

AMFC Workshop 2016

AMFC Technical Challenges and Status: From Single Cell to Stack System

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From Single Cell to System – Key Challenges

- AMFC Stack

- Selected issues / research needs defined at
2011 AMFC Workshop:

- Optimize operation conditions (basically effective water management)
 - Solution for carbonation issue
 - Higher anode activity
 - Membrane - operation at $T > 80^{\circ}\text{C}$; higher water mobility

- Advancement in state of the art 2011 → 2016

- 200mW/cm² MEA @0.5V →
 - 1000mW/cm² @0.5V (Elbit; [Zhuang *et al.*[1] under O₂])
 - 2kW net stack system →
 - 2kW net system (Cellera 2014)
 - **Presumed 10's of kW system by Daihatsu (albeit KOH-soaked MEA's)**

AMFC Status – Single (well-humidified) Cell

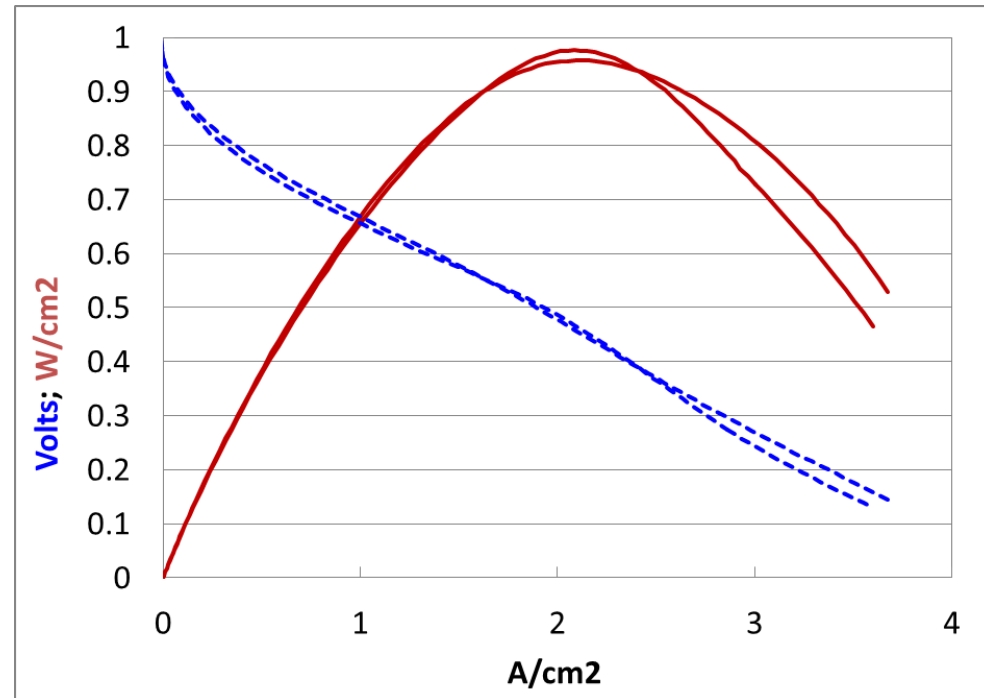
Polarization curve – 5cm² H₂/Air

Pt-free Ca, Pt-catalyzed An;
CO₂-free air

$$T_{\text{cell}} = T_{\text{air}}(\text{humf}) = 75^{\circ}\text{C}$$

$$P_{\text{air}}; P_{\text{H}_2} = 1; 3 \text{ bar(g)}$$

30μm thick, polyhydrocarbon
membrane



- Performance level of Proton Exchange Membrane (PEM) fuel cells is within reach, however:
 - Air humidification and overall water management are critical
 - CO₂ handling adds to system complexity in operation at lower T_{cell}

Selected Issues & Research Needs

- Higher anode activity
- Membrane - operation at $T > 80\text{C}$ / water mobility

- Anode activity: significant progress has been made
 - Near-Pt activity with Pd-based catalyst [2];
 - Pt-containing bimetallics show activity greater than Pt [3];
 - Advances in fundamental understanding of alkaline HOR [4,5]
- Anode challenge today: also substantially **water management**
- Membrane:
 - Tokuyama A201 – technology of ca. 2008 – is still the leading commercial “standard” membrane
 - i.e. “*membrane/ionomer issues*” – including the need for higher operation temperature and higher water mobility – have not been adequately resolved!

KEY BOTTLENECK !

Key System-Level Challenges

- **Water management**
 - *Target* : Operation with no external humidification
 - *Challenge* : Water generation on the fuel side creates propensity for anode flooding and cathode dry-out
- **CO₂ immunity**
 - *Target* : continuous operation with ambient air feed
 - *Challenge*: direct feed of ambient air causes loss of 50% of the power vs. operation on air free of CO₂

- These challenges have been addressed significantly, nevertheless,
- Substantial room remains for further improvement

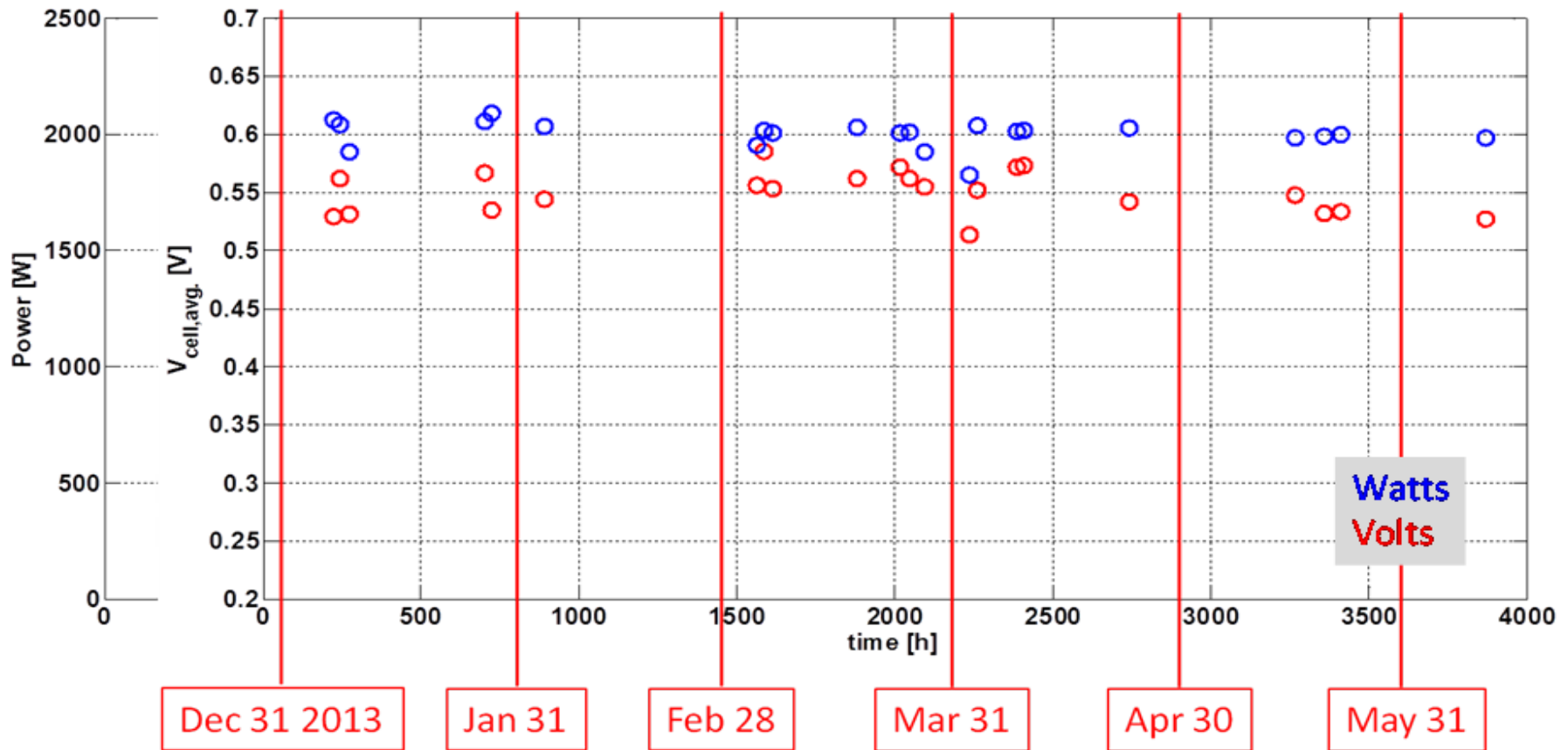
Field-tested 2kW AMFC System (Cellera)



- 6-month 2kW H₂/Air stack-system test
- Live site backup capability
- Aluminum hardware; air-cooled
- Cathode water exchanger / dry anode
- Pressure - ambient air / 1.5bar(g) H₂



AMFC Status – Stack operation

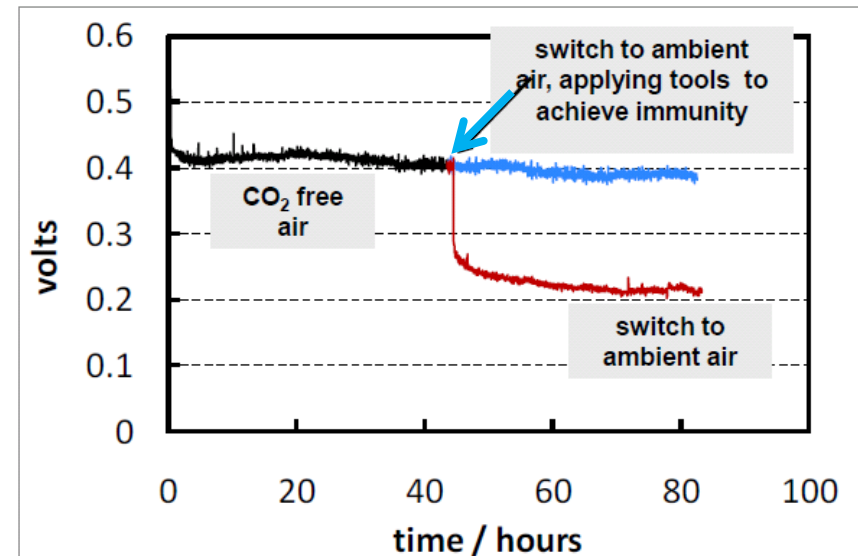


- No measurable degradation over 5000h (intermittent operation)
- Optimized shut-off/restart conditions proved critical

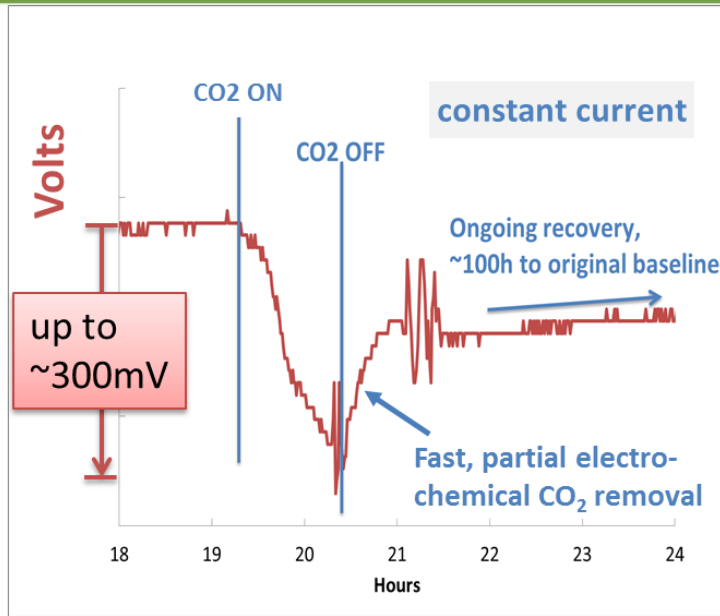
AMFC SYSTEM: CO₂ IMMUNITY

The “CO₂ Immunity” Subsystem

- CO₂ sequestration subsystem upstream the cathode developed and demonstrated at Cellera (now Elbit Systems) [6]
 - Two step process; each lowering the CO₂ level by ~10x
 - Thereby reducing CO₂ in the cathode inlet to <5 ppm
 - First step: Thermally regenerated polymeric active material
 - Second step: completes removal of ~99% of CO₂ with a strongly CO₂-bonding inorganic solid

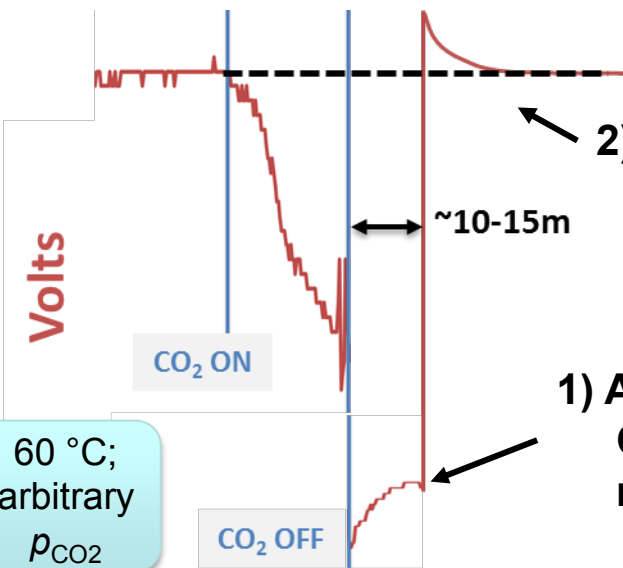


Handling CO2 contamination



Upper plot: Carbonation and de-carbonation (lowering p_{CO_2} under same constant current):

- ~100h to full recovery at any given current
- However: **significant partial recovery in 10's of minutes**
- Lower plot: Applying a current well above operation point: → **effective full recovery at the operation point**



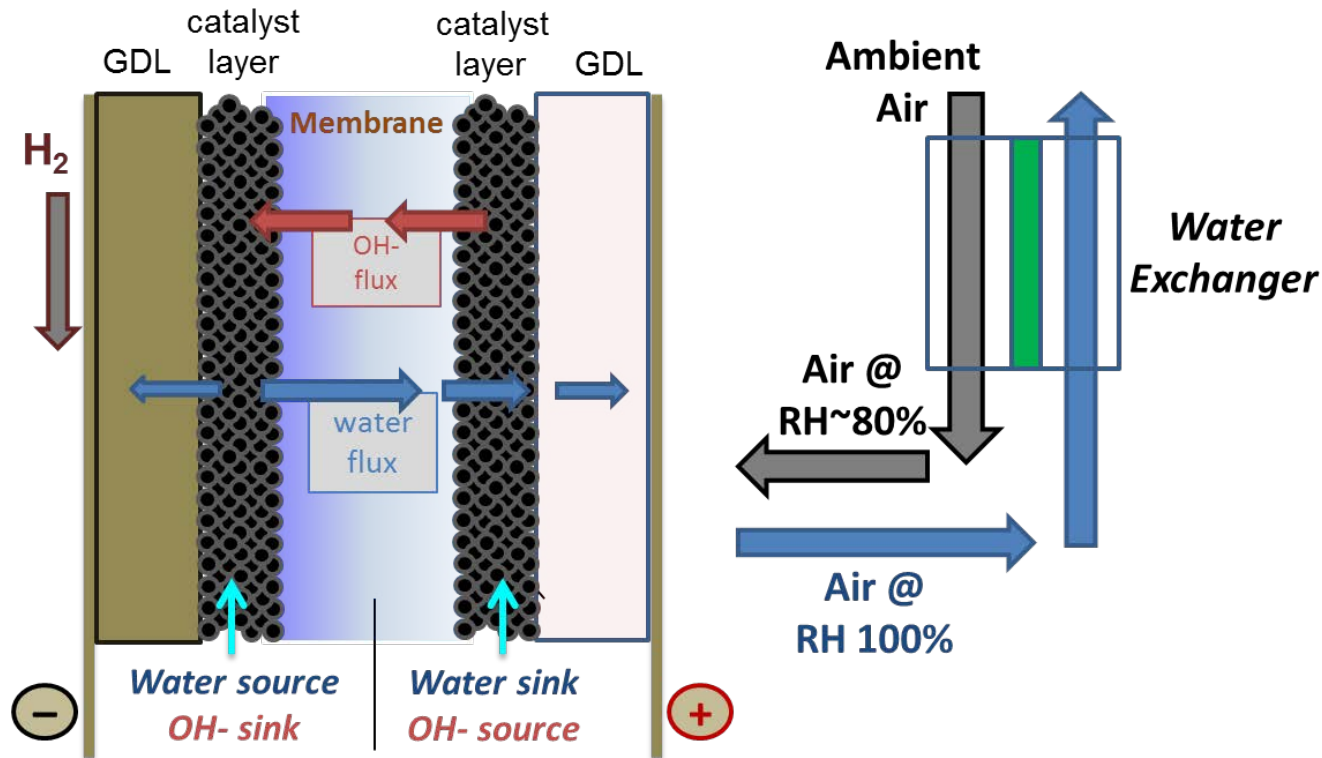
2) Return to original current, and voltage returns quickly to original value

1) At "CO₂ OFF", INCREASE CURRENT: Greater proportion of (H)CO₃⁽²⁾⁻ replaced at the anode by "new OH⁻"

The “CO₂ Immunity” Subsystem

- Corrective measures demonstrated
 - CO₂ sequestration subsystem upstream the cathode
 - De-carbonation within the cell by step of high current
- CO₂ sequestration technology is advancing independent of AMFC:
 - Isotherms with >30% w/w reversible CO₂ capture [7]
 - Improvements in T swing specs
(increasing adsorption T / decreasing desorption T)
- Addressing CO₂ sensitivity - path forward:
 - **Increase operation temperature** to facilitate decarbonation and allow higher “CO₂ slip”

AMFC SYSTEM: WATER MANAGEMENT

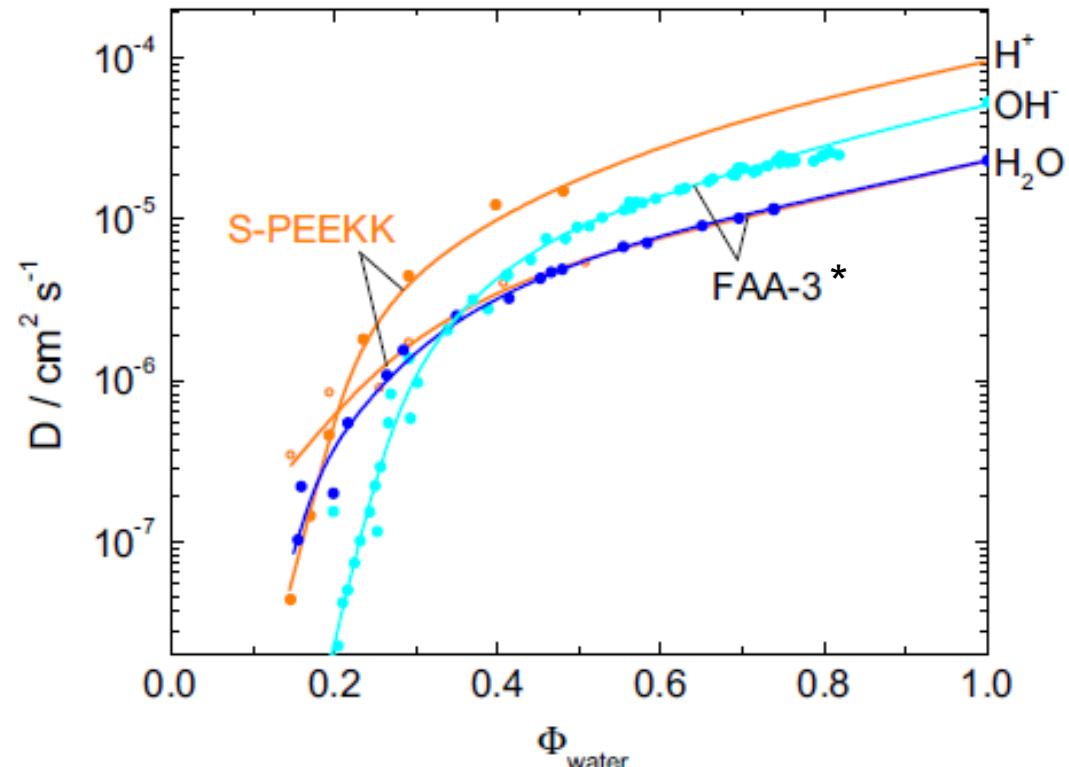


- AMFC Hydration challenge is especially significant because
 - The cathode is actively consuming water and
 - The cathode uses high gas flow (20% O_2 @ 2.0 stoichiometry) which causes substantial removal of water from the cell into sub-saturated air

AMFC System: Loss of water of hydration → strong impact on performance

- Diffusivities of H^+ and OH^- in the ionomer drop substantially with drop in the water content [8]

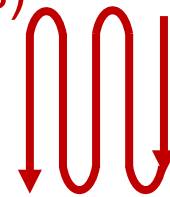
→ **Strong effect of partial dehydration** On conductivity for OH^- ion-conducting ionomers



* (FAA-3 membrane by Fumatech)

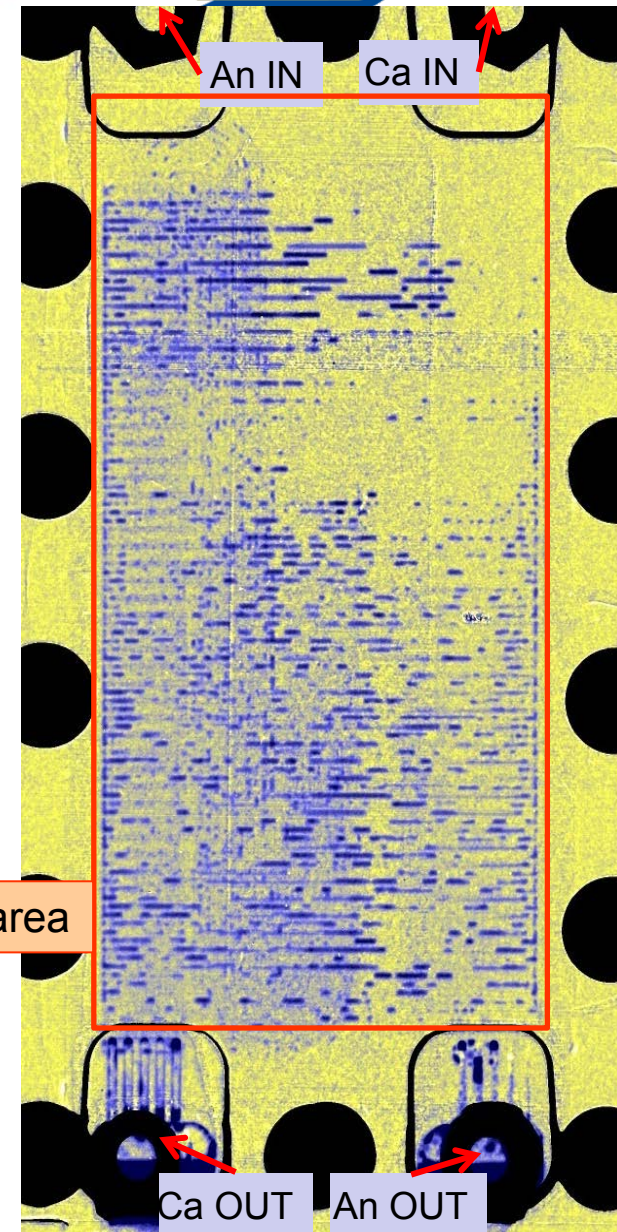
240 cm² Single-cell: Water Imaging

- Neutron Imaging “through-plane” (limited to single cell, giving a full lateral water distribution image)
- Horizontal single channels used for serpentine anode flow field
- Multi-serpentine (11 channels, 5 passes) flow field on cathode side
- Dry H₂; humidified air (80% RH); Cell T = 60°C



Yellow indicates “dry”;
more water → **more blue**

active area



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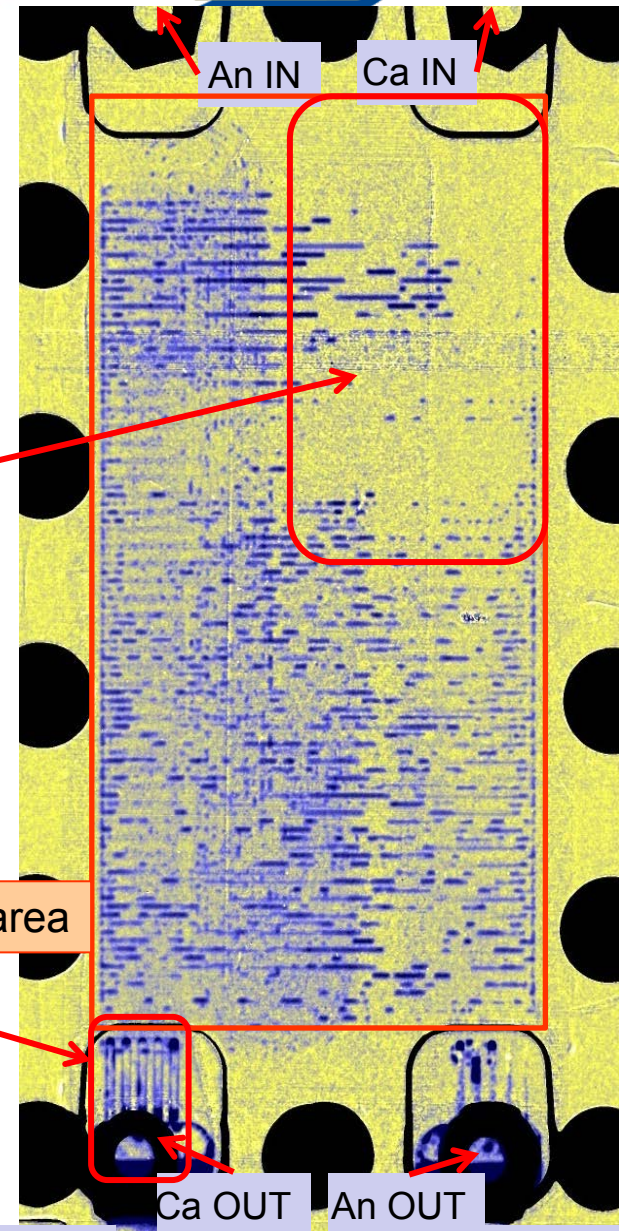
240 cm² single-cell: Water Imaging

- Operation with dead-ended anode and periodic gas purge (3s per 3 mins)

“Dry” section of MEA propagating from Cathode inlet

Excess water removal at Ca exhaust

active area



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Consequences

- Water exchanger on the cathode side is a key component of the AMFC water-management subsystem, **targeting highest dew point** for the cathode inlet
- **Fast rate of water transport** across the cell membrane into the cathode is critical for high AMFC performance

RESEARCH NEEDS

Membrane/ionomer upgrade is a key system requirement

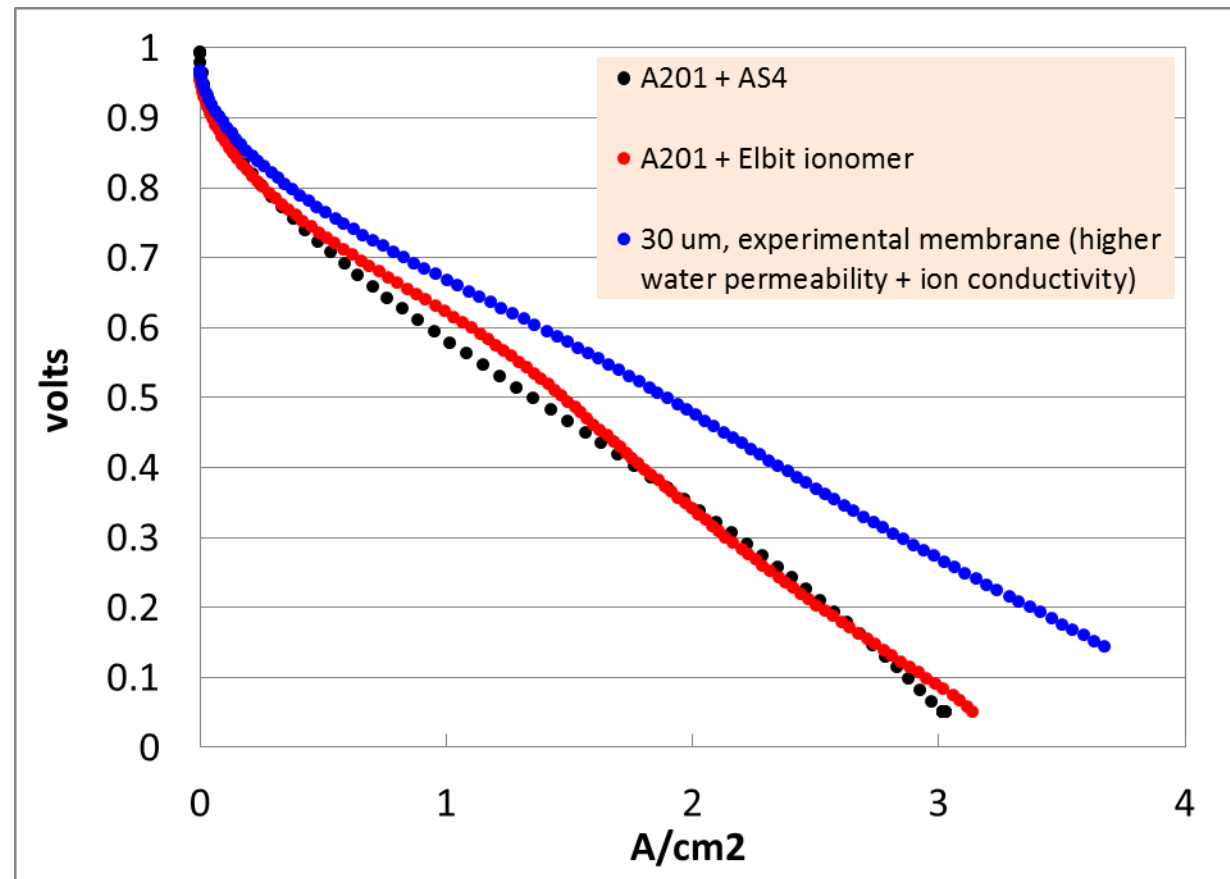
- [increase T_{cell}] × [decrease t_{mem}] × [increase σ_{ion}]
- With the main (system) benefits being:
 - **Facilitated water management**
 - **Reduced CO₂ filtration requirements**
- Obtained by
 - $\leq \sim 15 \mu\text{m}$ thick membranes of good mechanical integrity
 - Higher ionomer/membrane stability at 80 °C+

Influence of the membrane on AMFC performance

- Performance increase from optimized membrane properties (IEC/ion conductivity, water transport):

- Improved membrane characteristics play a significant role

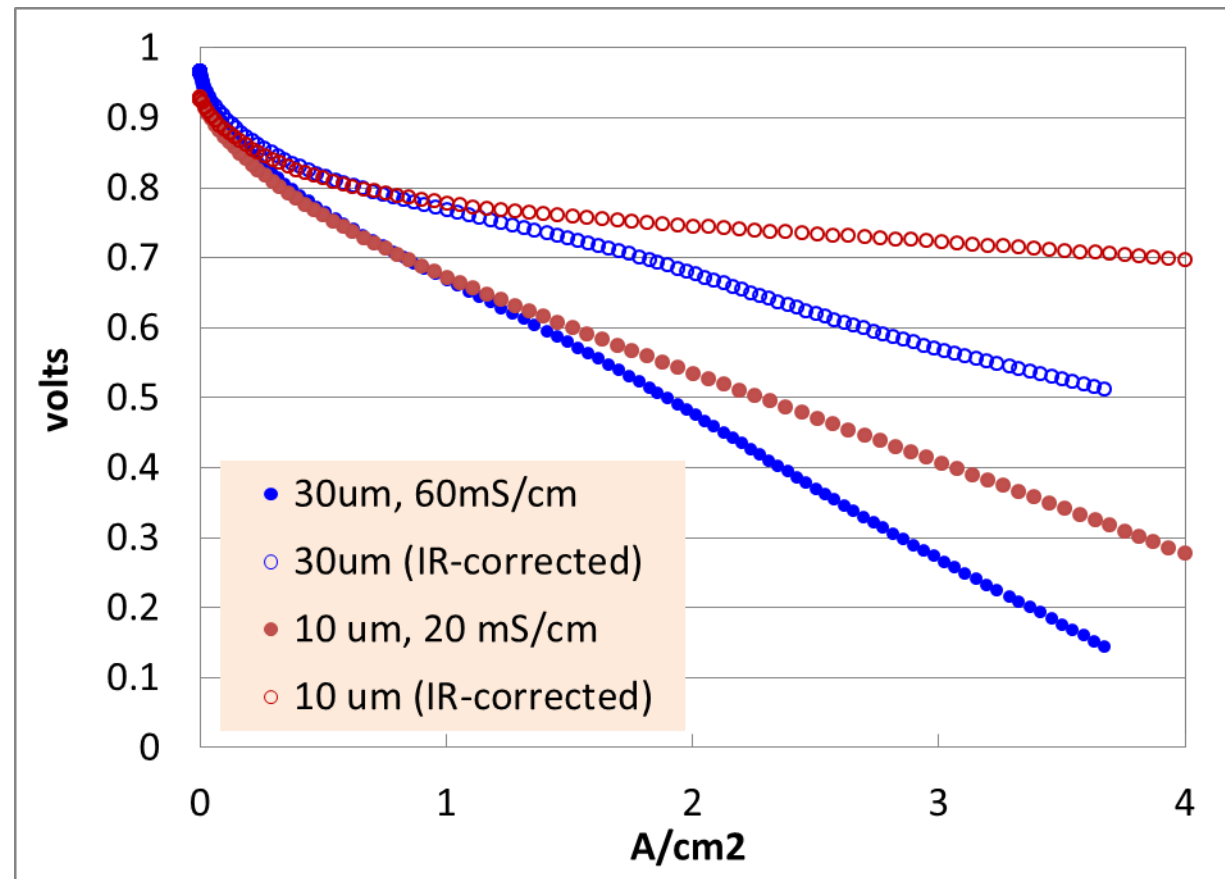
- Single cell / 5cm²
- Full Ca humidification
- 75C



Influence of the membrane on AMFC performance

- 30 micron membrane, ~ 60 mS/cm (OH⁻ at 75C)
- 10 micron membrane, ~ 20 mS/cm (OH⁻ at 75C)

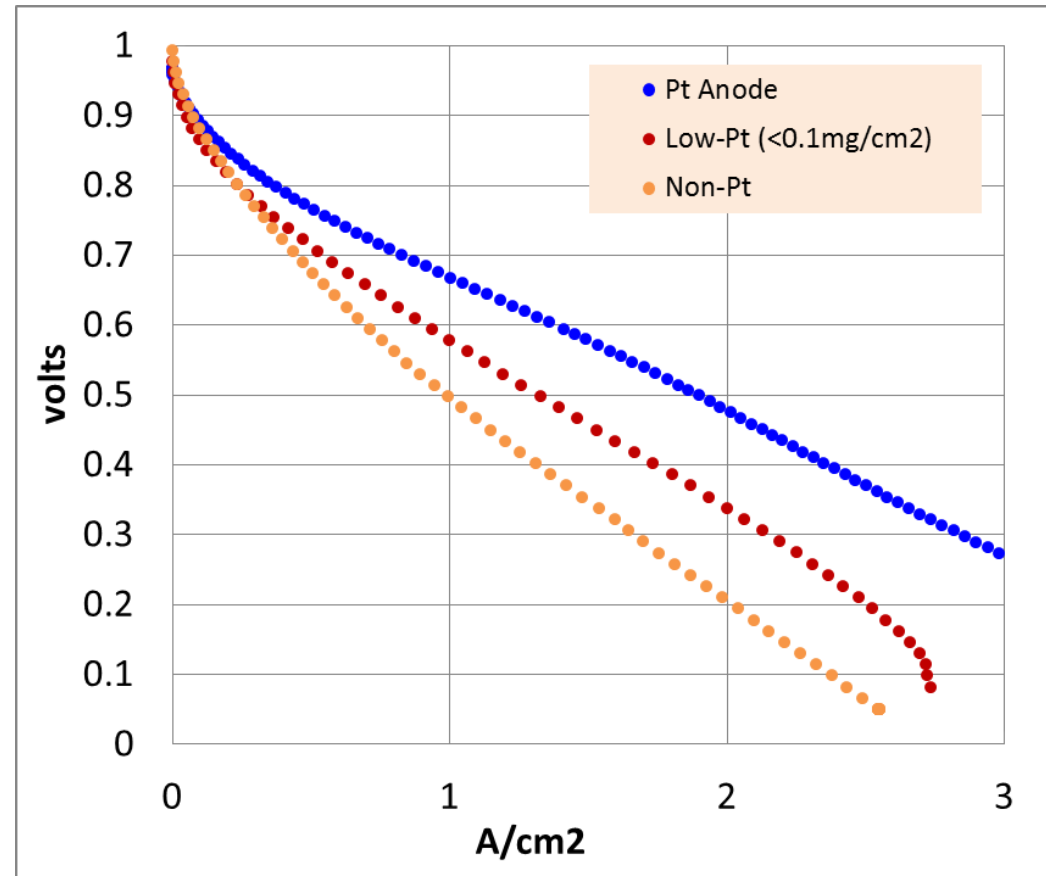
- **Thin membrane is potentially more beneficial than simple increase in conductance**



AMFC performance recorded with different anode catalysts

- Consequences of advancing to the low-cost AMFC anode – arising from low anode catalyst activity together with low catalyst utilization [9] and limited rate of H₂ access in a “flooded” anode*

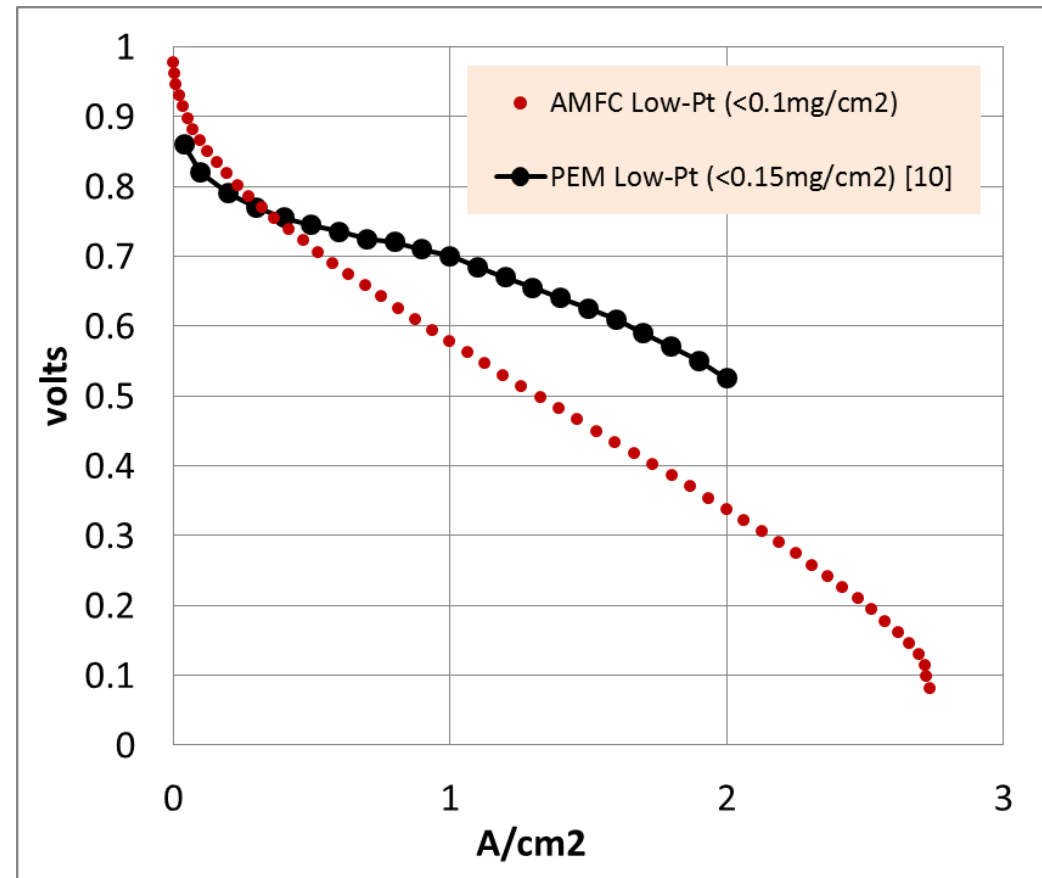
- Single cell / 5cm²
- Full Ca humidification
- 75C
- 30 micron membrane



* Reminder: 2x water generation rate

Present performance of AMFC and PEMFC of low cell Pt loading

- Performance boost still needed to match low-Pt PEM cells
- Membrane improvements can certainly help, but improved intrinsic activity and novel catalyst layer structures are clearly required



Concluding Remarks

- Primary goal today *from the system point of view* is:
Minimize the complexity and cost of applying system fixes to problems caused by materials properties limitations
- Reduce cathode dry-out losses through better internal water transport characteristics
- Allow higher temperature operation with advanced membranes which combine high T tolerance, water permeability and conductivity

Acknowledgements

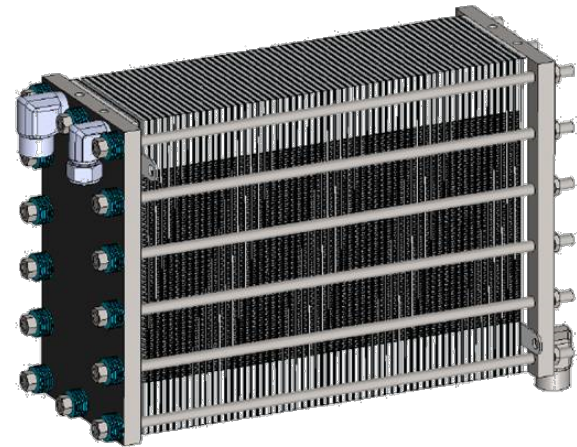
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