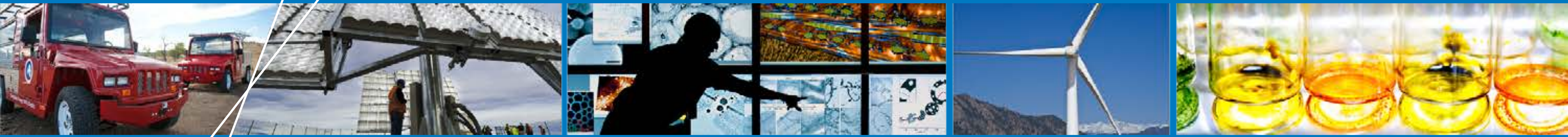
Advanced Ionomers & MEAs for Alkaline Membrane Fuel Cells



2013 DOE Hydrogen and Fuel Cells Program Review

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May 16, 2013

FC108

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

Timeline

- Start: March 2013
- End: March 2015
- % complete: ~1%

Barriers

A. Durability
B. Cost
C. Performance

Budget ($K)

DOE Cost Share	Recipient Cost Share	TOTAL
2000	500	2500

DOE funding	Budget ($K)
FY13	600

Partners – Principle Investigators

CellEra – Shimshon Gottesfeld
3M – Krzysztof Lewinski
Colorado School of Mines – Andy Herring

Relevance

DOE Milestones for Alkaline Membrane Fuel Cells (AMFCs)/ Goals

http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/fuel_cells.pdf pages 3.4-42 and 3.4-44

Task 1: Electrolytes	
1.4	Demonstrate an anion-exchange membrane that retains 99% of original ion exchange capacity for 1000 hours in hydroxide form at T > 80°C. (2Q 2013)

Task 3: Membrane Electrode Assemblies, Gas Diffusion Media, and Fuel Cells	
3.8	Demonstrate anion-exchange membrane technologies in MEA/single cells with non-PGM catalysts that maintain performance higher than 350 mW/cm^2 for 2000 hours at T > 80°C. (4Q, 2016)

Team Project Goals

- Synthesize novel perfluoro (PF) anion exchange membranes (AEMs) with high temperature stability and high water permeability
- Employ novel PF AEM materials in electrodes and as membranes in alkaline membrane fuel cells
- Demonstrate high performance, durability, and tolerance to ambient carbon dioxide.

Relevance

AMFC Potential Advantages

- Catalysis
  - Non-precious catalysis
  - Improved anode/cathode kinetics/durability
  - fuel choices
- System Issues
  - Electro-osmotic drag in opposite direction
  - Materials choices/ durability

Advantages of alkaline membrane vs. free electrolyte (KOH)

- Prevention of carbonate precipitates
- Liquid water tolerance without electrolyte migration
- Ability to withstand differential pressures
- Thinner separator layers possible
- Corrosion significantly mitigated
- Potential system design simplification

Relevance

2011 AMFC Workshop

Table 1. Select Highlights of Breakout Sessions

Breakout Session	Key Highlights
Anion Exchange Membranes – Stability	Membrane stability with Tokuyama membranes has been demonstrated to a level at or near commercial impact. AEM stability remains inferior to proton exchange membranes under conditions relevant to fuel cell operation.
Anion Exchange Membranes – Transport/Conductivity	Conductivity of AEMs is significantly lower than acid membrane analogues. Relatively little transport property data exist for AEMs, but water transport is likely to be an even larger issue in AMFCs than PEMFCs.
Electrocatalysis in High pH Environments	Oxygen reduction under basic conditions using high-performance, durable, non-precious electrocatalysts has been reasonably demonstrated, leaving anode catalysis as the primary concern in stark contrast to acidic systems.
MEA Issues	The most promising AMFC performance and durability reported to date has focused on H_2 as a fuel, and is now commonly achieved without the addition of free electrolyte. Performance of single cells has increased significantly with ~500 mW/cm^2 performance reported and durability in the thousands of hours.
System Issues	System issues will depend on system-specific requirements, but work in this area is necessary to determine how much improvement is needed in each of the other areas to produce viable devices. CO_2 from air or fuel has a major impact on system design and performance.

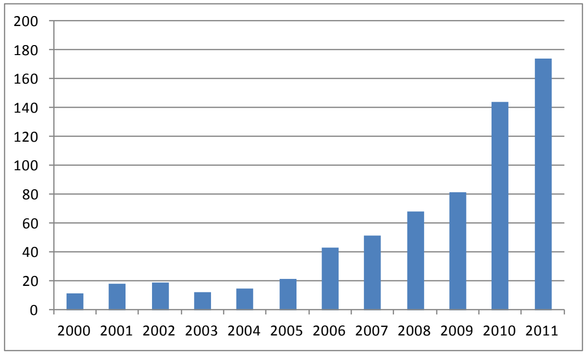


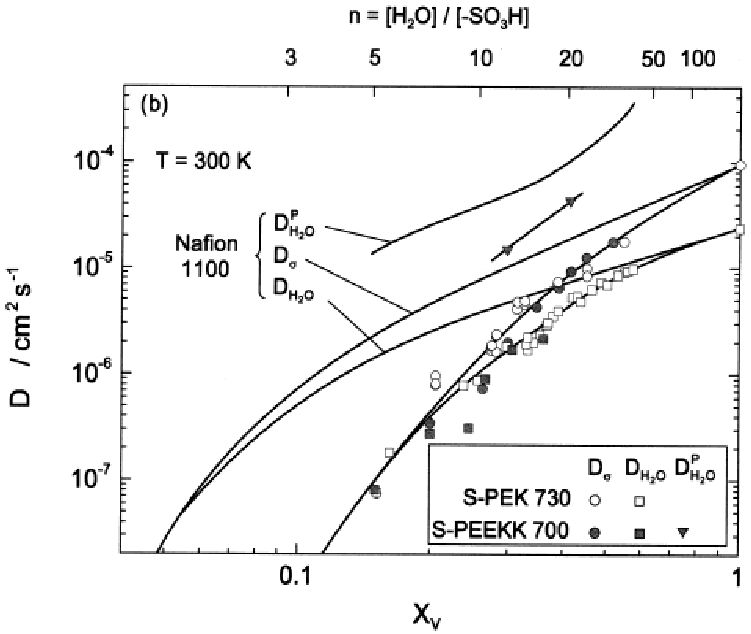
Figure 1. Publications with "alkaline membrane" and "fuel cell" from the ISI Web of Science search engine

http://www1.eere.energy.gov/hydrogenandfuelcells/wkshp_alkaline_membrane.html

Approach

Perfluoro (PF) Anion Exchange Membrane (AEM) Materials

The team will focus on achieving **higher-temperature, higher-power-density AMFC operation** through implementation of **novel alkaline perfluoro (PF) membranes and ionomeric dispersions**. The PF materials proposed are expected to enhance water transport capabilities and electrode performance/durability significantly, thereby enabling higher temperature and power density operation. The combination of high current density and operating temperature will improve the ability of these devices to tolerate ambient CO_2, potentially enabling complete tolerance to ambient CO_2.



Kreuer, K.D., et al., Chemical Reviews, 2004. **104**(10): p. 4637-4678

Most AEMs are based on hydrocarbon polymer chemistry. From significant work in the area of PEMs, water transport has been shown to be **significantly higher in PF polymers**, particularly at lower hydration levels.

Approach

Targeting high temperature operation

Why

- Performance and CO_2 (self-purge) significantly improved at increased T.

Concerns

- Stability of AEMs are an issue even at lower T
- Water management more "difficult" in AEMs and AEMs have a strong dependence on hydration

80°C as a target temperature

- Short term data suggests that CO_2 tolerance (self purge) and power density are adequate at 80°C for short periods of time until cells dehydrate. Higher T's too difficult to keep hydrated, lower T's have too high of a CO_2 solubility and decreased performance.

Background

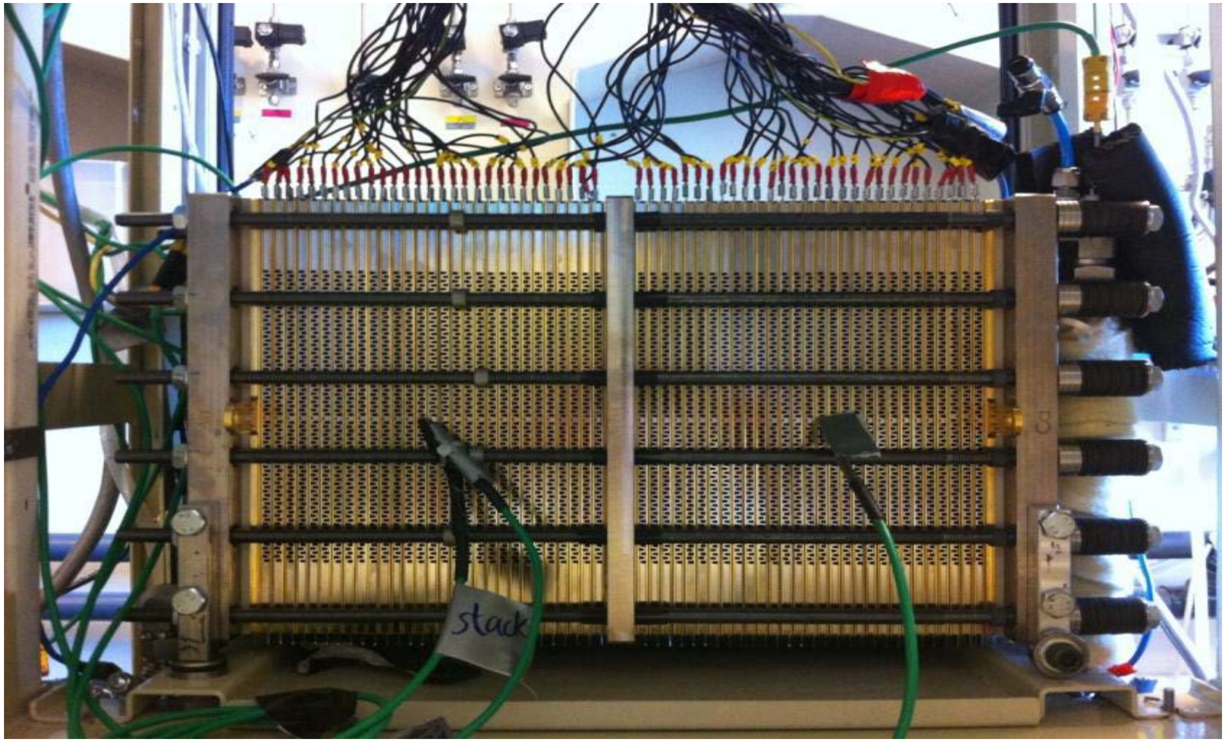
2.8 kW(gross) power AMFC Stack(CellEra)

Air cooling by fan;

No liquid electrolyte;

Elimination of Pt catalyst made possible ;

Hardware of low cost per kW



CHALLENGE

Further Increase Power Density by factor 2

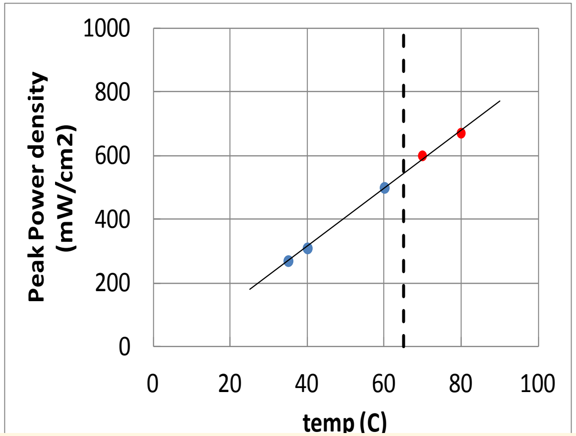
TO BE ADDRESSED IN THIS PROJECT BY NEW FAMILY OF OH- ION CONDUCTING IONOMERS WITH PER-FLUOROCARBON BACKBONE

- Length of 60 cell, air cooled stack = 21”
- Testing at Cellera for over 200 hours including stop/restart cycling -- completed
- Advanced preparations for first field test -- ongoing

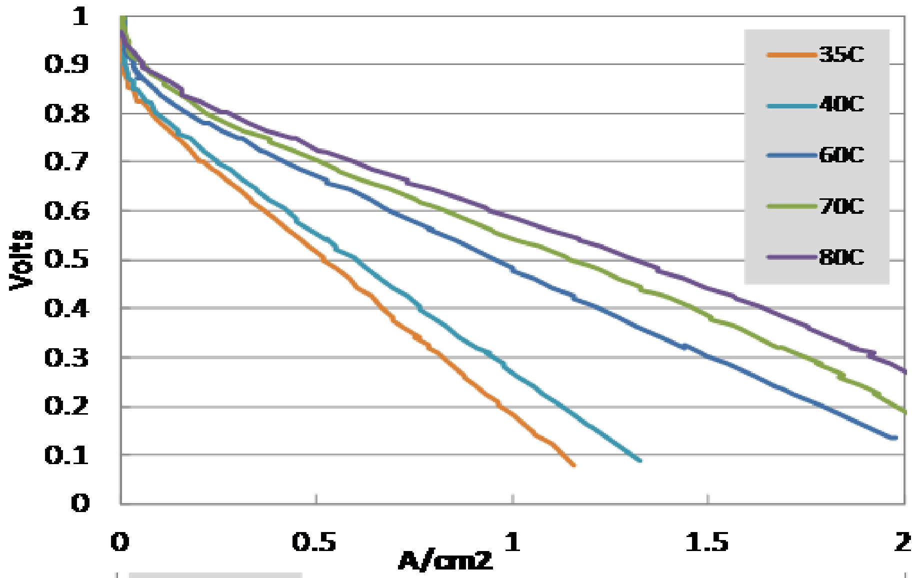
Background

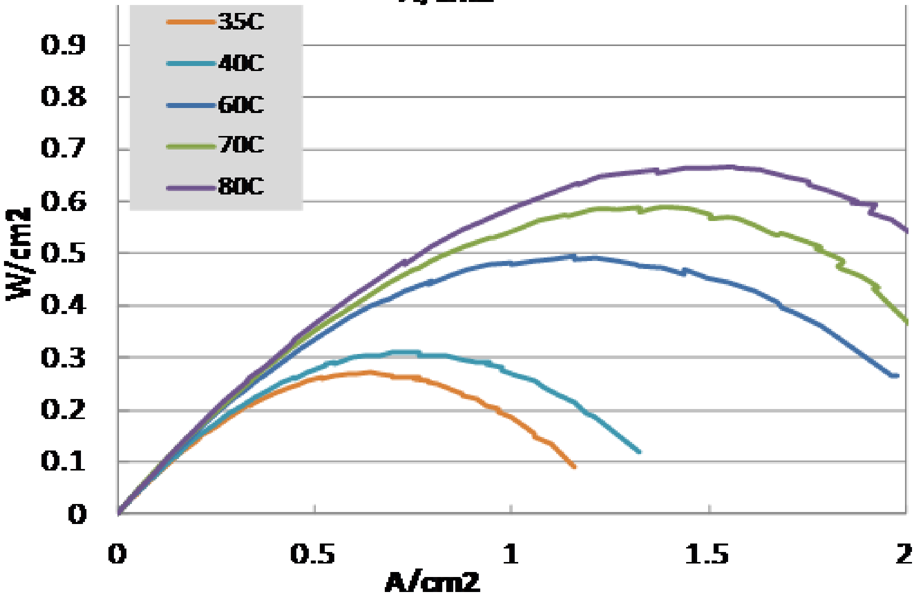
State-of-the-art AMFC Performance (CellEra)

- ✓ AMFC peak power is expected to rise by 40% when ionomer of better chemical stability allows to operate at 80°C
- ✓ A significant part of AMFC loss at present is apparently caused by limited water transport rate through the ionomeric membrane
  - both above aspects are to be addressed in this project



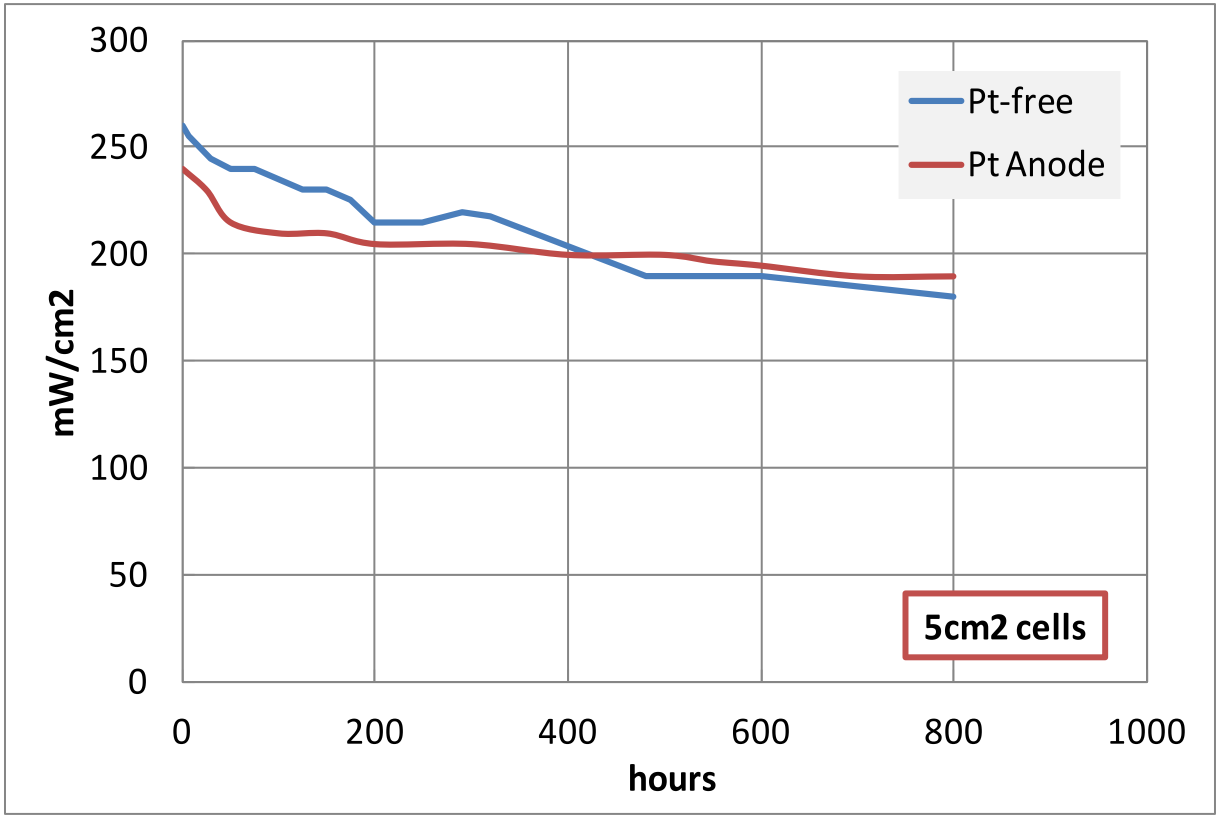
Temperature limit of stable operation (end 2012) designated by dashed line





Background

Pt-free AMFC operation (CellEra)

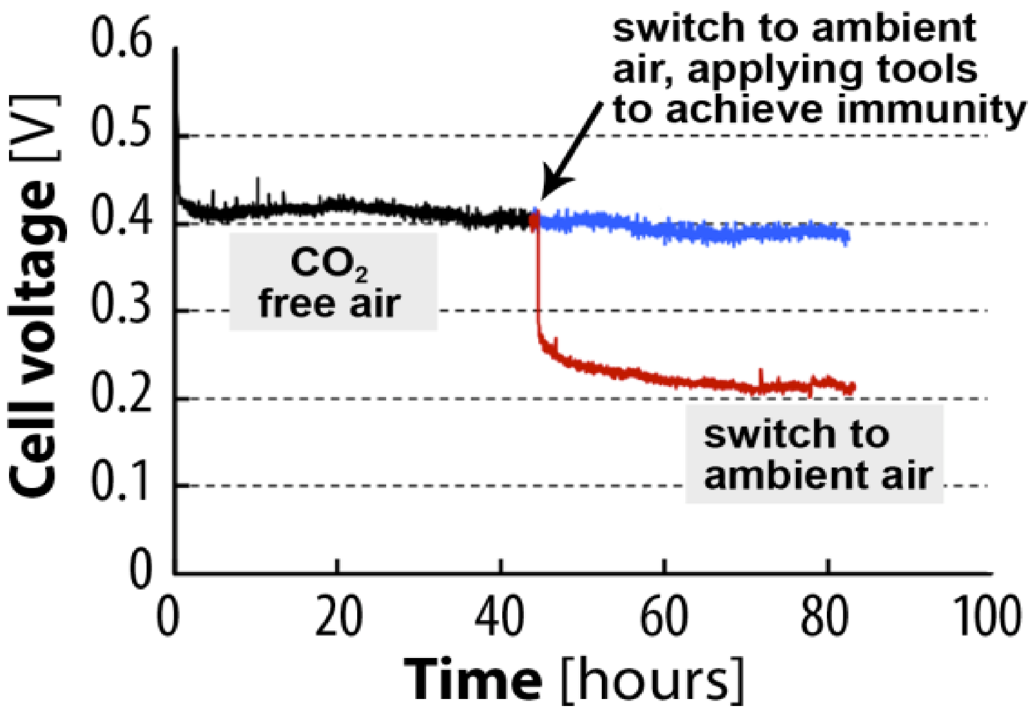


- **Achieving Pt-free CCMs of "Pt-like" performance , as seen above , required efforts centered on the AMFC anode. The cost of the components of the non-Pt catalyst generating this "Pt-like" performance, is estimated at 15$/kW , with room left for further cost reduction**

Background

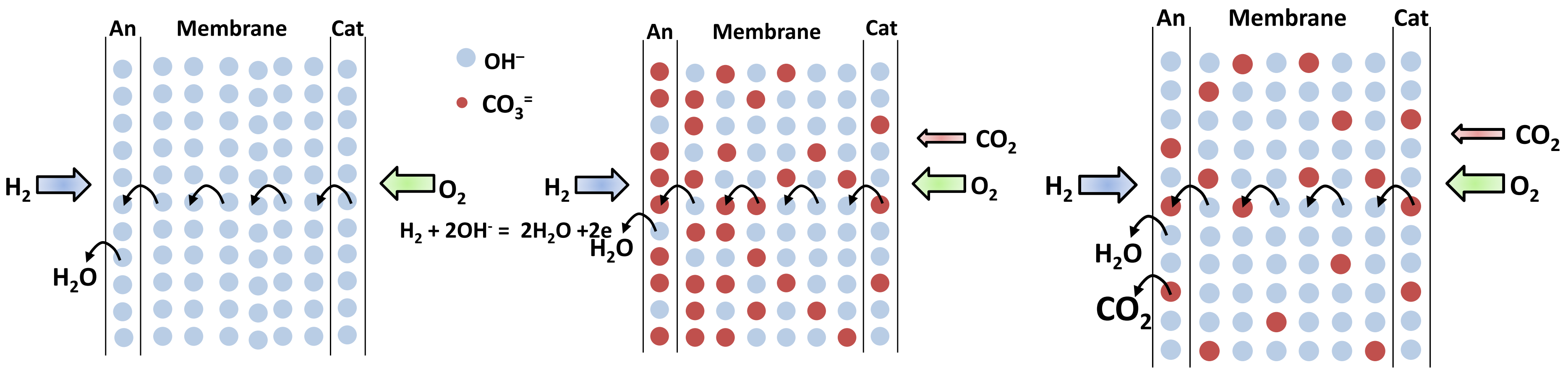
Impact of Ambient CO_2 (CellEra)

- Under specific conditions (50°C, fixed current density), cell voltage can decrease by 50% in the presence of ambient CO_2.
- These losses can be mitigated using system approaches at specific cost.
- Higher temperature operation can avoid or reduce these associated losses, by self purging of CO_2 from the AMFC.



Background

“Self-Purge” of Ambient CO_2



(1) CO_2 –free Cathode Feed

(2) Cathode Feed Has CO_2
Low temperature
Low current density

(2) Cathode Feed Has CO_2
High temperature
High current density

- High temperature can reduce CO_2 solubility within the membrane, higher current operation can reduce build up of CO_2 in membrane. Thinner membranes can also aid in CO_2 rejection.

Background

Perfluoro (PF) Anion Exchange Membrane (AEM) Materials

United States Patent [19]

Matsui et al.

[11] **Patent Number: 4,659,744**

[45] **Date of Patent: Apr. 21, 1987**

[54] **FLUOROCARBON ANION EXCHANGERS AND PROCESSES FOR THEIR PREPARATION**

[75] Inventors: **Kiyohide Matsui**, Sagamihara; **Yoshiyuki Kikuchi**, Tokyo; **Tamejiro Hiyama**, Sagamihara; **Etsuko Tobita**, Urawa; **Kiyosi Kondo**, Yamato; **Akira Akimoto**, Hohfu; **Toru Seita**; **Hiroyuki Watanabe**, both of Shin-nanyo, all of Japan

[73] Assignees: **Toyo Soda Manufacturing Co., Ltd.**, Shin-nanyo; **Sagami Chemical Research Center**, Tokyo, both of Japan

[21] Appl. No.: **624,029**

[22] Filed: **Jun. 25, 1984**

[30] **Foreign Application Priority Data**

Dec. 28, 1982 [JP] Japan 57-227443

[51] **Int. Cl.**[4] **B01J 41/14**; C08F 8/02

[52] **U.S. Cl.** **521/32**; 525/326.2; 525/326.4

[58] **Field of Search** 526/243; 521/32, 25, 521/31, 38

[56] **References Cited**

U.S. PATENT DOCUMENTS

2,801,224	7/1957	Greer	521/32
3,969,285	7/1976	Grot	526/243
4,081,349	3/1978	Hora et al.	521/32
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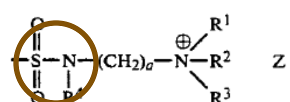
4,085,071	4/1978	Resnick et al.	521/32
4,093,568	6/1978	Seko et al.	521/32

Primary Examiner—Joseph L. Schofer
Assistant Examiner—Peter F. Kulkosky
Attorney, Agent, or Firm—Oblon, Fisher, Spivak, McClelland & Maier

[57] **ABSTRACT**

A fluorocarbon anion exchanger which is composed of a fluorocarbon polymer comprising a perfluorocarbon main chain and a pendant chain attached to the main chain, characterized in that the pendant chainhas a terminal group represented by the formula:



(I)

5 Claims, No Drawings

Sulfonamide linkage

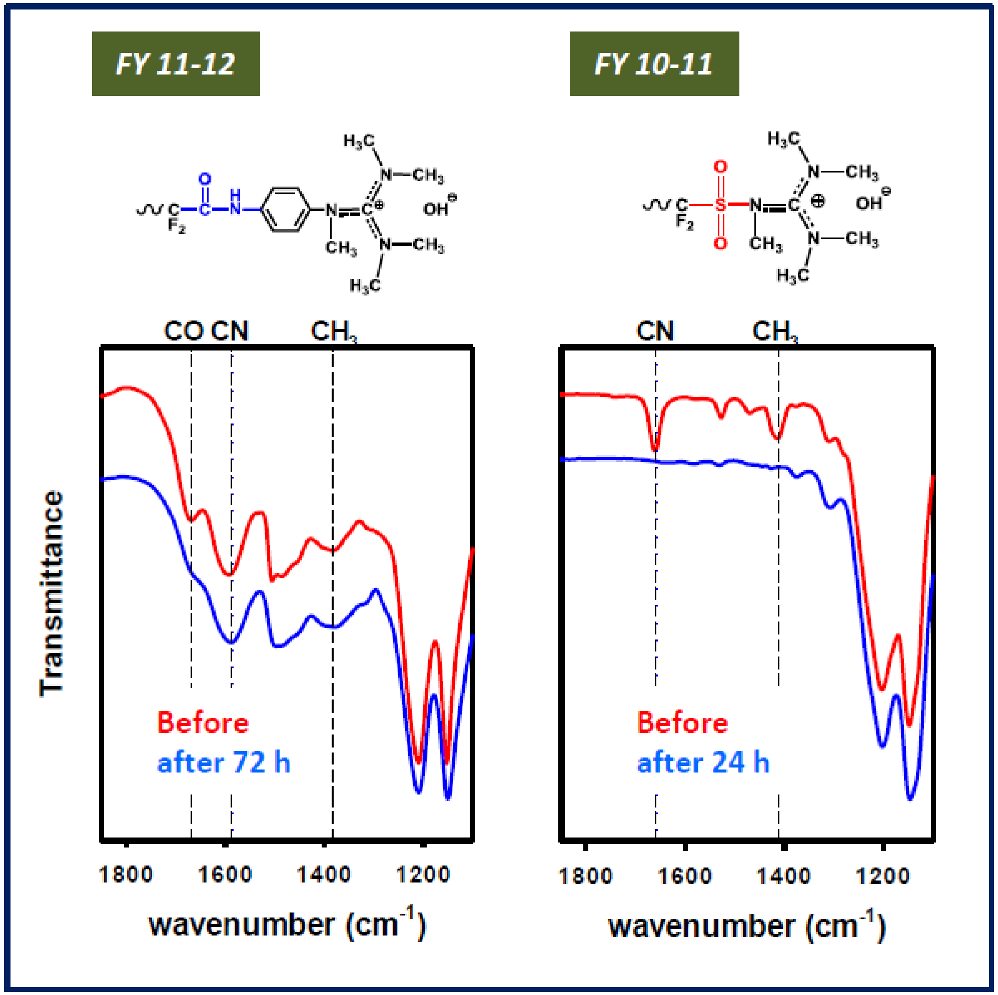
PF AEM materials were first reported in the mid 80's by Toyo Soda.

Tosflex® was a commercial membrane available for purchase in the 90s.

Many cation modifications had been reported, but chemistries were limited to a sulfonamide linkage from the sulfonyl fluoride precursor form.

Background
Perfluoro (PF) Anion Exchange Membrane (AEM) Materials

Stability after soaking in 0.5 M NaOH at 80°C



LANL has recently investigated guanidium as a cation for inclusion into PF AEMs.

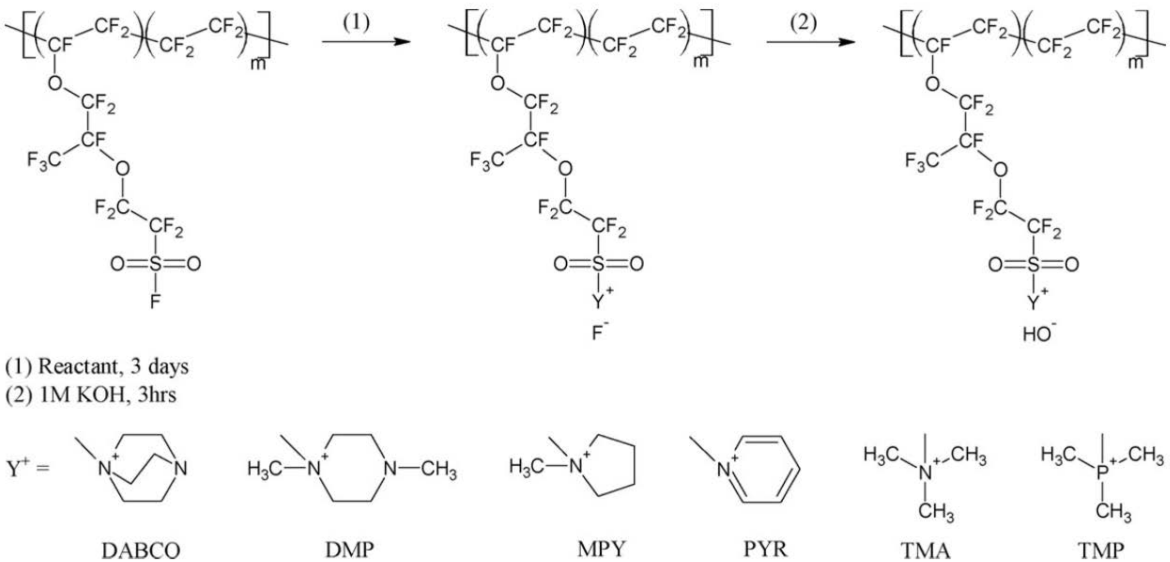
Sulfonamide linked systems showed poor base stability.

PF materials were a limited subset of the materials investigated. Two linking chemistries were presented, with only a single cation. A limited amount of data is available regarding these materials (including water transport data which were not a key focus of these studies).

Acidic proton of the amide link appears to have increase stability but may have resulted in non conducting membrane.

http://www.hydrogen.energy.gov/pdfs/review12/fc043_kim_2012_p.pdf

Background
Perfluoro (PF) Anion Exchange Membrane (AEM) Materials



Scheme 1. Synthesis of Nafion-based AEMs with various cations.

Salerno and Elabd, J. APPL. POLYM. SCI. 2013, DOI: 10.1002/APP.37874

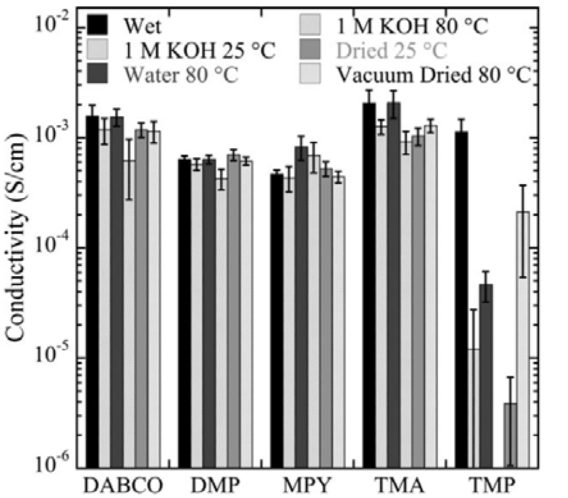


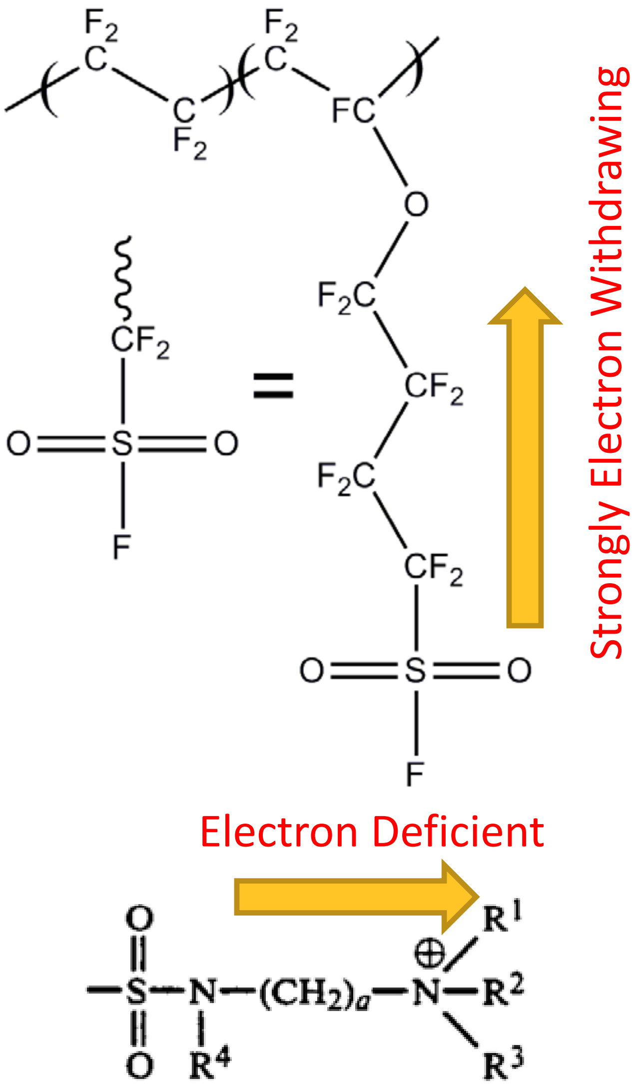
Figure 6. Chemical stability measured by through-plane ionic conductivity of hydrated AEMs after exposure to various conditions for 24 h.

Very recent work at Drexel investigated PF AEMs with direct linkages of the cation to the highly electron withdrawing fluorinated sidechains.

The most relevant durability conditions reported were for 80°C, but only 24 hours.

Background

Perfluoro (PF) Anion Exchange Membrane (AEM) Materials



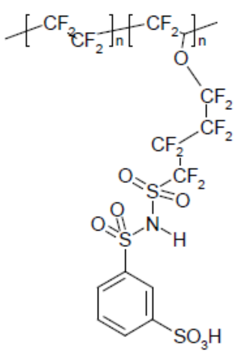
We start with the sulfonyl precursor form (SPF) of a perfluorosulfonic acid (PFSA) polymer. As it is readily available and can be modified through several chemical approaches.

The high electron withdrawing character of the PF backbone and side chain is ideal for proton exchange membrane fuel cells, as it makes acids more acidic and can be used to form chemically stable covalent linkages.

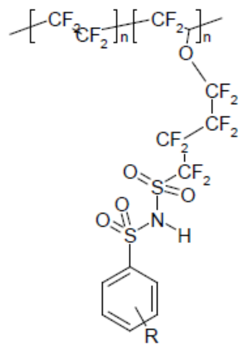
For PF AEMs, the high electron withdrawing character of the polymer is a challenge as it makes bases less basic and can result in low stability chemical bonds.

Background

Perfluoro (PF) Anion Exchange Membrane (AEM) Materials

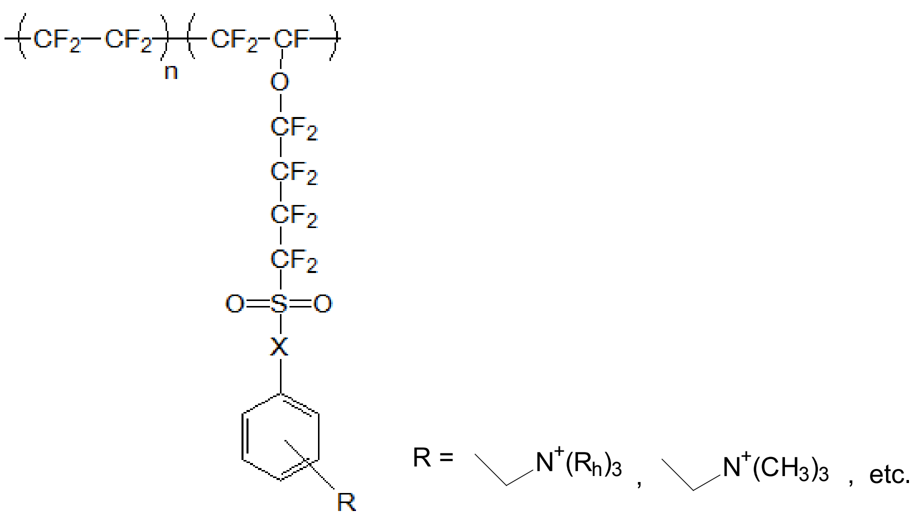


Meta bis acid



A variety of other Polymers have been prepared and evaluated

http://www.hydrogen.energy.gov/pdfs/review11/fc034_hamrock_2011_o.pdf



Our focus in the area of membrane synthesis is the development and application of novel tethering strategies and incorporation of spacer groups to improve stability. We will leverage 3M's vast experience with the modification of PF polymers for acidic ionomers, as well as further advance proven approaches.

These materials will made into membranes and ionomer dispersions that will be used in fuel cell testing.

Collaborations

National Renewable Energy Lab: Bryan Pivovar (PI), Clay Macomber, Dan Ruddy
Role/ Relevant background: AEM technology, advanced cations/tethers, chemical synthesis

3M: Krzysztof Lewinski, Mike Yandrasits, Steve Hamrock
Role/ Relevant background: Perflouro, polymer, dispersion and membranes

CellEra: Shimshon Gottesfeld, Dario Dekel
Role/ Relevant background: Chemical Synthesis

Colorado School of Mines: Andy Herring, Mei-chen Kuo
Role/ Relevant background: AEM MEAs, electrocatalysis, cell/system testing

Work Plan

- **PF Ionomer Synthesis *(NREL/CSM, 3M)***
  - Cation Tethering to SFP through S-N Linkage *(NREL/CSM, 3M)*
  - Development and Application of Alternative Chemistries *(NREL/CSM, 3M)*
- **PF AEMs and Ionomeric Dispersions *(3M, NREL/CSM)***
  - Sub-Task 2a: Membrane Casting *(3M, NREL/CSM)*
  - Sub-Task 2b: Polymer Dispersion Preparation *(3M, NREL/CSM)*
  - Sub-Task 2c: Membrane Characterization *(NREL/CSM, 3M)*
- **MEA fabrication/Fuel Cell Testing *(CellEra, NREL, 3M)***
  - Sub-Task 3a: Water Management and CO_2 Tolerance Studies *(CellEra)*
  - Sub-Task 3b: PF AEM and Ionomeric Dispersions in MEA Fabrication and Fuel Cell Testing *(CellEra, NREL, 3M)*
- **Detailed Assessment of Cost and Manufacturability *(CellEra, 3M, NREL)***

FY 13 Milestone	**Synthesize 3 unique perfluoro anion exchange polymer chemistries from the sulfonyl fluoride form precursor.**	**9/13**