# Anionic-exchange membrane development for application in alcohol alkaline fuel cells

Shakes Nonjola

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## Historical background



Willow

Sir William Robert Grove
(July 11, 1811 - August 1, 1896)
Photo: The Bridgeman Art Library, London (The Royal Institution, London)

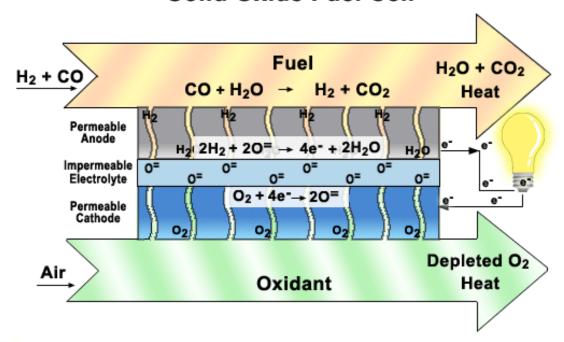
- Fuel cell (FC) first demonstrated over 160 yrs ago.
- F.T Bacon (1930) developed alkaline fuel cell (AFC).
- AFC first generation technology used by NASA for space missions.
- Also early demonstration for transportation applications.



#### What is a Fuel Cell?

 Conversion of chemical energy directly into electrical energy and heat using electrochemical process

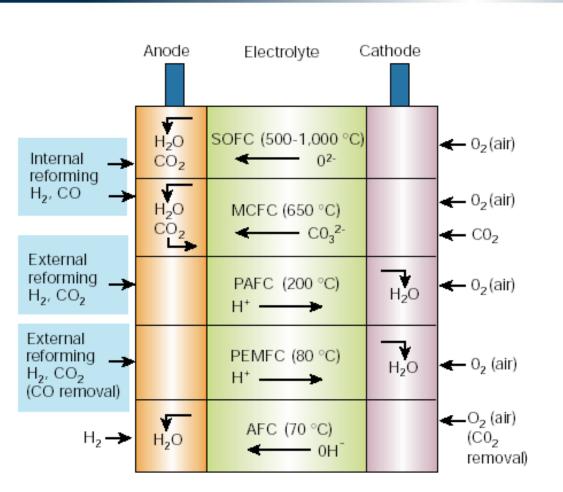
#### Solid Oxide Fuel Cell



Solid State Energy Conversion Alliance (SECA)



## Fuel Cell Types



- Alkaline (AFC) developed for the Apollo program
- Polymer membrane (PEMC) leading candidate for transportation
- Phosphoric acid (PAFC) 200kW units commercially available for combined heat and power (CHP)
- Molten carbonate (MCFC) and solid oxide (SOFC) can work directly with hydrocarbon fuels – 200+kW demonstration units

Taken from B.C.H. Steele & A. Heinzel, Nature, 414 (2001) p345.



## Advantages of Fuel Cell

- Fuel cells generate power continually, eliminating the need for backup generators.
- They are efficient, converting approximately 40%-50% of the available fuel to electricity compared to 20%-40% for traditional fossil fuel-fired power plants.
- Emit 60% less carbon dioxide than combustion-fired reciprocating engines per unit output, and operate at lower noise levels.
- Fuel flexible and can operate with most hydrocarbons, such as natural gas, methanol, ethanol, propane, diesel, and gasoline.

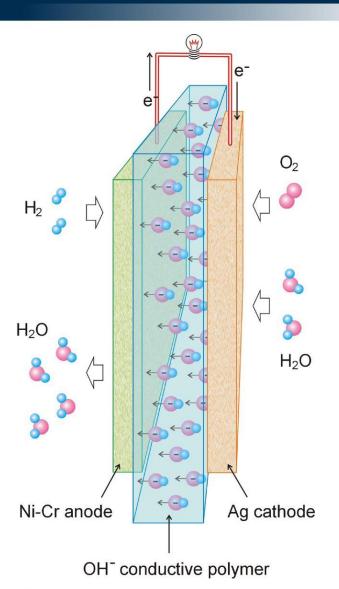


## **Technical Challenges**

- CO tolerant electrocatalysts
- Better membranes for PEMFC, AFC and DMFC
- Intermediate temperature high performance electrodes (SOFC)
- Low cost fabrication processes



#### Alkaline Fuel Cell Overview



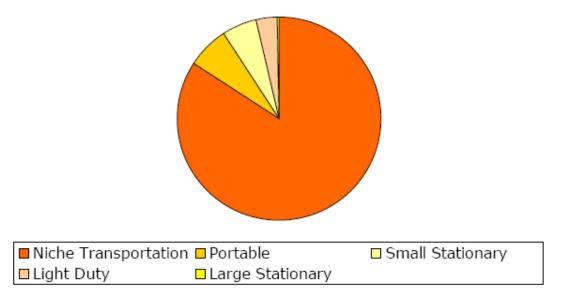
- All AFC uses an alkaline electrolyte (KOH) to operate.
- AFC systems are low temperature FC (60 and 90 °C)
- Variety of non Pt metals can be used.
- Demonstrate efficiency between 45 and 60 %, and can produce ~ 20kWe.
- AFC systems are easily poisoned by CO<sub>2</sub> – reduces electrolyte conductivity.
- Also reduces lifetime replaced at faster rate than other FC types.



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## Applications of AFC

- Originally used by NASA to provide electric power and drinking water to the shuttle
- Currently used in niche transportation, powering forklift trucks, boats and submarines.
- Have to be more cost effective and reach over 40 000 hrs operating times (8 000 hrs currently).



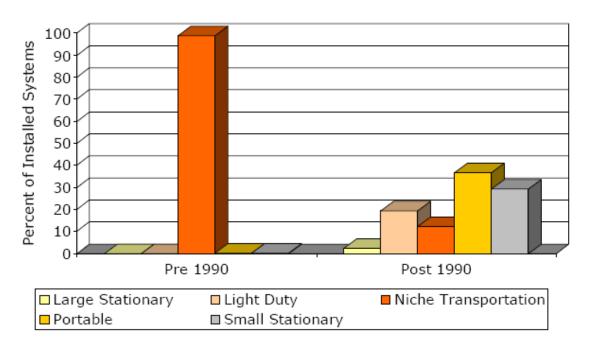
Taken from Fuel Cell Today (2006)



Total Number of AFC Units Installed Globally by Application

### **Current AFC Market**

- AFC market is limited compared to other FC technologies.
- Over 80% before 1990
- 1980s transportation sector favoured PEMFC systems.
- Approx. 10 yrs back AFC technology revive and develop capability in other applications



Taken from Fuel Cell Today (2006)

AFC Systems Installed Globally Split by Date Introduced and Application



## Way Forward

- R & D of AFC systems has an important role to play.
- Trends show that companies and organisations re-examine existing AFC technology.
- ~70% organisations involved in AFC operate as commercial entities and ~30% as academic institutions, government agencies/investors.
- High percentage indicates that companies are working towards commercialisation of AFC technology.



## Membrane Development

- Polymer electrolyte fuel cell (PEFC) most developed in the past 2 decades.
- PEFC acidic membrane (Nafion) as an electrolyte.
- Nafion based FCs several obstacles such as: dependence on Pt catalysts and MeOH crossover in DMFC.
- Anion exchange membranes were developed non Pt catalysts and OH a source of fuel.
- To date no suitable alkaline electrolytes is readily available.







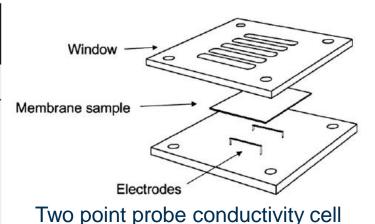
## Anionic-Exchange Membrane

- Designed and synthesized alkaline polymer, quaternary ammonium polysulfone (QPSf).
- Thermally stable > 120 °C.
- Ion exchange capacity regulated > ~1 quaternary ammonium group per structure unit.
- Polymer structure was confirmed by NMR and FTIR.



## Conductivity Measurements

Table 2 – Specific conductivities of QPSf and Nafion membranes.				
Membrane	c <sub>KOH</sub> (mol dm <sup>-3</sup> )	$\sigma$ (S cm <sup>-1</sup> )		
QPSf	0 (H <sub>2</sub> O)	0.0016		
	0.5	0.0192		
	1.0	0.0210		
	1.5	0.0675		
	2.0	0.0833		
	2.5	0.0533		
Nafion 117	H <sub>2</sub> O	0.112		

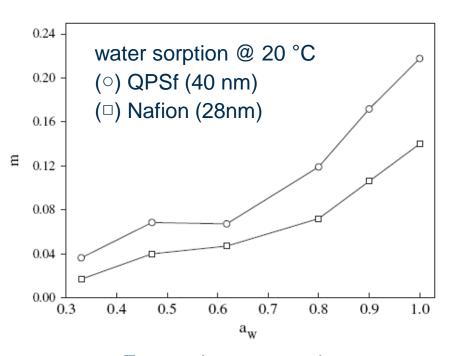


- To confirm QPSf suitability for FC application.
- Nafion high conductivity than QPSf.
- Increasing [KOH] increases conductivity of QPSf.
- Decrease at higher [KOH] due to displacement of ammoniun group by HO-.

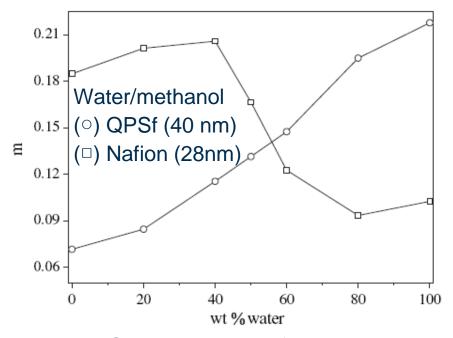
Corti et al. Hydrogen Fuel Cell, 35 (2010) p 5489.



## Water and Methanol Uptake



- Exposed to vapour phase.
- QPSf has higher water uptake than Nafion.



- MeOH concentration from 0-100 wt%.
- Pure MeOH uptake by QPSf is ~3 times lower than Nafion
- MeOH permeation in QPSf will be lower than in Nafion.
- Water is preferably sorbed over MeOH by QPSf.
- Nafion sorption increases with MeOH content in water/MeOH mixture



## **Mechanical Properties**

Table 1 – Young's m	odulus of hyd	drated QPS	f and Nafion
membranes.			

Membrane	E (GPa)
QPSf Nafion 117 Nafion 117 <sup>a</sup>	$\begin{array}{c} 0.25 \pm 0.11 \\ 0.29 \pm 0.08 \\ 0.09 – 0.25 \end{array}$

- Elastic modulus of QPSf is similar to that of Nafion
- QPSf and Nafion are mechanically feasible to construct MEA for FC.

[a] Tang et al. Mat. Sci. Eng A, 2006, vol 425, p297.



#### Conclusion

- QPSf were successfully synthesized.
- QPSf membrane exhibited excellent mechanical properties and chemical stability comparable to that of Nafion 117.
- Results indicated that QPSf membrane is a good candidate as electrolyte in alkaline direct methanol fuel cell
- Performance studies will be addressed in the forthcoming paper.



## **Thank You**

