



02 Fuel Cell

Introduction

Advances in nanotechnology offer immense potential towards the development and production of innovative materials with improved, customized properties, requested by the industry. The benefits and valuable contributions of polymer based nanoparticles have been demonstrated in diverse areas such as coatings, construction, adhesives, food, packaging, cosmetics, life science and energy. To match the application requirements, the physical and chemical properties of the end-product can be adapted by the effective combination of properly chosen materials.

SPECIFIC POLYMERS main focus is the development of energy-cost-efficient and high throughput synthetic strategies for the preparation of polymeric particles. We are specialized in the production of silica nanoparticles grafted poly(sodium 4-styrenesulfonate) as innovative & suitable substitute to the Nafion® in fuel cell membranes.

Toward a more powerful & efficient fuel cell membrane

Main aspects take into account for the preparation of a new performing fuel cell membrane are:

- Adapted to Proton Exchange Membrane Fuel Cell (PEMFC) technology
- High Ion Exchange Capacity (IEC)
- Energy-/cost-efficient and high throughput synthetic strategy
- Feasible access to up scaling production

In this way SPECIFIC POLYMERS, in joint collaboration with the CEA, identified a suitable technology consisting in incorporate silica nanoparticles grafted poly(sodium 4-styrenesulfonate) into a fluorinated membrane based PVDF.

→ PVDF advantages: mechanical strength, electrical insulation resistant to acid environment, low gas permeation, low cost material and large amount accessibility

→ SiO₂-g-PSSNa advantages: high proton conductivity, high ion exchange capacity, thermal stability, water uptake, low-cost components



Focus on the SiO₂-g-PSSNa SP-59P-9-001

Within this project, SPECIFIC POLYMERS worked on the synthesis of the silica nanoparticles grafted poly(sodium 4-styrenesulfonate). Different synthetic approaches and techniques were confronted but, we decided to polymerize the sodium 4-styrenesulfonate via Atom Transfer Radical Polymerization (ATRP) directly from the silica nanoparticles. This grafting method is called "grafting from".

Particles functionalization

To reach the SiO₂-g-PSSNa, the first step consists in functionalizing the silica nanoparticles. The chloromethylphenylethyltrimethoxysilane (CMPETMS) is used as coupling agent since the alkoxy silane moiety will react onto Si-OH surface functions while the chlorinated atom will be involved into ATRP step. The grafted density of each silica nanoparticles can be tune by adjusting the amount of CMPETMS.

Polymerization step

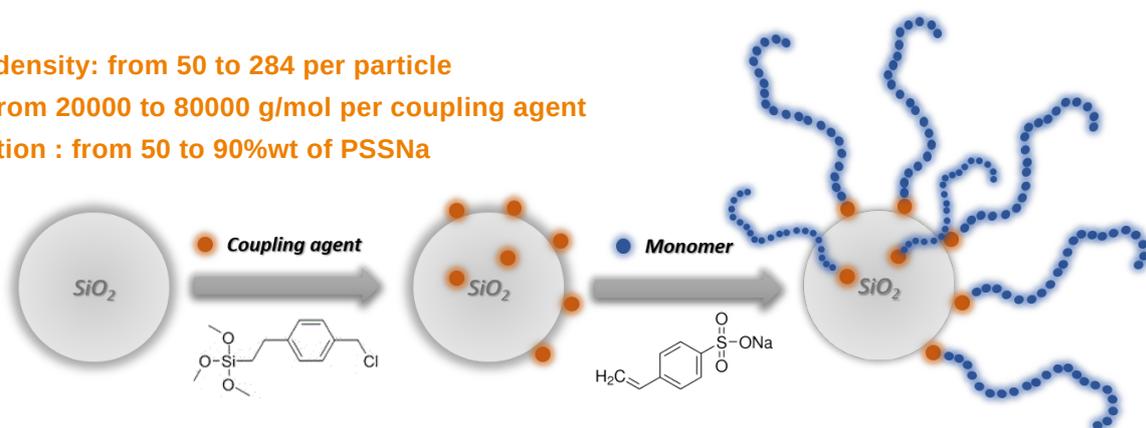
To obtain faithful SiO₂-g-PSSNa targets, ATRP conditions are maintained for 24h at 45°C. This method is chosen for the polymerization step owing to its considerable advantages such as:

- No free polymer (polymerization from particles and no free initiator)
- High molecular weight control
- Narrow molecular weight distribution
- High degrees of chain end functionalities

Product Specificities

- **Theoretical grafting density: from 50 to 284 per particle**
- **Brush polymer: Mn from 20000 to 80000 g/mol per coupling agent**
- **Theoretical composition : from 50 to 90%wt of PSSNa**
- **IEC : Up to 4.6meq/g**

SP-59P-9-001
Batch up to 100g



Process scale up

After completion of the particle development in a research batch-scale it might be important for our customers to scale-up the process. Our team of experts can support them up to commercial production, according to their specific needs. Within this scope, SPECIFIC POLYMERS, in joint collaboration with the CEA, is currently working on the SiO₂-g-PSSNa scaling-up. Academics or industrials could order the SiO₂-g-PSSNa at SPECIFIC POLYMERS while the nanocomposite hybrid membrane could be provided by the CEA.



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Fuel cell performance

Nanocomposite hybrid membranes (NHM) were prepared by casting process in DMSO. These membranes are composed by 56%wt of PVDF and 44%wt of SiO₂-g-PSSNa. The performance evaluation was performed face to the commercial Nafion® NRE211.

Performance at 60°C

As observed (**Figure 1**), the open circuit voltage (OCV) of NHM is around 1.07V which shows first that the leakage current is low (very good electrical insulation) and then hydrogen permeation is lower than Nafion® NRE211 membrane. The power density gain is 40% at 0.7V compared to Nafion® NRE211. According to complex impedance measurement, this gain is mainly related to a 50% drop in membrane resistance (HFR) while charge transfer resistance (CTR), associated with the activity of the electrode, is identical (**Figure 2**).

In addition, the membrane resistance of the NHM is constant over the entire range of current density while the resistance of the Nafion® NRE211 tends to increase for low current densities.

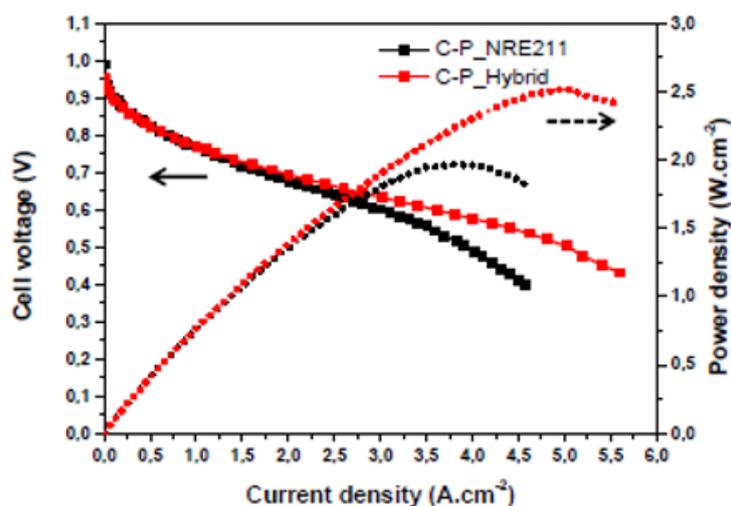


Figure 1: Polarization curves under dry H₂/O₂ and 50%HR H₂/Air conditions

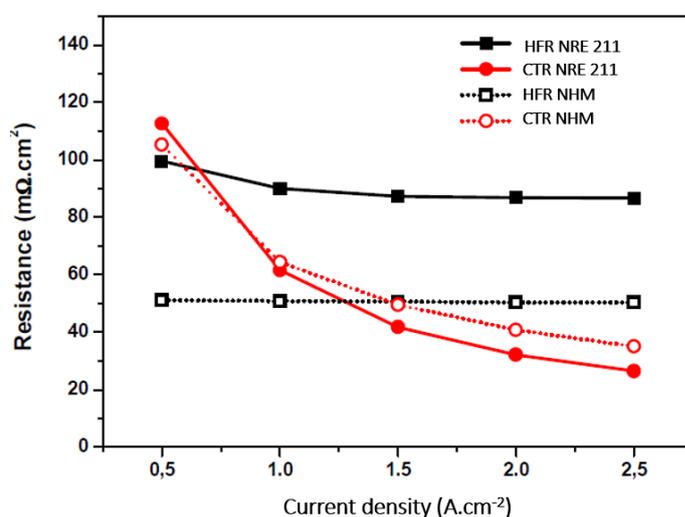


Figure 2: Resistances evolution according to current density



Durability at 70°C and 1.0A/cm²

The new generation of nanocomposite hybrid membranes shows improvement of:

- Physical properties (high proton conductivity, low H₂ permeability and good mechanical strength)
- Fuel Cell performance at 70°C (0,77W/cm²@1,0A/cm² under O₂ and 0,66W/cm²@1,0A/cm² under Air)
- Durability à 70°C (voltage decay 14 μV/h under O₂ i.e. 5500 hours of operation) (**Figure 3**)

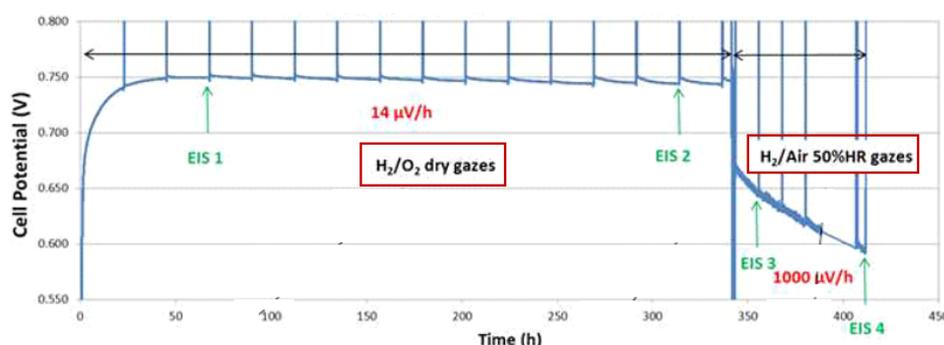


Figure 3: Durability at 70°C and 1.0A/cm²

Microstructure Observation

Performances of Nafion® membranes are mainly related to the nanostructuring of the material. Indeed, the dual properties induced by first, the hydrophobic perfluorinated back-bone and then, the hydrophilic sulfonic moiety, enable the formation of proton conducting network in the membrane volume (percolation). Regarding the NHM, this outstanding ability is maintained. Thus, in this membrane, PVDF acts as hydrophobic barrier while SiO₂-g-PSSNa as conductive network.

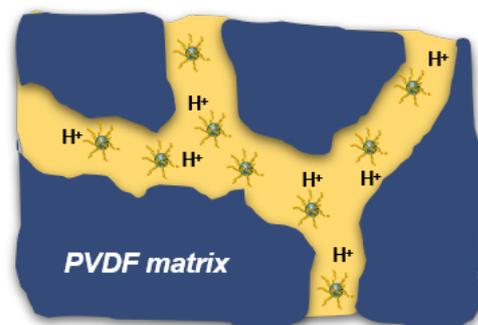


Figure 4: Schematic representation of the nanocomposite hybrid membrane

Functional properties

Membrane	Nafion® NRE211	Hybrid Membrane
Density (g.cm ³)	1.95	1.40
Water Uptake (%Wt)	18	100
Swelling (z and x,y) (%)	11 8	33 35
IEC (meq.g ⁻¹)	0.95	1.86
Hydratation number (25°C) (?)	11	30
Proton conductivity immersed (25°C) (mS/cm)	48	67
H ₂ crossover at 25°C (mA.cm ²)	0.8	0.3
HFR (1 A.cm ²) (mW.cm ²)	95	48
CTR (1 A.cm ²) (mW.cm ²)	67	67
OCV (V)	1.02	1.07
Cell potential (1 A.cm ²) (V)	0.745	0.785
Power density (0.7V) (W.cm ²)	0.95	1.40

Outlooks

Finally it must notable that, due to its low H₂ permeability, this membrane should be a good candidate for PEM Electrolyser application.