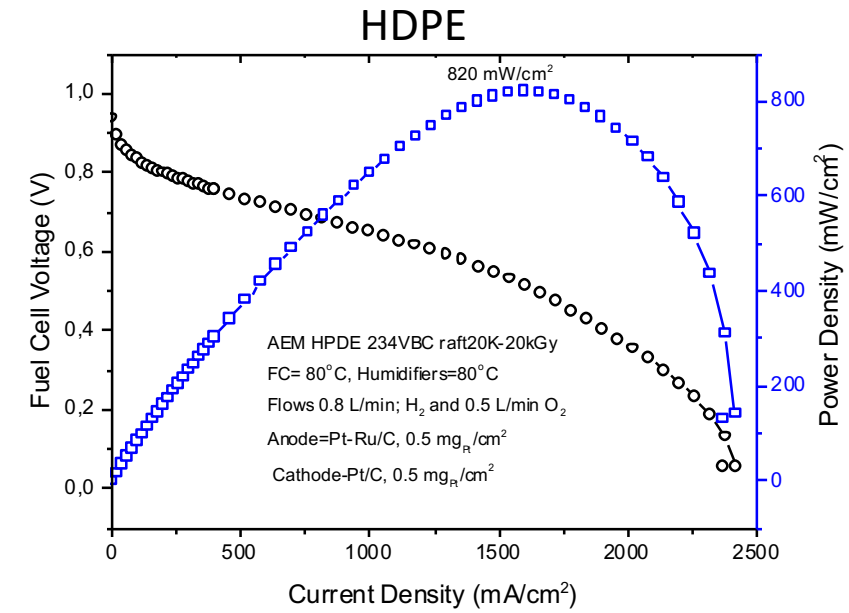
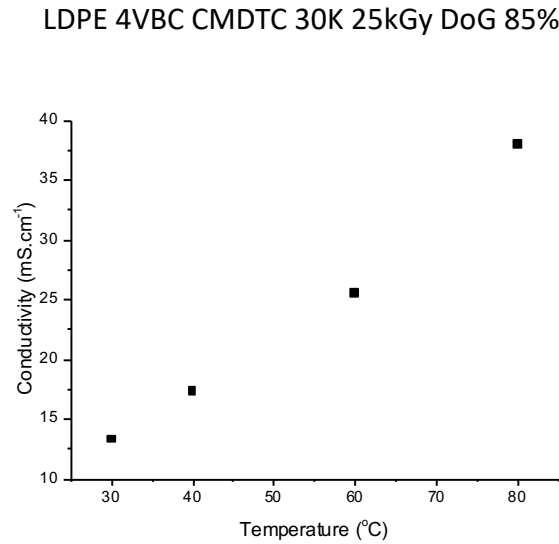
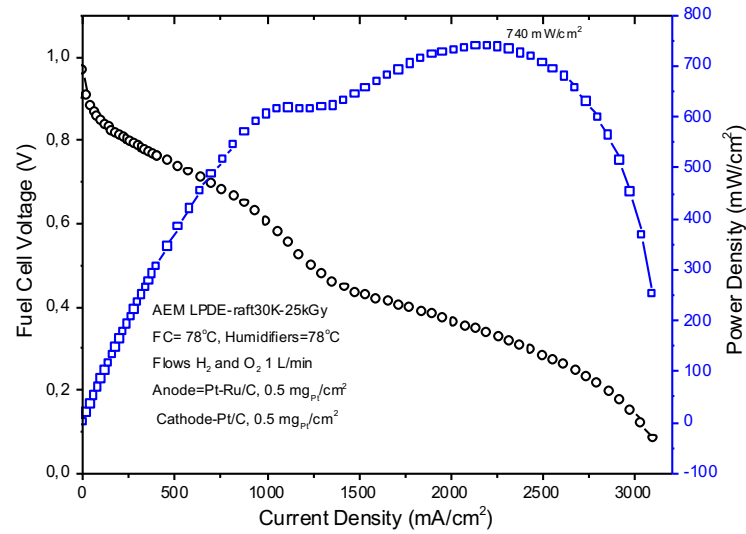
CMDTC-4VBC 30kGy



CMDTC-234VBC 30kGy



LDPE and HDPE RIG by VBC by Direct Method



Summary

- Low Density Polyethylene, LDPE, biaxially oriented films (Goodfellow, 25 μm) and HDPE 10 μm were used for radiation induced grafting by vinylbenzil chloride monomer.
- We studied the influence of solvents, monomer concentration and absorbed radiation dose on degree of grafting (DoG) of 4-VBC onto LDPE.
- RIG prepared membranes were characterized on their physical, chemical, mechanical and electrochemical properties.
- Polymeric film base used for RI grafting and type of monomer chosen affects final properties of AAEM.
- Solvent type and concentration affects DoG
- DoG affects all studied properties.
- RAFT agent decreases DoG with increasing concentration and it reduces drastically this parameter compared to conventional RIG polymerization.
- Optimization of parameters of RIG of VBC onto LDPE still have not been reached here.

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Fuel Cell membranes Group



RIG membranes SETRD Group



Thank you!

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