New materials as key enabling technologies for fuel cells and water splitting

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TRUSTED PARTNER FOR BUSINESS





- State of the art: Fuel cells
- Proton Exchange Membrane Fuel Cell (PEMFC)
- LIST-MRT activities:
 - 1. Synergy MWNTs/polymers
 - 2. Highly Ionic Conductive Short Side Chain ionomer for next fuel cell generation
 - 3. Water splitting



- Limitation of fossil energy resources
- Increasing CO₂ emissions
- Global warming



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https://nation.com.pk

FUEL CELL TYPES





Solid Oxide Fuel Cell (SOFC), Molten Carbonate Fuel Cell (MCFC), Alkaline Fuel Cell (AFC), Phosphoric Acid Fuel Cell (PAFC), Proton Exchange Membrane Fuel Cell (PEMFC), Direct methanol Fuel cell (DMFC)

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H. Vaghari et al. Sustainable Chemical Processes 2013, 1, 16

PROTON EXCHANGE MEMBRANE FUEL CELL: HOW IT WORKS





PROTON EXCHANGE MEMBRANE FUEL CELL SET UP

PEM FC hardware available at LIST



PEMFCs have a unique set of advantages for use in vehicles:

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- sufficiently low working temperature (80°C)
- a good energy density *versus* other fuel cell types
- robust and relatively simple mechanics
- ability to run on pure hydrogen
- ability to use ambient air as the oxidant.

PEMFC COMPONENTS



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LIST – MRT CURRENT RESEARCH LINES





- Pt loading
- Support corrosion

Highly Ionic Conductive Short Side Chain ionomer for next fuel cell generation

• Polymer electrolyte membrane

ELECTRODES: PLATINUM



PLATINUM REQUIREMENTS:

- ACTIVITY
- SELECTIVITY
- STABILITY
- POISONING RESISTANCE



Global Fuel Car Vehicle & Annual FCV Platinum demand



High cost and limited availability of Pt resources!

Source: WPIC Research R. Borup et al., Chem Rev., 2007, 107, 3904

HOW TO DECREASE THE PLATINUM LOADING?

Current strategies

Preparation methods	Advantages	Drawbacks
Modified thin film	Relatively higher Pt utilization; no obvious distortion or deformation of the catalyzed layer due to low-hot-pressing temperature, 80 C, and pressure; without adding any additional organic solvent; more intimate membrane/electrode interface and interfacial continuity between them; more economical process	Relatively high-Pt-loadings; limits the Pt loading under 0.05 mg cm−2; difficult to control the Pt particle size; uniformity of Pt deposition in large scale
Electrodeposition	Relatively higher Pt utilization; deposition of Pt theoretically happens at solely active zone (ionic and electronic pathways of substrate) of membrane, and NCL diminishes inactive catalyst sites; possible to increase the Pt/C ratio up to 75 wt.% near the surface of the electrode; most of Pt is in close contact with the membrane	Relatively higher Pt loadings; concerns on the scalability for mass scale manufacturing; complex processes and relatively high-Pt-loadings; CI- ions produced in process are known to poison Pt and reduce the catalytic activity
Sputter deposition	Lowest Pt loadings; Allows the Pt deposition onto various substrates such as GDL, membrane and NCL (or Nafion-bonded NCL); denser Pt layers; possible to fabricate nano-scale; Pt layer with uniform distribution; simple and easy to scale-up; cheap direct deposition method	Relatively lower Pt utilization; poor adherence of Pt to substrate; short durability, i.e., physical weakness; greater probability of dissolution and sintering of Pt; multi-Pt electrocatalyzed layer structure in MEA for higher performance; even smaller particle sized Pt probably hinders water transport
Dual ion-beam assisted deposition	Relatively lower Pt loadings and higher Pt utilization; significantly different morphology, largely amorphous for better performance; low-density Pt deposits	Complex processes and/or steps involved; concerns on the scalability for mass scale manufacturing; low-specific power density
Electroless deposition	Effective for PtRu binary anode electrocatalyst	Higher fabrication cost
Nano-carbons as catalysts	Relatively lower Pt loadings and higher Pt utilization	Strongly dependent on Pt loading methods; high price of synthesis of nano-carbons

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THREE-PHASE-BOUNDARY

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A *three phase boundary* is a region of contact among three different phases, consisting of Pt/Carbon Black, the ionomer and the gas-diffusion path for oxygen reduction reaction in the cathode catalyst layer





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J. C. MeierBeilstein J. Nanotechnol. 2014, 5, 44

LAYER BY LAYER DEPOSITION



A more recent approach



Advantages:

- deposition on surfaces of almost any kind and any shape
- broad processing window
- fine number of parameters
 (concentration, adsorption time, ionic strength, solvent composition, temperature...)

LbL allows:

- to increase the porosity in the multilayer structure
- to limit any material loss
- high values of Pt utilization

WHERE LBL CAN BE APPLIED?





Carbon black CX-72

Sample

Multi walled carbon nano tubes

Carbon black

Multi walled carbon nano tubes



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HOW TO PROTEC THE CARBON SUPPORT



Mussel-inspired polydopamine layer



- strong bond between pDopa and Pt precursor thanks to the presence of catechol and amino groups
- π - π interaction between dopamine and graphitized carbon structures
- hydrophilicity of pDopa and the customised thickness of pDOPA films

M. Rahimnejad et al., RSC Adv. 2017, 7, 47380 T. Lee et al., J. Mater. Chem. A, 2014, 2, 6167

ELECTRODE PREPARATION





140°C, 30 min



OH



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Pt nanoparticule

Pt/MWNTs



Pt/MWNTs-pDOPA

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H. Long et al., Journal of Power Sources 2016, 307 569e577

ELECTROCHEMICAL SURFACE AREA





The Fuel Cell life of the system with pDOPA is longer than the system w%o pDOPA

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LIST – MRT CURRENT RESEARCH LINES





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FUEL CELL COST



Membrane Electrode Assembly

Membrane electrode assembly (MEA):

- polymer electrolyte membrane (PEM)
- catalyst layers (CL)
- gas diffusion layers (GDL) attached on the outer surface of the catalyst layer







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- o Restrictive thermal stability
- Severe methanol permeability
- Difficult to further chemical modification
- Large dependence of proton transport process on %RH

POLYMER ELECTROLYTE MEMBRANE

State of the art



Category	Structure	Physical properties	In situ performance
Perfluorinated membranes	 Fluorinated backbone like PTFE Fluorocarbon side chain Ionic clusters consisting of sulfonic acid ions attached to the side chains 	Membranes are strong and stable in both oxidative and reductive environments	 Membrane is durable upto 60,000 h Proton conductivities in well humidified membranes are 0.2 S/cm at PEMFC operating temperatures Cell resistance of 0.05cm2 for 100 m thick membrane with voltage loss of only 50mV at 1 A/cm2 is achievable
Partially fluorinated membrane	•Hydrocarbon or aromatic side chain grafted onto the backbone, which can be modified Fluorocarbon base	Membranes are relatively strong in comparison to pf, but degrade fast	 Less durable than perfluorinated ones Low performance On suitable modification, yield membranes with comparable proton Conductivities
Non-fluorinated hydrocarbon membranes	Hydrocarbon base, typically modified with polar groups	 Membranes posses good mechanical strength Poor chemical and thermal stability 	 Poor conductors of protons Exhibit low durability on account of swelling obtained by incorporation of polar groups into the polymer matrix
Non-fluorinated aromatic membranes	Aromatic base, typically modified with polar/sulfonic acid groups	 Good mechanical strength • Good water absorption Chemically and thermally stable even at elevated temperatures 	 Good water absorption Relatively high proton conductivity is attainable Conductance of SPPBP at 65 mol% of sulfonation is 10−2 S/cm that is retained at temperatures above 100 °C
Acid–base blend membranes	Incorporation of acid component, into an alkaline polymer base	Stable in oxidizing, reducing and acidic environments • High thermal stability	 Good dimensional stability Exhibit proton conductivity comparable to Nafion® Durability of the membranes is still to be proven

PERFLUOROSULPHONIC ACID MEMBRANES



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HIGHLY IONIC CONDUCTIVE SHORT SIDE CHAIN IONOMER FOR NEXT FUEL CELL GENERATION

Plasma radical assisted polymerization via Chemical Vapour Deposition



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D. Lenoble, Centre de recherche Pubblic - Gabriel Lippmann, Lux. 91934, 2013



	PRAP-CVD	WET CHEMISTRY	
Conformity	High	Low	
Solvent	No	Yes	
Temperature	Low	High	
Step	1	Multiple	
Treatments of 3D shaped samples	Yes	No	
Uniform film thickness	Yes	No	
Shrinkage	No	Yes	
Agglomeration	No	Yes	
Waste	No	Yes	





By PRAP-CVD it will be possible

- deposit the membranes directly on the electrode
- surpass commercial membrane and bypass current issues in terms of conformity, adhesion and affinity between the membrane and the electrodes

lonomer	LSC PFSA	SCC PFSA	PRAP-CVD
	(Nafion™)	(Aquivion™)	membrane
Equivalent Weight (g/mol)	1100	870	<800
Conductivity (S/cm)	0.078	0.2	> 0.2
Water uptake (wt.%)	27.5	35.3	> 30





Water splitting is the chemical reaction in which water is broken down into oxygen and hydrogen



A bridge project submission is ongoing...

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✓ LIST IS HIGHLY INVOLVED IN THE ENERGY TOPIC:

✓ FUEL CELL COMPONENTS ARE INVESTIGATED
 INVESTIGATION (CORE PROJECTS)

✓ WATER SPLITTING (BRIDGE PROJECT)



Fonds National de la Recherche Luxembourg

FNR-CORE « EnergyCell » C13/MS/5897111



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