Development of PGM-free Catalysts for Hydrogen Oxidation Reaction in Alkaline Media

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Overview Slide

- **Timeline**:
  - Start date: 06/01/2015
  - End date: 05/31/2017
  - No cost extension: 08/31/2017
  - PI change is approved: New PI is Prof. Plamen Atanassov
- **Budget Data**:
- Total Project Value: $ 759,998 (Federal), $ 250,000 (cost share); Total $ 1,009,998
- Cost Share Percentage: 33%
- Total Funds Spent*: $ 601,778

  * On 04/01/2017
- **Barriers/Targets:**
  - Activity (catalyst, RDE, MEA)
  - Integration in MEA (catalyst, ionomer)
  - Manufacturability (catalyst, ionomer, MEA)

- **Partners and PIs**

Los Alamos National Laboratory, Los Alamos: Dr. Yu Seung Kim

EWII Fuel Cells LLC, Albuquerque: Ms. Madeleine Odgaard

Pajarito Powder LLC, Albuquerque, Dr. Barr Halevi

Relevance: Objectives and Targets

- **Objectives:** Development of PGM-free electrocatalysts for HOR in alkaline media; the catalysts will be scaled up to 50 g batches; a new type of ionomer for AEMFC will be synthesized and full integration of PGM-free catalyst with ionomer into the MEA will be performed.

- **Relevance to DOE Mission:** This will enable integration of the PGM-free anode materials into the optimized MEA structure. It can be expected that performance of PGM-free based AEMFC will be significantly improved ca. peak power density up to 250 mW cm^{-2}.

- **Targets**
  - RDE peak current density > 1 mA cm^{-2}
  - RDE current density at 0.01V > 0.085 mA cm^{-2} (1st Go-no-Go)
  - **MEA peak current density 250 mW cm^{-2} (H_2/O_2 configuration) – 2nd Go-no-Go design point**

Approach: Technical Details

- **Overall technical approach:**
  - **Comprehensive materials development strategy encompassing:**
    - Novel new catalysts for Hydrogen Oxidation Reaction in alkaline media
      - High Performance Catalysts
      - Tailored Catalysts for Understanding Structure Property Relationships
    - Controlling Metal/Alloys support interactions
      - Efficient mass transport of charged and solute species
    - Ensuring Stability via careful control of reaction center's electronic structure
  - **Synthesis of novel alkaline exchange ionomers**
    - Development of several synthetic approaches (copolymerization, chloromethylation, etc.)
  - **Scaling Up the catalyst synthesis**
    - Technology transfer from small lab-scale batches to 50 g batch level
    - Inter-batch reproducibility on the level of 10% by activity
  - **Integration of scaled-up catalysts and ionomers into AEMFC MEA**
    - Influence of additives onto MEA performance
    - Design of catalyst layers by deposition method
- **Program Technical Barriers and Approach to Overcome them:**
  - **Meeting and Exceeding Program Activity Target of HOR in a fuel cell tests of peak power density – 250 mW cm^{-2}.**
    - (a) Development of new classes of materials
    - (b) Scaling-up the technology
    - (c) Understanding mechanism of HOR electrocatalysis
    - (d) Integration of electrode materials into high-performance MEAs

Approach: Milestones

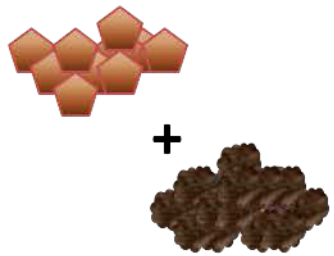
Date	Milestone	Status	Comments
March 2016 (PPC)	Scale-up of UNM synthetic approach up to 50g batches - Match physical-chemical characteristic of UNM catalysts	100% completed	Materials were synthesized and characterized by SEM, TEM, XRD, BET and XPS
September 2016 (LANL)	Preparation of fluorinated ionomer dispersion - Conductivity: > 10 mS/cm at 80°C at 100% RH	100% completed	Ionomers synthesized on the level of 20+ ml and characterized
August 2016 (EWII)	Manufacturing MEA Gen 1 - Peak PD > 50 mW cm^{-2}	100% completed	Gen 1 MEAs made from UNM inks and evaluated
March 2017 (EWII)	Manufacturing MEA Gen 2 - Peak PD > 100 mW cm^{-2}	100% completed	Gen 2 MEAs made from EWII inks and evaluated

Accomplishments and Progress

Synthetic Approach

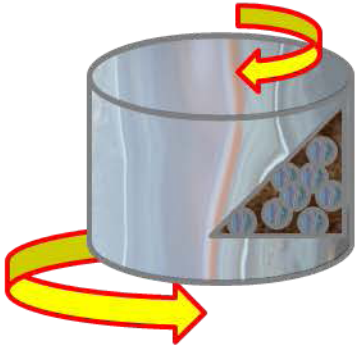
Thrust Area 1: Tasks 1-2 (UNM)

1. Combine solid nitrates and Mo-salt

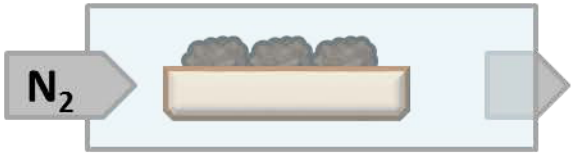


2. Grind

3. Ball mill

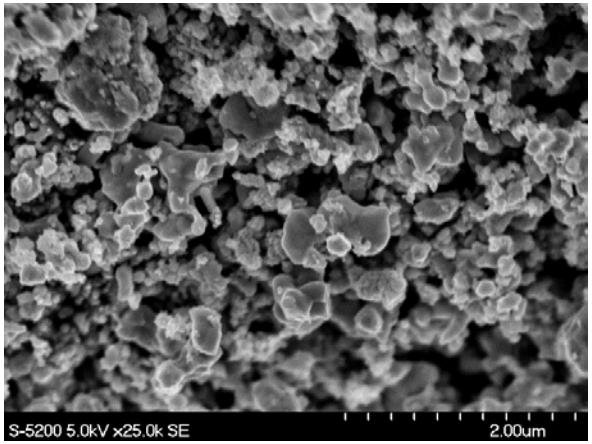


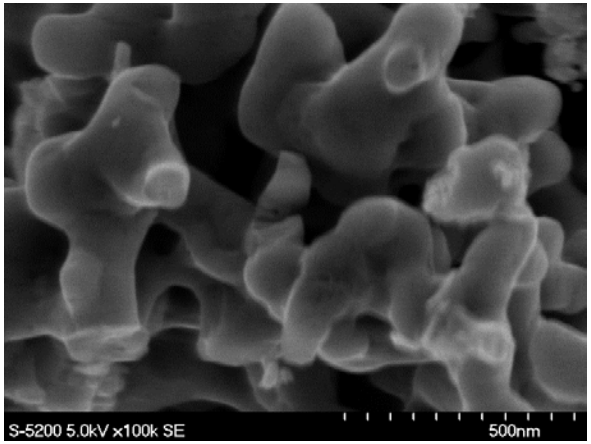
4. Dry at 250 °C for 1 h



5. Reduction at 550 °C for 4 h

NiMoCu material synthesized by SSM

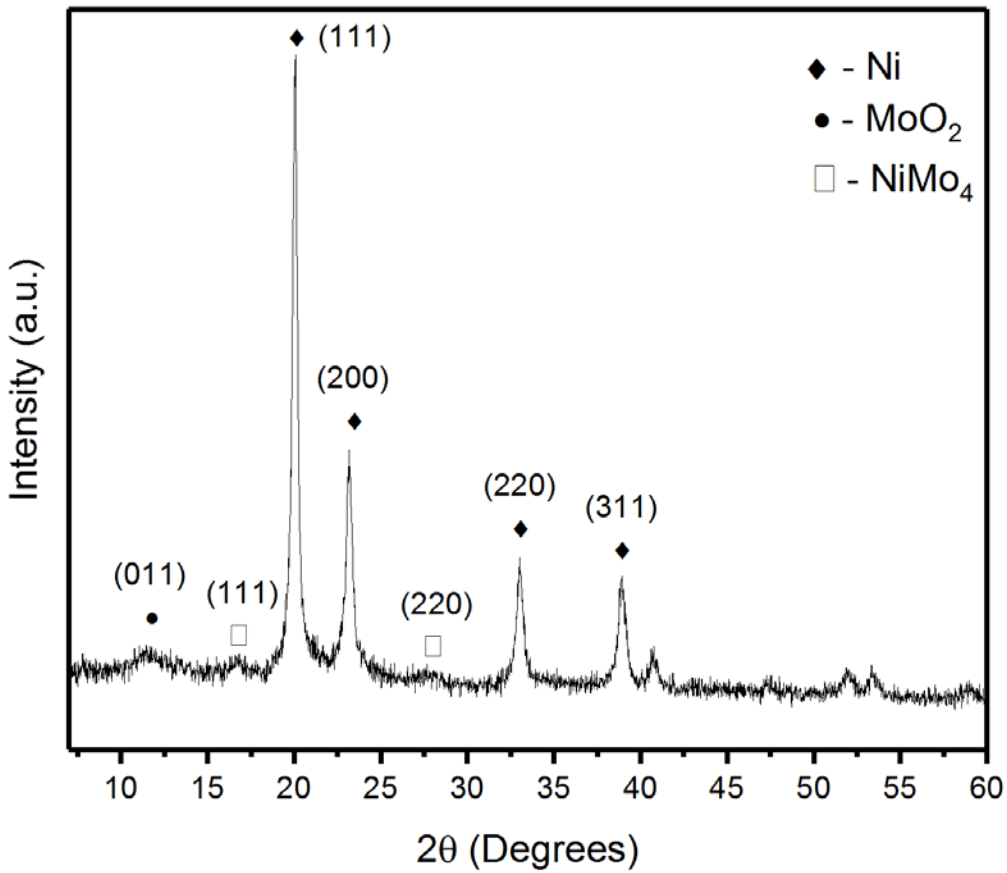


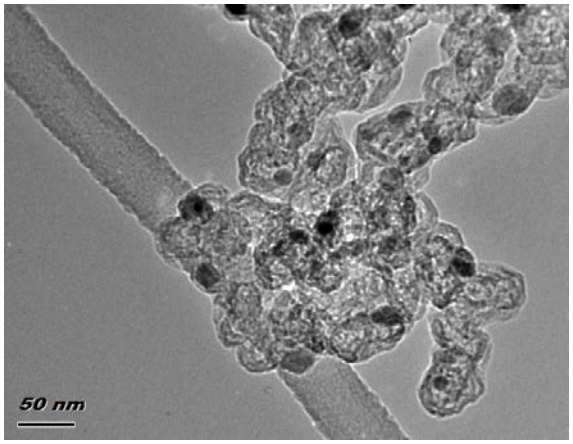


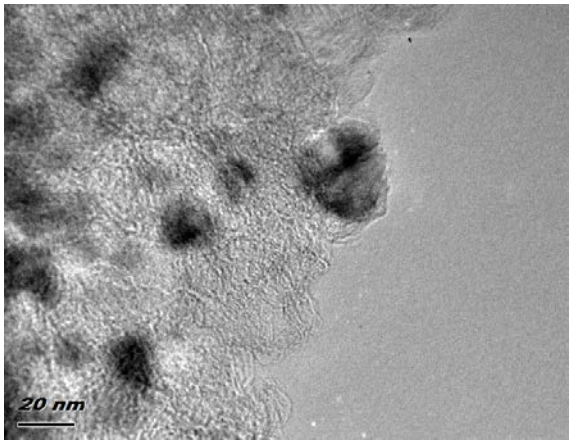
- Materials synthesized
- Characterization done
- Morphology control achieved

Accomplishments and Progress

NiMo-based supported catalysts



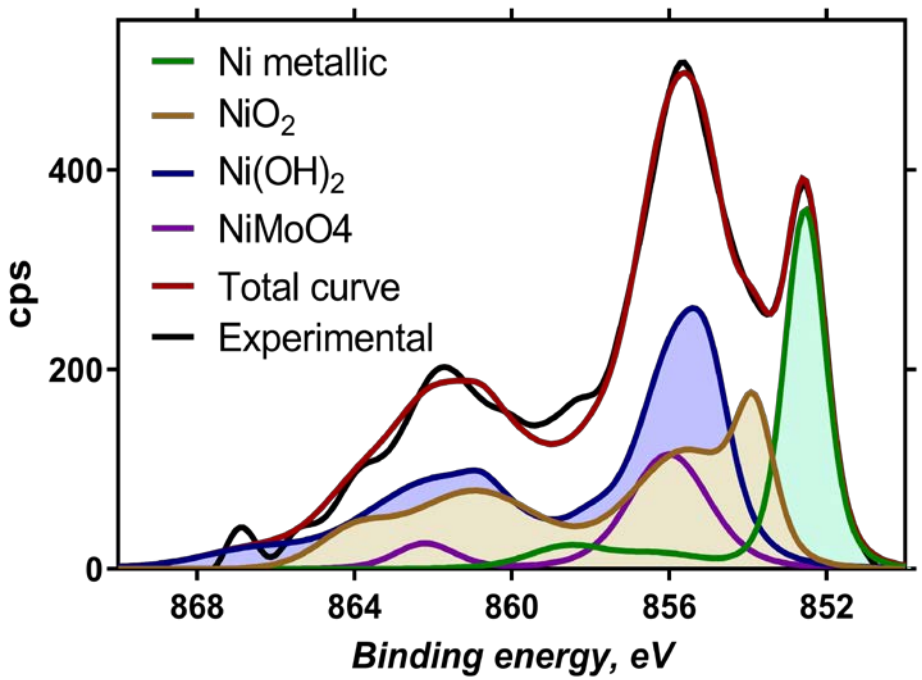


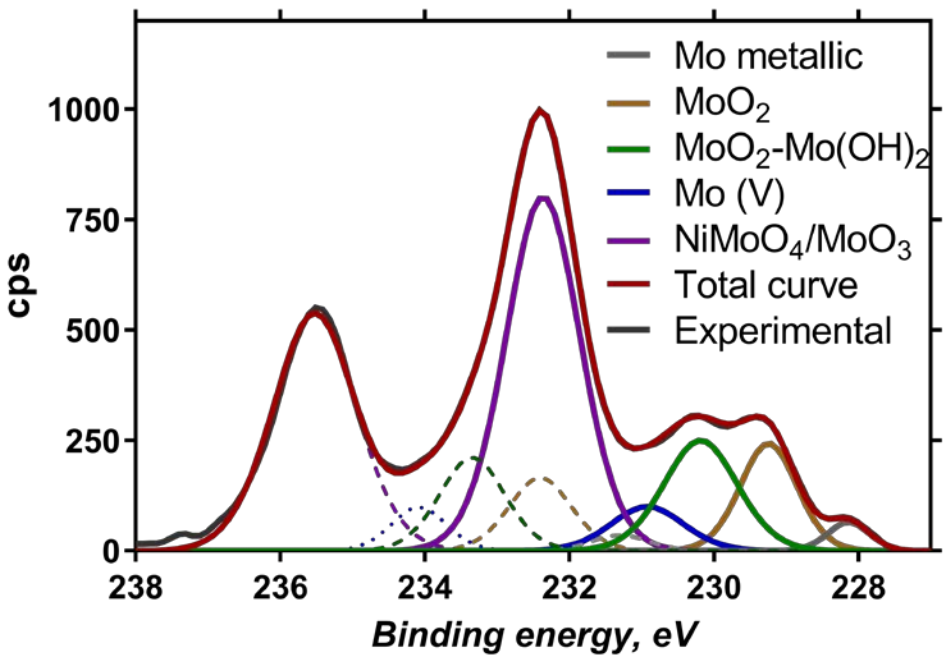


Material is a mixture of NiMo alloys and MoO_2

Accomplishments and Progress

Surface chemistry of NiMo/KB



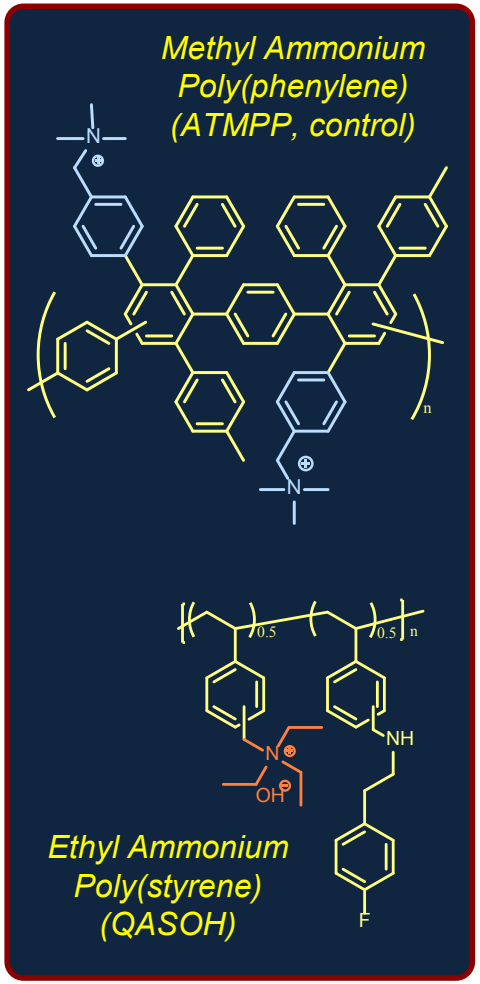


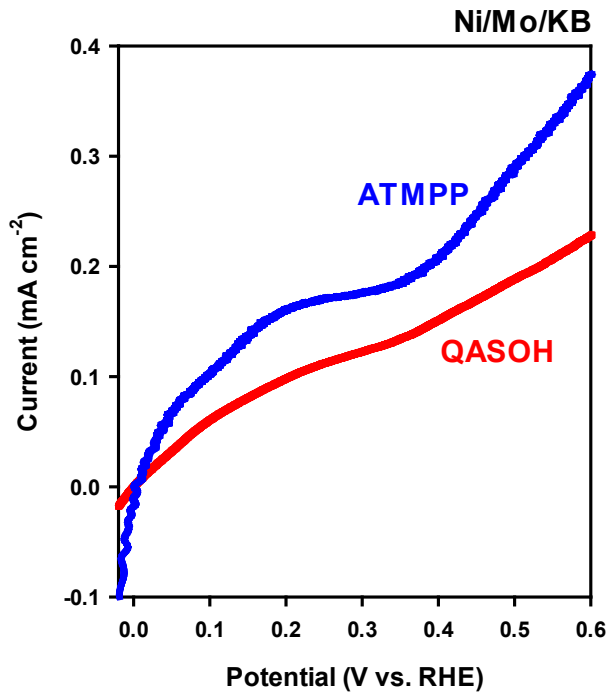
Surface of catalyst is covered with Ni and NiMo oxides

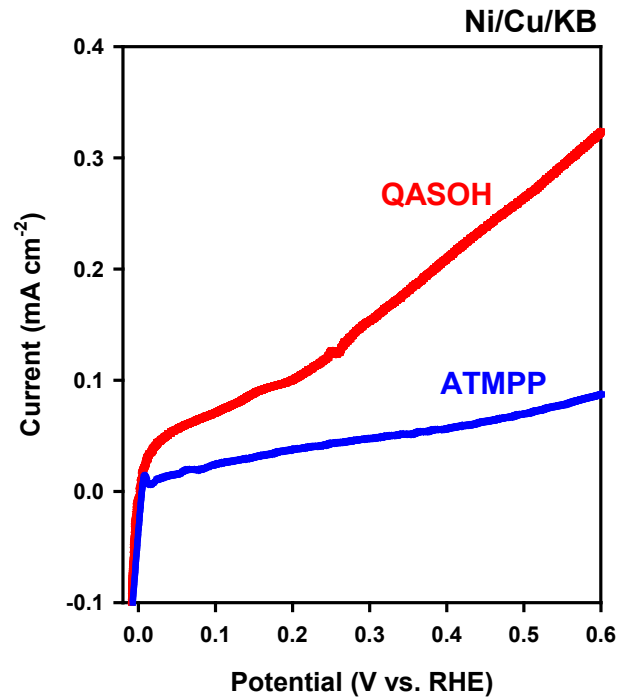
Accomplishments and Progress

Ionomeric Binder for NiM HOR Catalysts

Performed employing ionomer-coated nanoparticle microelectrode (100 µm of diameter) at 100% RH, at room temperature and ambient pressure, with H_2/ Catalyst Loading: 0.1 mg_{metal}/cm^2. *Pre-treatment:* 1. Chronoamperometry at 1.4 V for 20 second, 2. Linear scan voltammetry between -0.1 V and 1.4 V, at 5 $mV.s^{-1}$ 3. Chronoamperometry at 0.1 V for 30minute, 4. Repeat 1. Voltammogram shown below after 0.1 V 30 min.





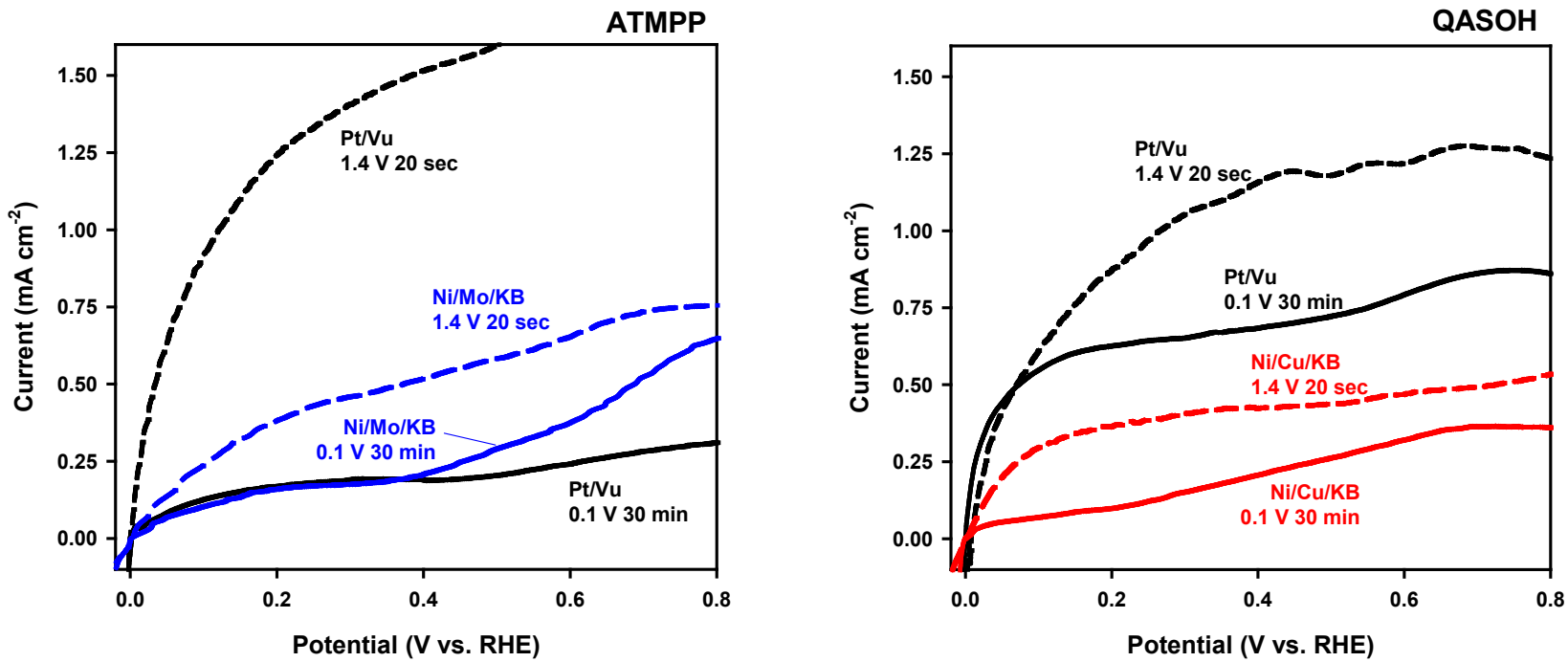


- NiMo/KB performed better with ATMPP; NiCu/KB performed better with QASOH.
- Research Highlight: Synthesized high-performing fluorinated ionomer (QASOH) (see details Technical Backup Slide)

Accomplishments and Progress

HOR Catalytic Activity Comparison

Performed employing ionomer-coated nanoparticle microelectrode (100 μm of diameter) at 100% RH, at room temperature and ambient pressure, with H_2/ Catalyst Loading: 0.1 mg_{metal}/cm^2. *Pre-treatment:* 1. Chronoamperometry at 1.4 V for 20 second, 2. Linear scan voltammetry between -0.1 V and 1.4 V, at 5 $mV.s^{-1}$ 3. Chronoamperometry at 0.1 V for 30minute, 4. Repeat 1. Voltammogram shown below after 0.1 V 30 min.



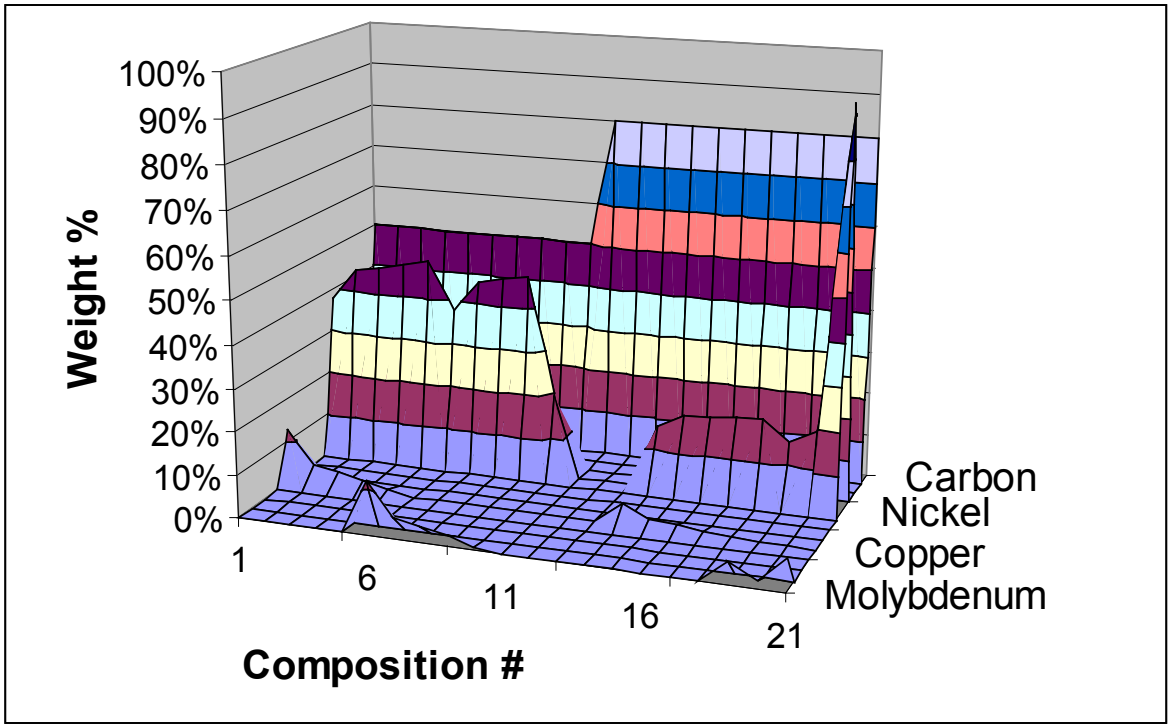
- HOR activity of Pt/Vu is significantly inhibited by cationic group adsorption; NiMo/KB is the least cationic group adsorbed catalyst.
- QAPOH (ethyl ammonium cationic group) is less cationic group adsorbing ionomer.
- Research Highlight: At a HOR potential (0.1 V vs. RHE), the HOR activity of NiMo/KB-ATMPP and NiCu/KB-QASOH catalyst-ionomer is comparable to that of Pt/Vu-ATMPP.

Accomplishments and Progress

Scale-up of Ni-M Catalysts

Thrust Area 3: Task 4 (Pajarito Powder)

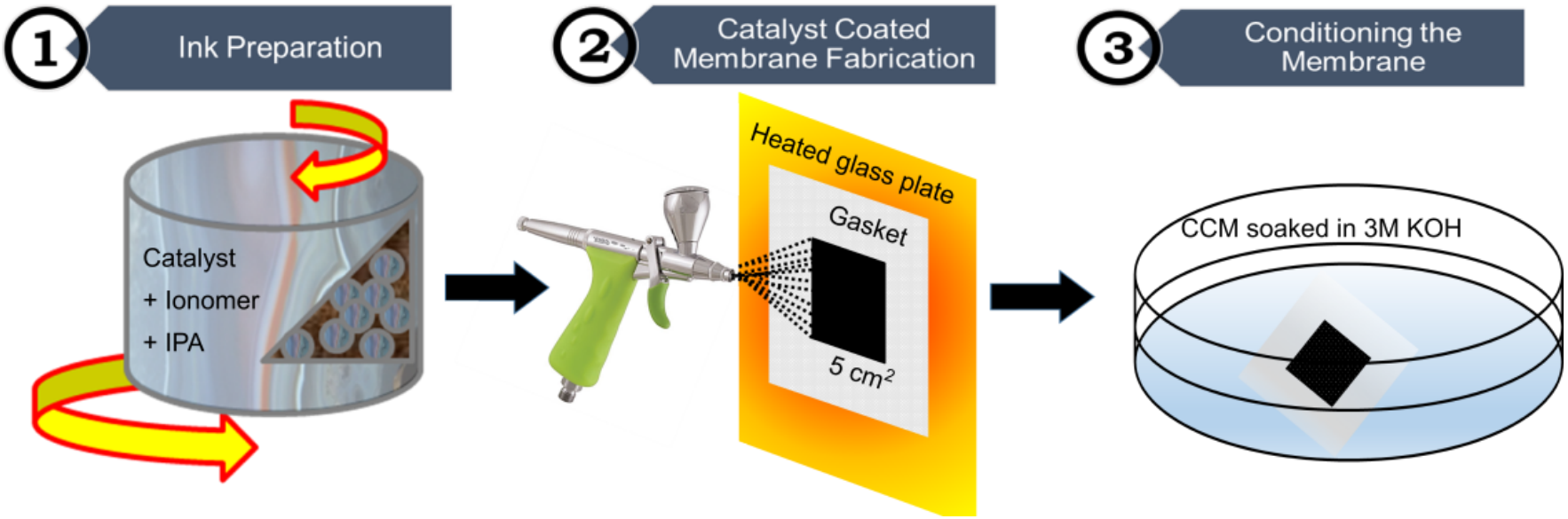
- Carbon supported catalysts screening (80% completed)
  - Synthesis and characterization of 20 and 50wt% $Ni_WMo_XCu_Y$ (W,X,Y=0 to 1) on carbon supports (KD600, XC305)
  - **NiMo/KB and NiCu/KB catalysts synthesized on the level of 25g**



Accomplishments and Progress

Fuel Cell Tests: Initial Data

MEA fabrication with Tokuyama ionomer



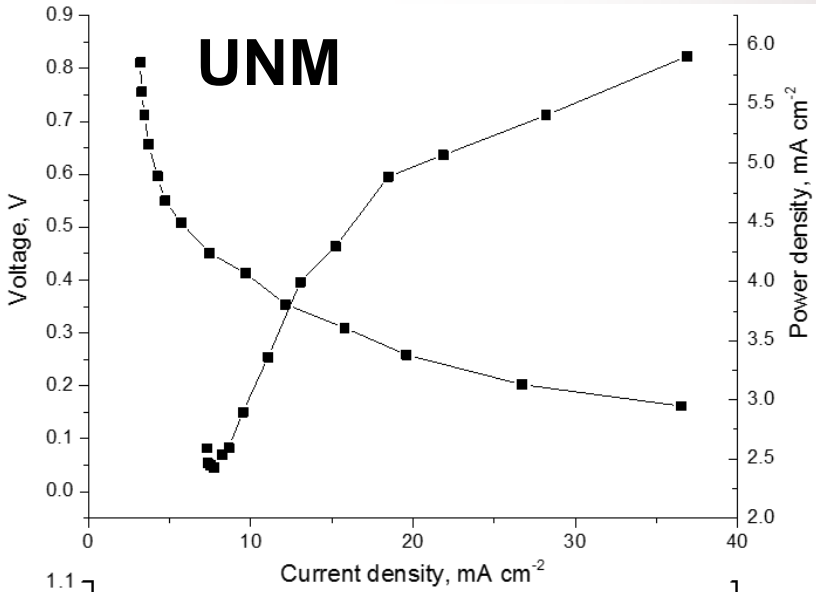
Mixture of catalysts, Tokuyama ionomer and alcohols were dispersed by ball-milling: 450RPM, t=20 min.

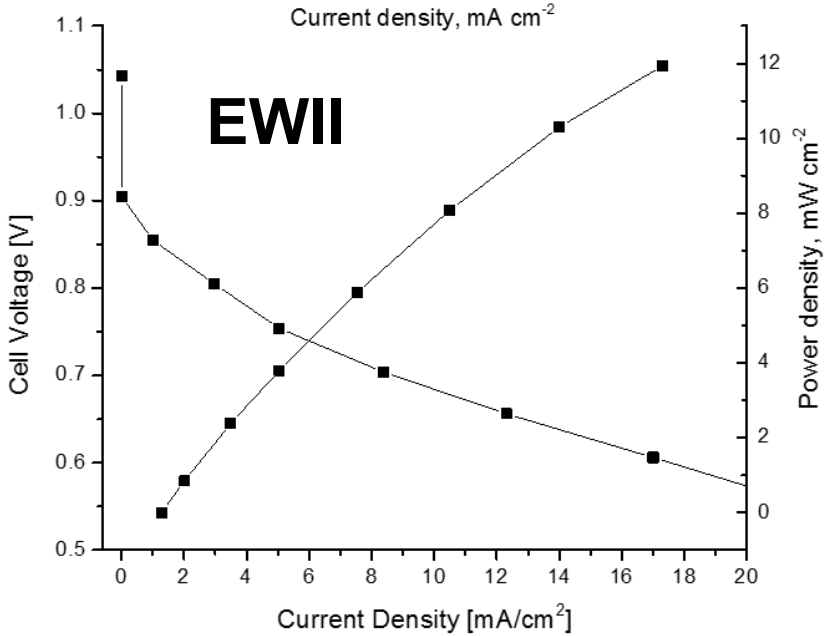
CCM sprayed. Converted to OH^- form by soaking in 3M KOH

- **Ink prepared by ball-milling was stable during the hand-spraying**
- **Membrane did not change the shape during the CCM fabrication**
- **No hot pressing required using CCM method**

Accomplishments and Progress

Initial MEA performance NiMoCu





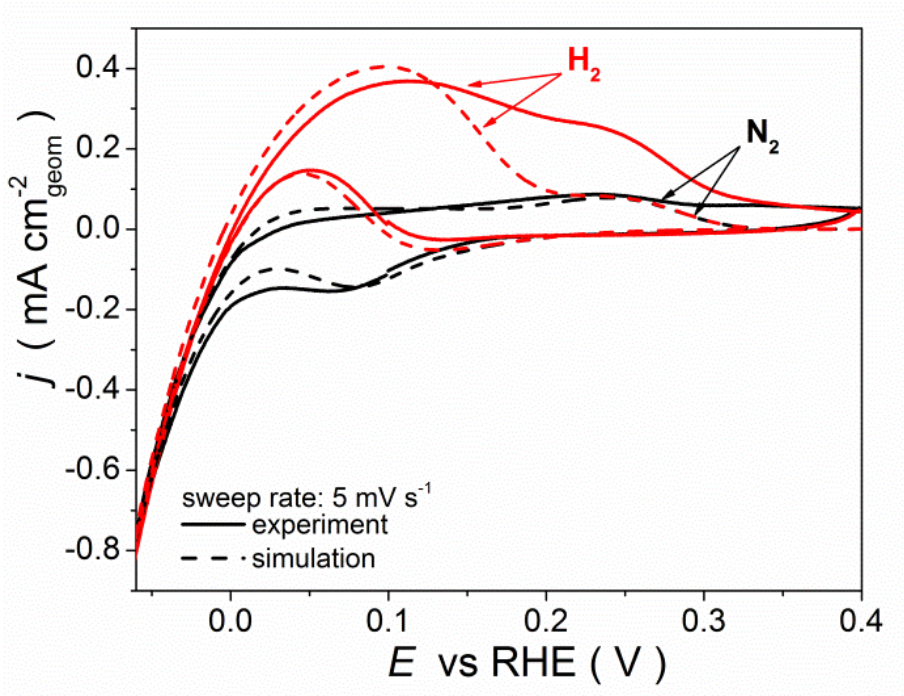
Fuel Cell Operating Conditions:

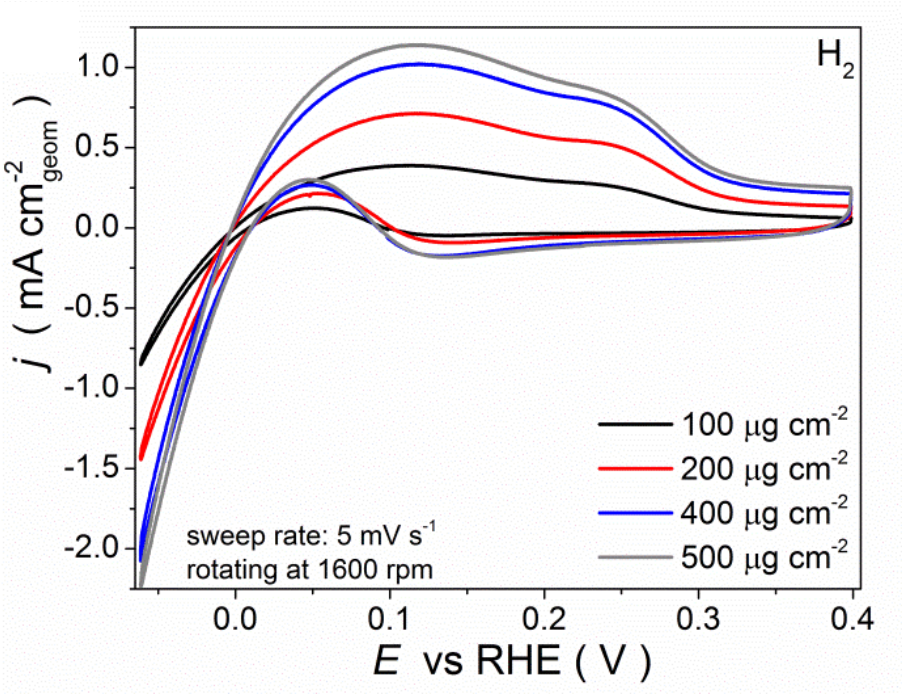
- Catalyst Loadings
  - Anode: 4 mg cm^{-2} 20 % AS5
  - Cathode: 0.4 mg$_{pt}$ cm^{-2} 20% AS5
- GDL: SGL GDL 25 BC
- Membrane: Tokuyama A201
- Back pressure: 20 psi$_g$
- Cell temperature: 60 ^oC
- Humidifiers: 60 ^oC anode / 60 ^oC cathode
- Humidity: 100% for anode and cathode
- Gas flow rates: 0.25 L min^{-1} for anode and 0.2L cathode

- ➢ Performance of both MEAs (UNM and EWII) was low
- ➢ From unsupported to supported NiMo/NiCu catalysts

Accomplishments and Progress

NiMo/KB HOR: RDE





Sample	T / °C	m_{M+C} / µg cm^{-2}	A_{ECSA} / cm^2_{Ni}	j_0 / µA cm^{-2}_{ECSA}	i_o / A g_M^{-1}	Reference
NiMo/KB	25	100	1.6 ± 0.2	27 ± 2	4.5 ± 0.2	This work
Ni/N-CNT	r.t.	350	6.2	28	3.47	[1]
Ni/CNT	r.t.	350	5.2	9.2	0.96	[1]
CoNiMo	r.t.	-	-	15	-	[2]
Ni_{pc}	25	-	0.5	2.2	-	[3]
20% Pd/C (com)	20			52 ± 2	38 ± 4	[4]

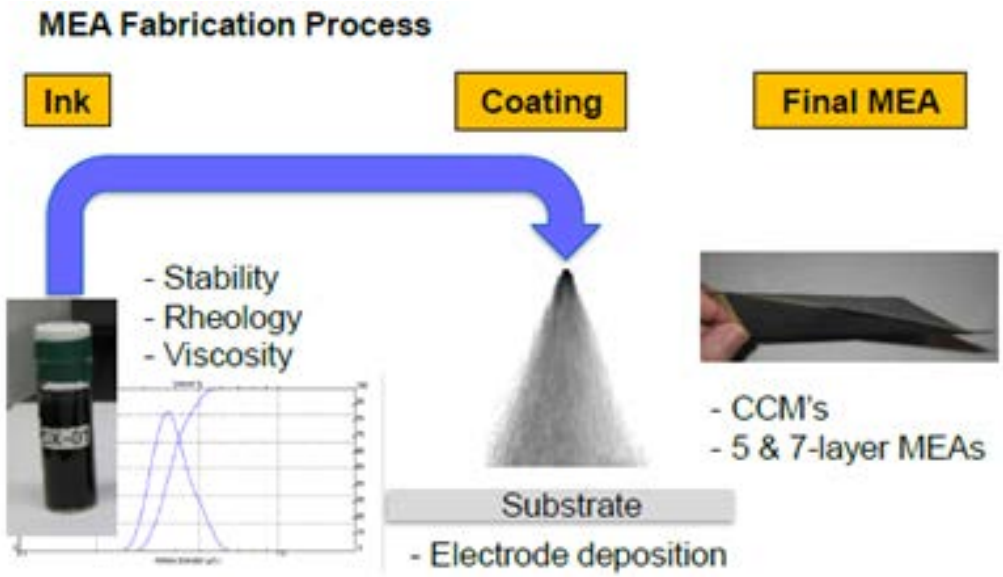
- **NiMo/KB has activity similar or higher than state-of-the-art PGM-free Ni-based HOR catalysts**

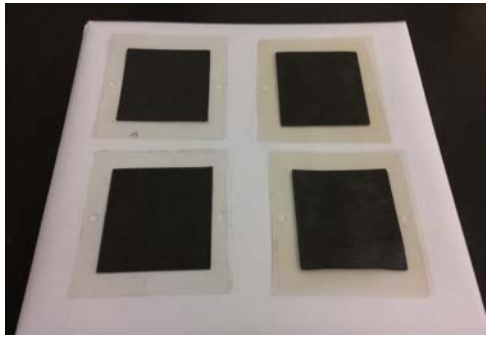
[1] W. Sheng et al. J. Electrochemical Society 157 (2010) B1529-B1536.
[2] Z. Zhuang et al. Nature communications 7 (2016).
[3] S. A. S Machado et al. Electrochim. Acta 39 (1994) 1385-1391
[4] J. Zheng et al. J. The Electrochemical Society 163, 6 (2016) F499-F506.

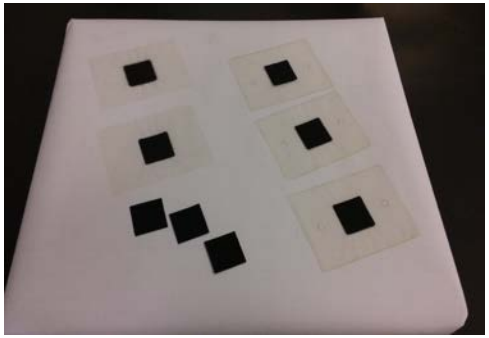
Accomplishments and Progress

MEA manufacturing

Thrust Area 4: Task 5 (EWII Fuel Cells)

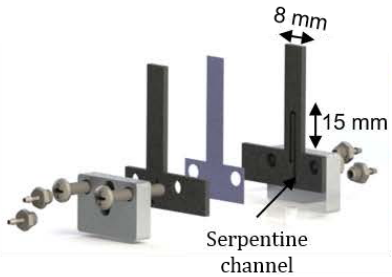




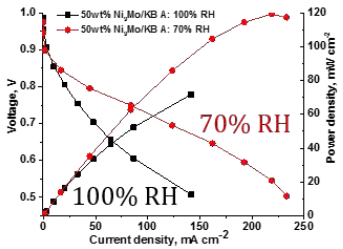


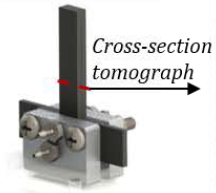
Accomplishments and Progress

In-Operando X-Ray CT

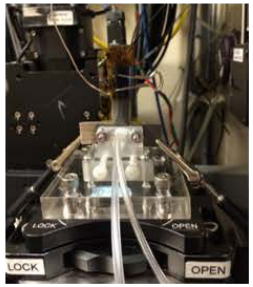


- In-operando micro X-ray CT study under two RH conditions at Beamline 8.3.2 ALS
- Severe flooding in all the components observed at 100% RH near OCV currents
- When RH reduced to 60 % almost no condensed water observed in GDLs and some is observed in the CL



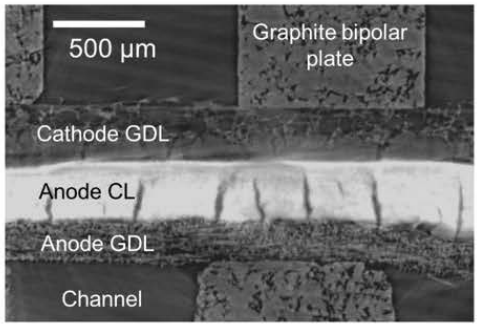


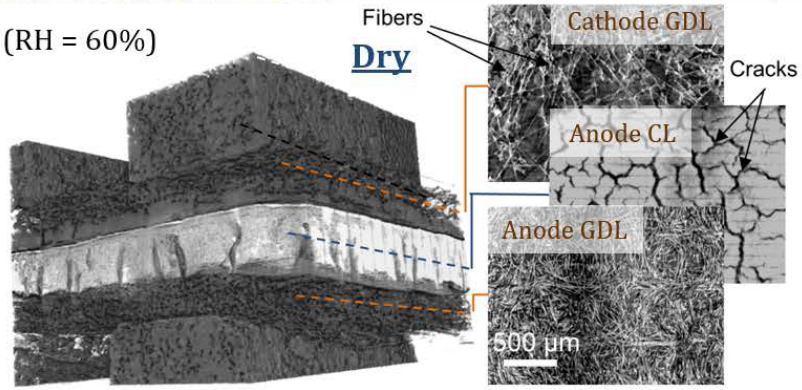
Assembled cell at the beamline stage



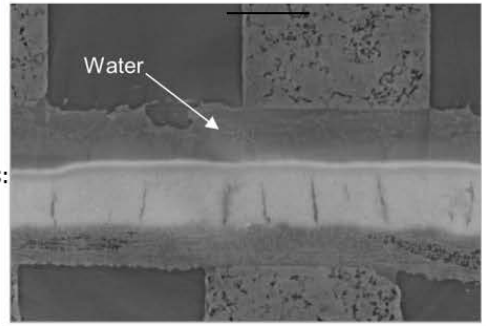
In-operando conditions:
0.2/0.2 slpm H_2/O_2, near OCV current, SGL 24 BC (cath) Freudenbergh H2315 (anode)

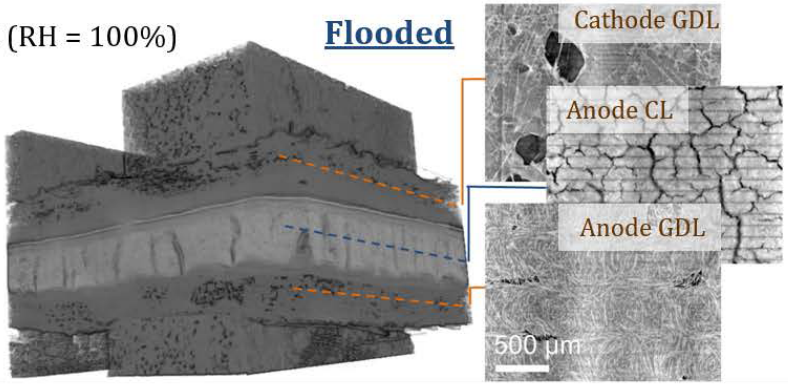
T = 43°C (RH = 60%)





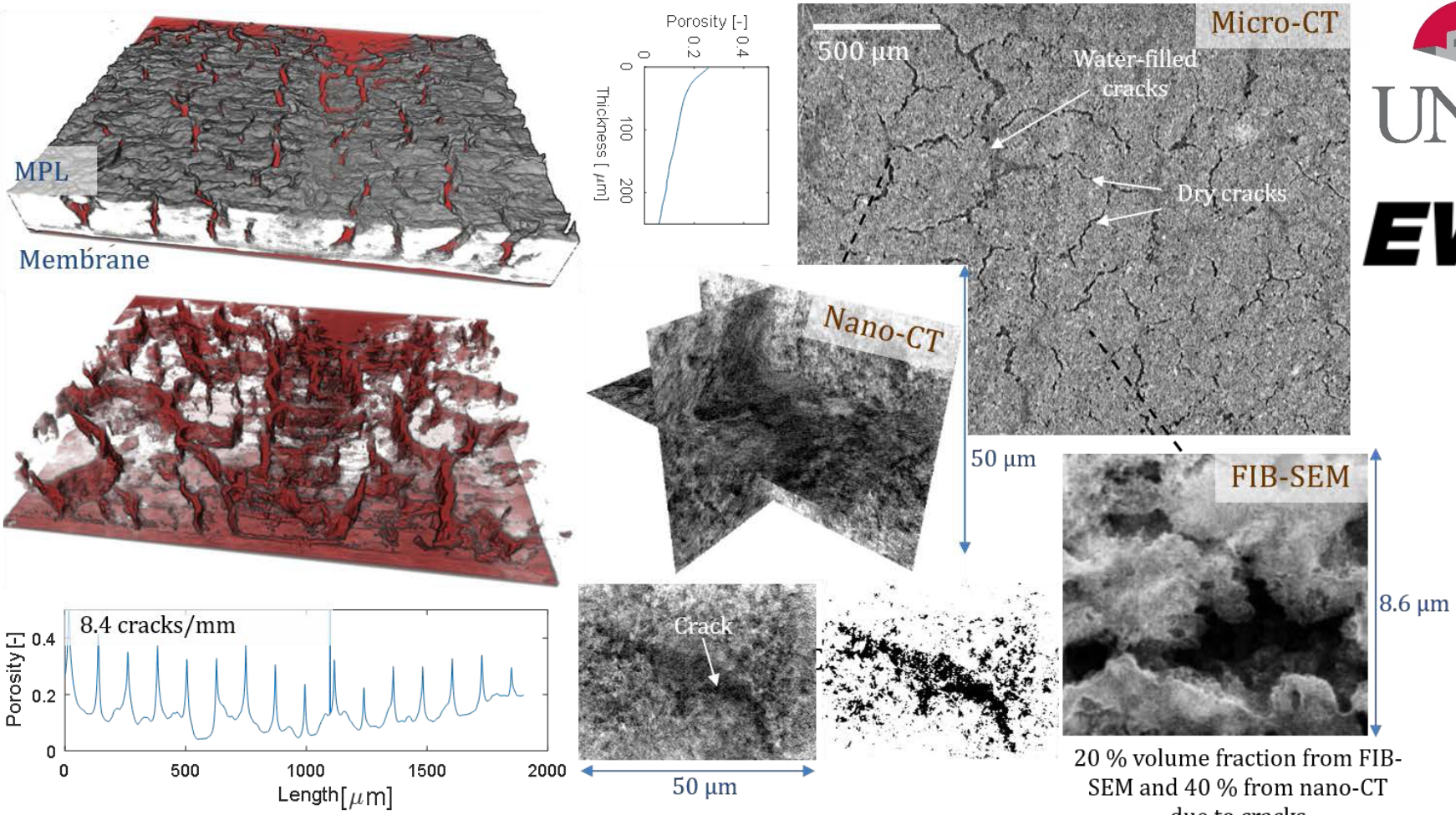
T = 30°C (RH = 100%)





Accomplishments and Progress

Morphology Across Scales

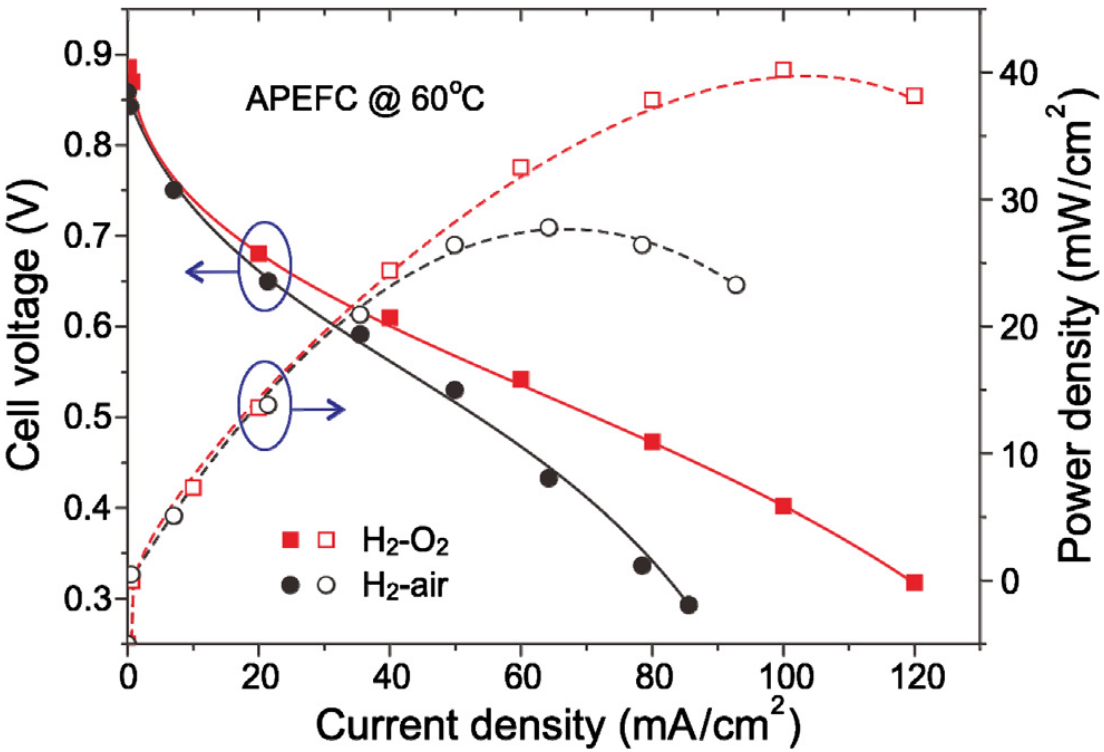


20 % volume fraction from FIB-SEM and 40 % from nano-CT due to cracks

- Periodic crack formation (fractal), with average 125 μm spacing (can aid in water management)
- Water is clearly visible within the cracks with micro-CT
- Crack size ranges with median thickness of 12 μm
- In crack-free regions larger voids are present as confirmed by FIB-SEM

Accomplishments and Progress

Literature data on Ni-based anodes



Fuel Cell Operating Conditions:

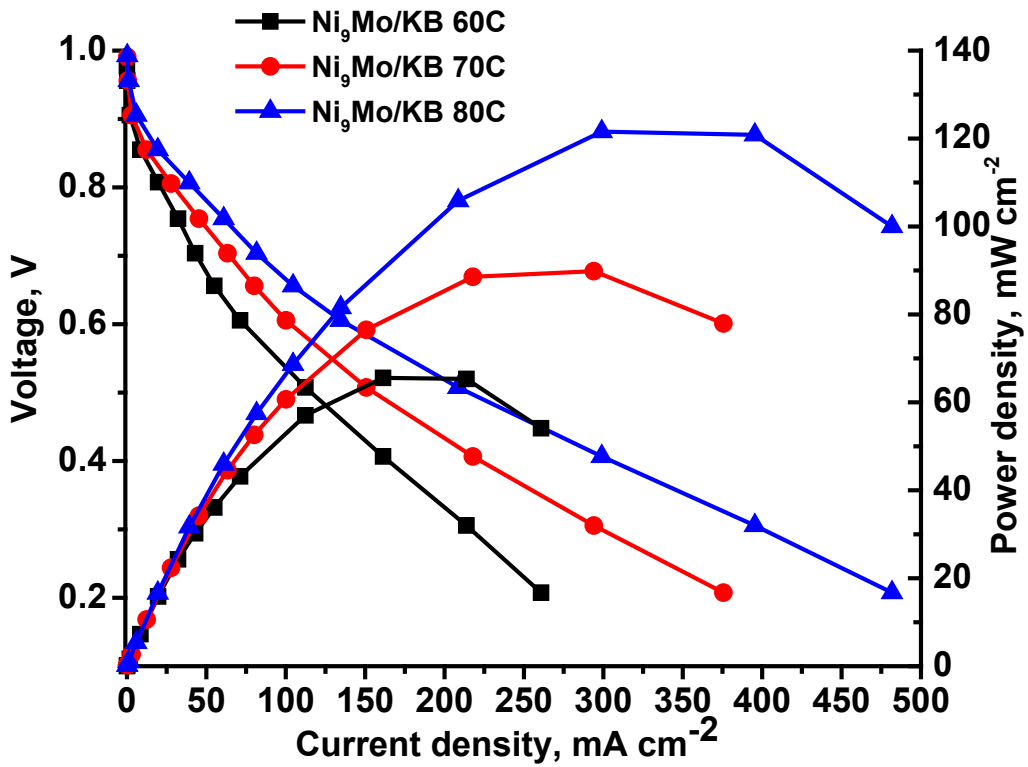
- Catalyst Loadings
  - **Anode: NiW 17.5 mg cm^{-2}**
  - Cathode: CoPPY/C 2 mg_{pt} cm^{-2}
- GDL: SGL GDL 25 BC
- Membrane: xQAPS
- Back pressure: 20 psi_g
- Cell temperature: 60 °C
- Humidifiers: 60 °C anode / 60 °C cathode
- Humidity: 100% for anode and cathode
- Gas flow rates: 50 ccm for anode and 50 ccm cathode

Q. Hu, G. Li, J. Pan, L. Tan, J. Lu, L. Zhuang "Alkaline polymer electrolyte fuel cell with Ni-based anode and Co-based cathode" Int. J. of Hydr. Energy 38 (2013) 16264-16268.

Using completely PGM-free MEA peak power density of ~40 mW cm^{-2} was shown by L. Zhuang group

Accomplishments and Progress

NiMo/KB Fuel Cell Performance



Performance:

- Peak power density: **120 mW cm^{-2}**
- OCV: ~1V
- Resistance: 200 mOm

Fuel Cell Operating Conditions:

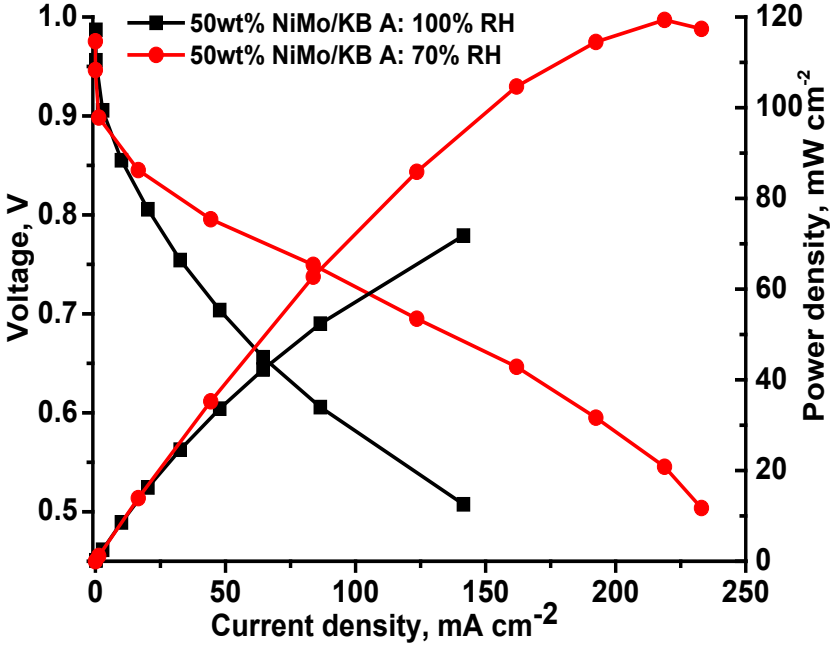
- Catalyst Loadings
  - Anode: 4 mg cm^{-2} 35 % AS4 NiMo/Kb
  - Cathode: 0.2 mg$_{Pd}$ cm^{-2} 25% AS4 Pd/XC72R
- GDL: SGL GDL 29 BC
- Ionomer: Tokuyama AS4
- Membrane: Tokuyama A201
- Back pressure: 20 psi$_g$
- Cell temperature: 60-80 ^{o}C
- Humidifiers: 60-80 ^{o}C anode / 60-80 ^{o}C cathode
- Humidity: 100% for anode and 100% cathode
- Gas flow rates: 0.2 L min^{-1} for anode and cathode

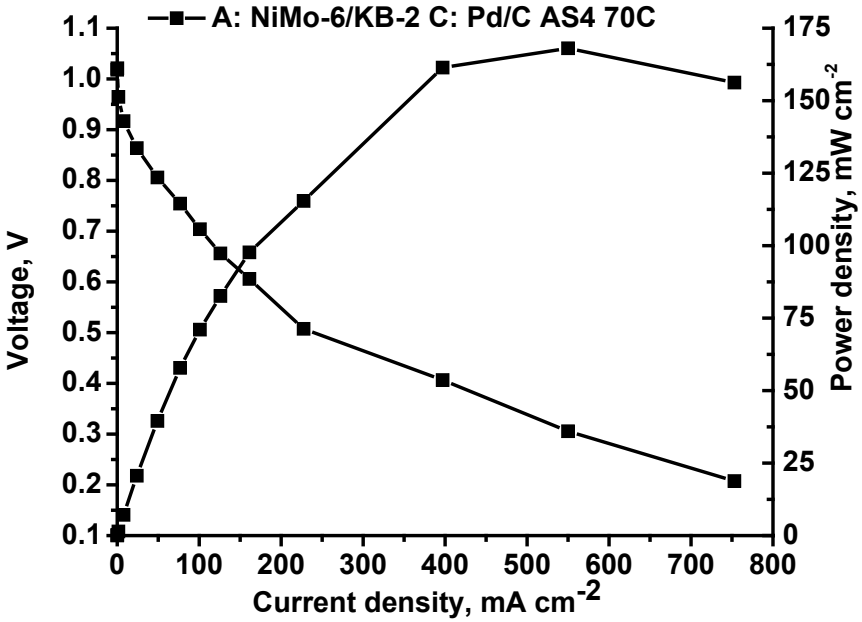
Fuel Cell MEA Construction:

- The Pd cathode was made with our standard ink recipe (50/50 IPA and Water) and hand spray
- The NiMo/KB cathode was made by CCM (UNM hand spray) and tested in 5cm^2 cell
- The fuel cell MEA was constructed with no hot pressing
- MEA was transferred into OH$^-$ form and tested after activation

Accomplishments and Progress

NiMo/KB Fuel Cell Performance





Catalyst Loadings:
Anode: 3.5 mg cm^{-2} 35 % AS5 Ni-Mo/Kb
Cathode: 0.2 mg_{pd} cm^{-2} 25% AS4 Pd/C

Membrane: Tokuyama A201, Back pressure: 20 psi_g
Cell temperature: 70 ^{0}C, Humidity: 100% for anode and cathode
Gas flow rates: 0.2 L min^{-1} for anode and 0.25L min^{-1} for cathode

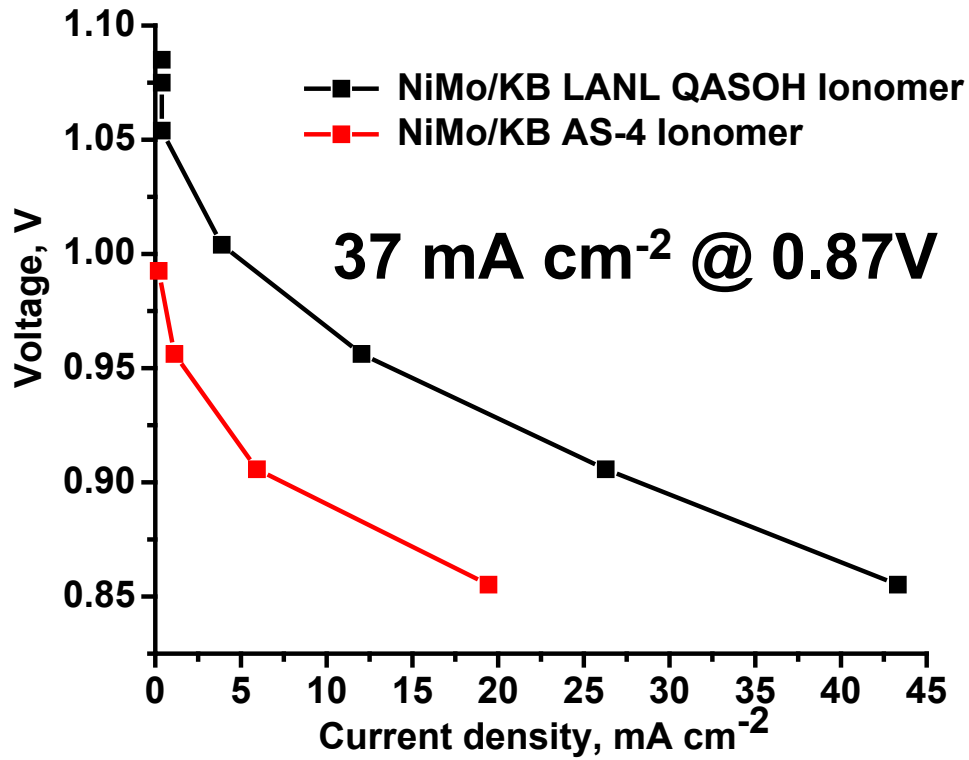
Strong influence on anode RH was observed.
Peak power density was ~175 mW cm^{-2}

Accomplishments and Progress

NiMo/KB LANL Ionomer

Performance:

- Current density: **45 mA/cm^2 at 0.85V OCV: ~1.1V**



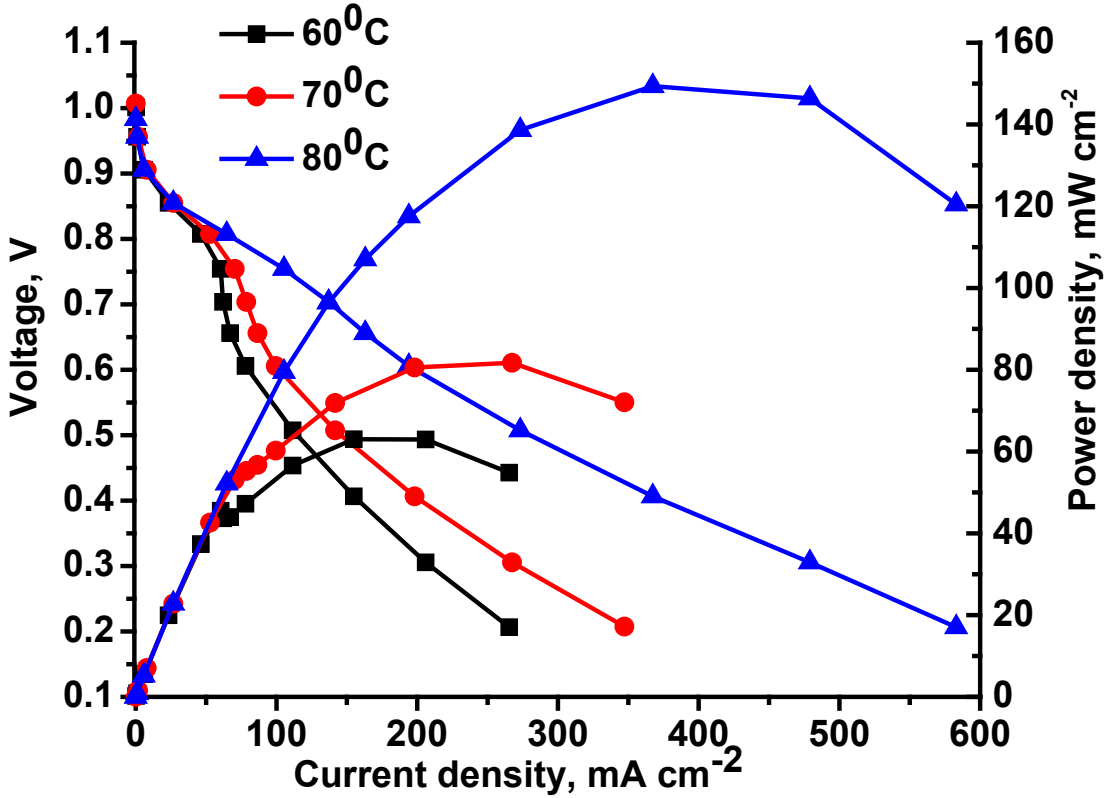
Fuel Cell Operating Conditions:

- Catalyst Loadings
  - Anode: 4 mg cm^{-2} 30 % LANL NiMo/Kb
  - Cathode: 0.2 mg$_{Pd}$ cm^{-2} 25% AS4 Pd/XC72R
- GDL: SGL GDL 29 BC
- Ionomer: **LANL QASOH**
- Membrane: Tokuyama A201
- Back pressure: 20 kPa$_g$
- Cell temperature: 80 ^{o}C
- Humidifiers: 80 ^{o}C anode /80 ^{o}C cathode
- Humidity: 100% for anode and 100% cathode
- Gas flow rates: 0.2 L min^{-1} for anode and 0.25L min^{-1} for cathode

LANL ionomer gave performance close to DOE 2020 PGM-free PEMFC target of 44 mA cm^{-2} at 0.9V

Accomplishments and Progress

Study of NiCu/KB Anode



Performance:

- Peak power density: **150 mW cm^{-2}**
- OCV: ~1V

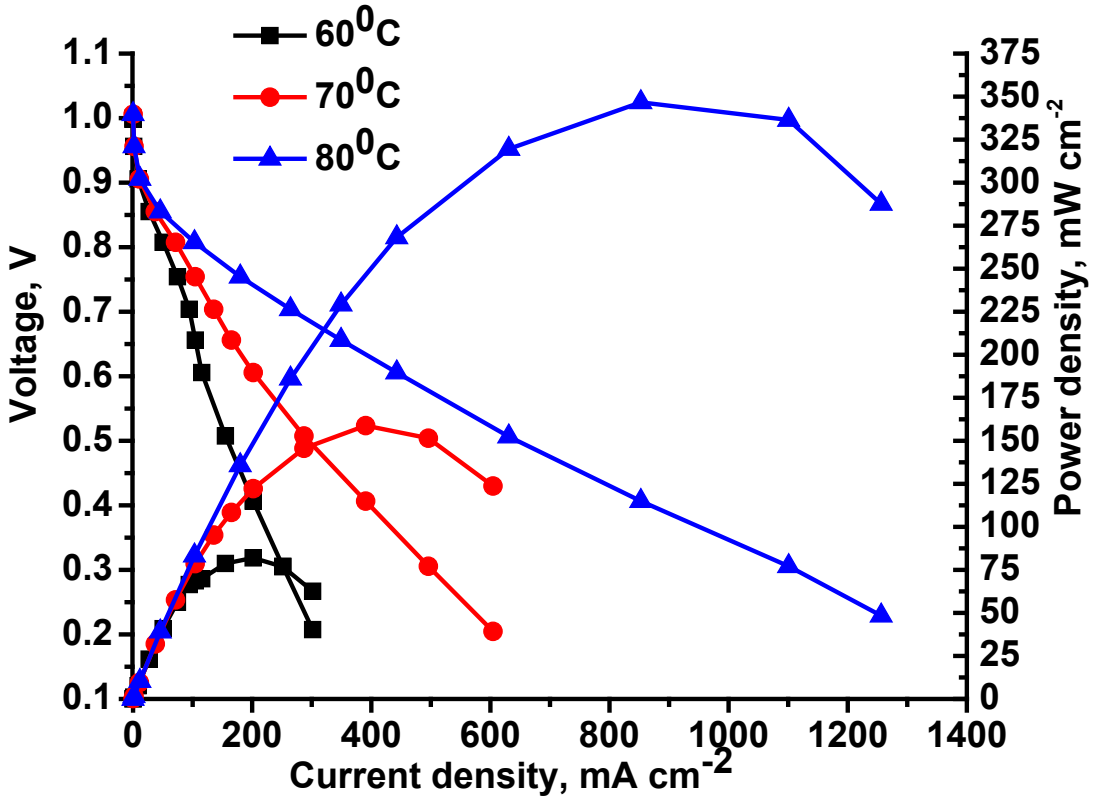
Notes:

- **OCV was lower compared to NiMo/KB**
- **Slow MEA activation**
- **Ionomer ratio is not optimal**

NiCu/KB shown higher performance in fuel cell tests compared to NiMo/KB

Accomplishments and Progress

NiCu/KB Go-no-GO Design Point



Performance:

- Peak power density: **~350 mW cm^{-2}**
- OCV: ~1V

Fuel Cell Operating Conditions:

- Catalyst Loadings
  - Anode: 4 mg cm^{-2} 30 % AS4 NiCu/KB
  - Cathode: 0.2 mg$_{Pd}$ cm^{-2} 25% AS4 Pd/XC72R
- GDL: SGL GDL 29 BC
- Ionomer: Tokuyama AS4
- Membrane: Tokuyama A201
- Back pressure: 20 psi$_g$
- Cell temperature: 60-80 ^{o}C
- Humidity: 100% for anode and 100% cathode
- Gas flow rates: 0.2 L min^{-1} for anode and cathode

MEA utilized NiCu/KB as a PGM-free anode met 2nd GnG design point (250 mW cm^{-2}): 350 mW cm^{-2}

Collaboration and Partners

Catalyst design, characterization, project management:
Alexey Serov (Project Lead), Sarah Blair, Sadia Kabir, Morteza Talarposhti, Kateryna Artyushkova, Plamen Atanassov

Ionomer development and DFT calculations:
Yu Seung Kim (PI), Hoon Chung, Kwan-Soo Lee, Joseph Dumont, Ivana Matanovic

MEA Design:
Madeleine Odgaard (PI), Debbie Schlueter, Steven Lucero

Scaling Up:
Barr Halevi (PI), Alia Lubers, Henry Romero, Samuel McKinney

Prof. Iryna Zenyuk

Hawaii Natural Energy Institute
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Dr. Tatyana Reshetenko

Prof. Elena Savinova

Remained Challenges and Barriers

- Optimize NiCu system: Ni:Cu ratio and support
- Re-optimize NiCu/C:Ionomer ratio
- Develop MEA fabrication method at EWII to integrate NiCu/C into the catalyst layer
- Mitigation of anode flooding
- Influence of CO_2 (in air) on MEA performance

Summary Slide

- **Results**

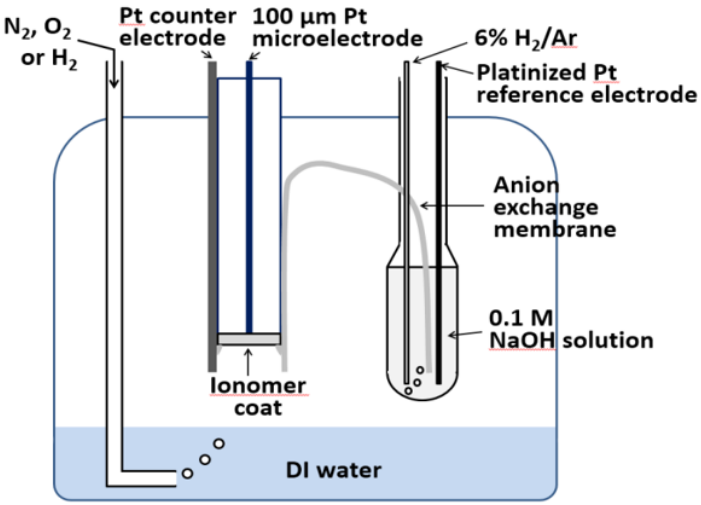
- Three classes of PGM-free catalysts were synthesized: NiMoCu (unsupported), NiMo/KB and NiCu/KB
- Morphology of catalysts was controlled and maintained to meet milestone criteria (particle size <70 nm and surface are 20 m^2 g^{-1})
- LANL met milestone requirements by ranking functional groups in ionomers. DFT calculations were found to be in good agreement with experiment. Ionomer was synthesized in amount required for MEA manufacturing
- Pajarito Powder scaled up the SSM up to 50 g level and met criteria on electrochemical performance of the samples
- EWII achieved in Gen 1 and Gen 2 MEAs power densities higher than 100 mW cm^{-2} and met the milestones
- **Team met 2nd Go-no-Go design point (250 mW cm^{-2}) with actual peak power density of 350 mW cm^{-2}**

Future Activity

- Synthesis of NiCu on different support
- Re-optimization of NiCu/C to ionomer ratio
- Integration of NiCu/KB into the catalyst layer
- Perform extended durability study
- Perform PGM-free MEA tests using non-simulated air
- Finishing articles and presenting project results on ECS meeting.

Technical Back-up Slides

Microelectrode experiments

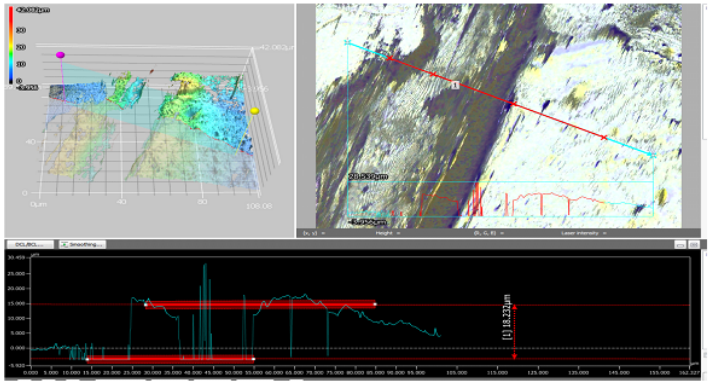


Microelectrode set-up for alkaline HOR study

Membrane thickness measurement by Laser Profilometry

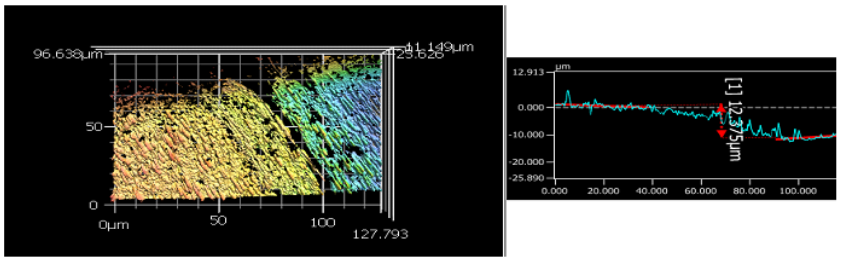
ATMPP film on Microelectrode

Thickness ~ 18µm



QS film on Microelectrode

Thickness ~ 12µm



Alkaline membrane – HOR catalyst characterization

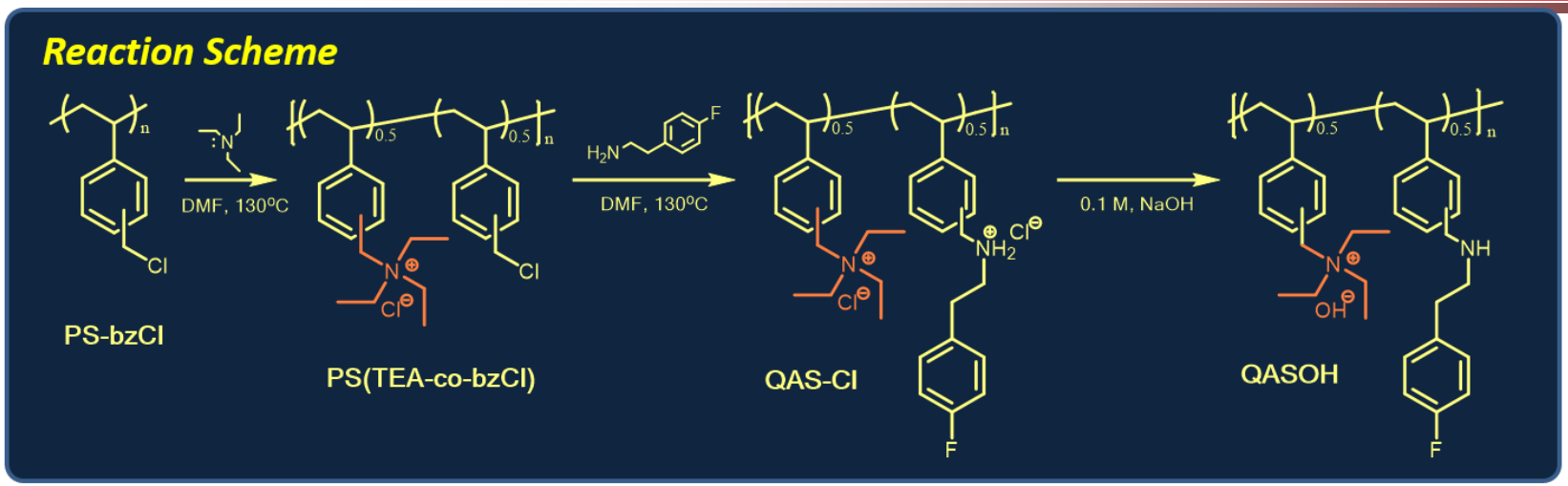
Performed experiments ionomer coated microelectrode of 100 µm of diameter in a 100% RH environment, at room temperature and pressure, with N_2 and H_2.

Procedure: 1. Chronpamperometry at 1.4 V for 20 seconds.
2. Linear scan voltammetry between -0.1V and 1.4V, at 5 mV.s^{-1}
3. Chronpamperometry at 0.1 V for 30minutes.
4. Repeat 1.

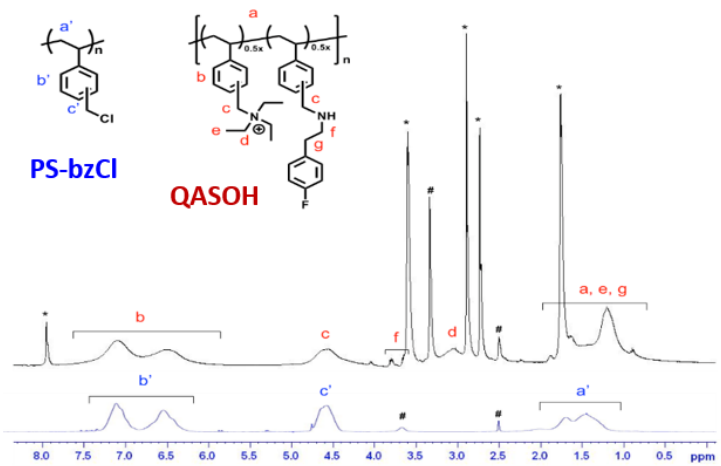
For detail procedure, see J. Electrochem. Soc. 162, F499-F506, 2015

Synthesis Ionomers

Reaction Scheme



^{1}H NMR Characterization



- Tetraethyl ammonium functionalized fluorinated polystyrene is successfully synthesized (IEC = 2.0 meq/g, Molecular weight: 88,400, hydroxide conductivity 14 mS/cm at 30°C).
- The copolymer having the hydrophobic/hydrophilic composition of 50:50 can be dissolved in alcoholic solvents.
- 30 g of 5 wt.% ionomer dispersion was delivered to UNM for MEA production.

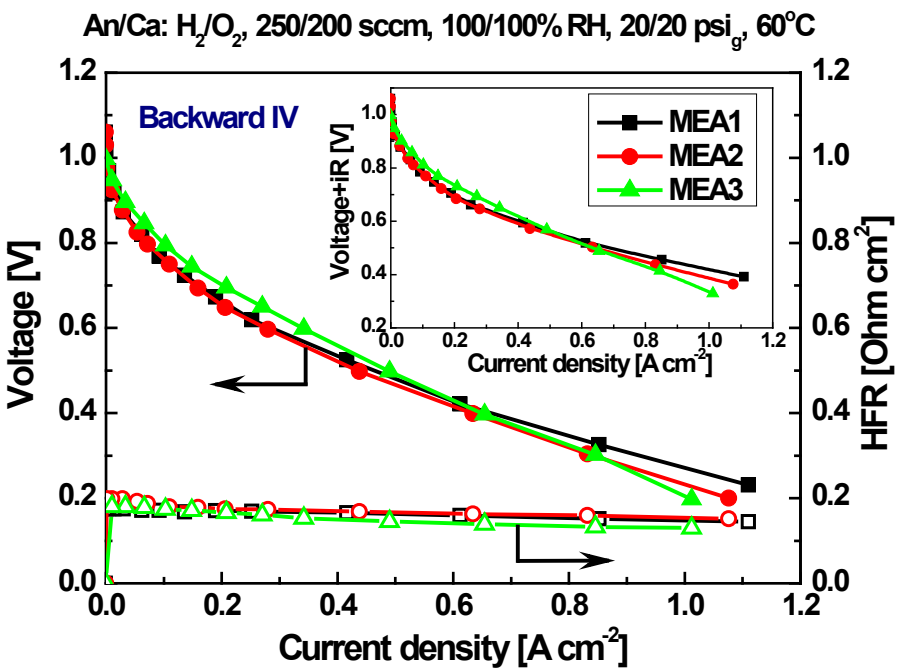
QAS-Cl; δ 7.8-6.1 (br, 12H, -Ar**H**), 5.0-4.2 (br, 4H, -ArC**H$_2$**N-), 5.0-4.2 (br, 4H, -ArC**H$_2$**N-), 3.9-3.6 (m, 2H, -NC**H$_2$**CH$_2$Ar), 3.05 (br, 6H, -ArCH$_2$N(C**H$_2$**CH$_3$)$_3$), 1.8-0.3 (br, 17H, -CH$_2$CHAr-, -N(CH$_2$C**H$_3$**)$_3$, ArC**H$_2$**CH$_2$N-); QAS-Cl copolymer was dissolved using THF, DMF, and Water represented by *; DMSO-d$_6$ is represented by #. PS-bzCl; δ 7.4-6.2 (br, 3H, -Ar**H**), 4.8-4.3 (br, 2H, -ArC**H$_2$**Cl), 2.2-1.1 (br, 3H, -C**H$_2$**C**H**Ar-).

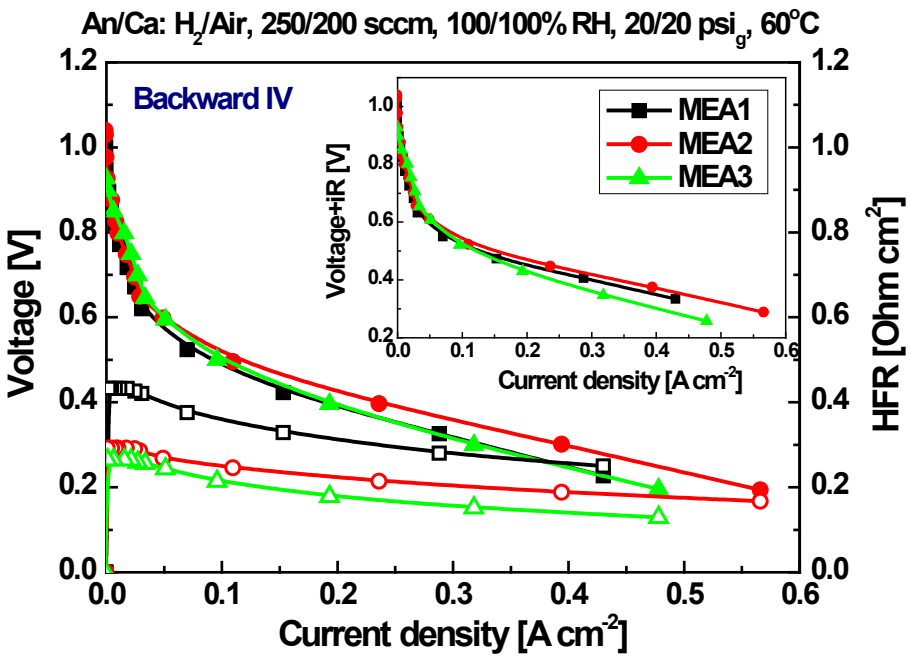
Reproducibility, IV curves at H_2/O_2 and Air

Pt/C on Anode and Cathode Study

Hawaii Natural Energy Institute
www.hnei.hawaii.edu

Polarization curves recorded in both directions increasing and decreasing current show hysteresis, when backward IV curves has better performance than forward due to the better humidification.

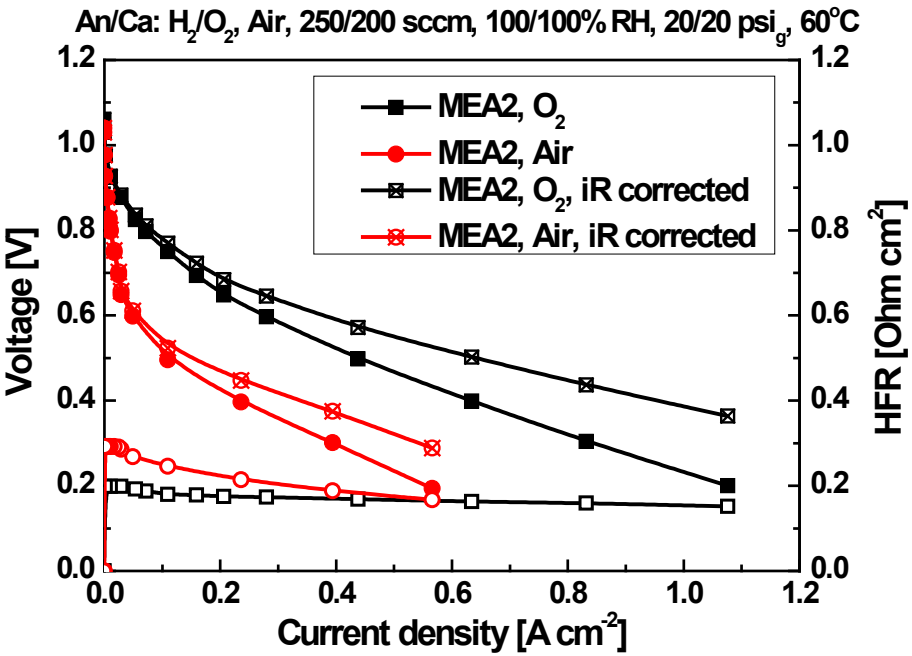


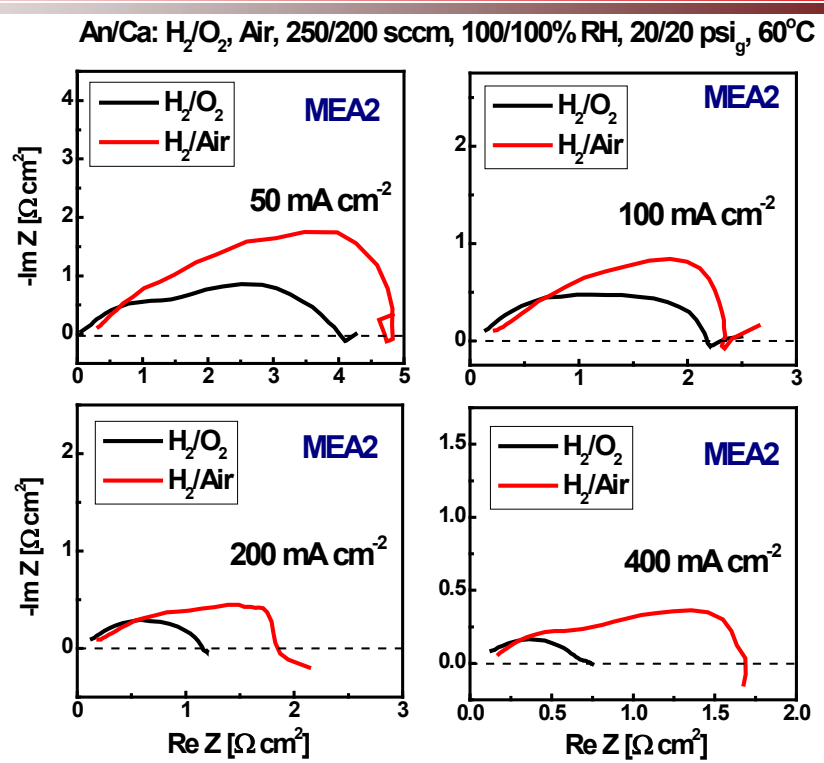


Three MEAs were tested in H_2/O_2 or H_2/Air and at 100/100% RH conditions. The data showed close performance and HFR of these samples for H_2/O_2 gas configuration. However, at H_2/Air HFRs of the samples varied from 0.13 to 0.43 Ohm cm^2. The observed deviations in performance are likely due to variations in HFR (presence of CO_2), mass transfer properties of electrodes etc. In general, we obtained reproducible performance for AMFC.

Performance at H_2/O_2 and Air

Pt/C on Anode and Cathode Study





1. Performance at H_2/O_2 gas configuration is higher than for H_2/Air.
2. HFR at H_2/O_2 seems to be lower than for H_2/Air due to possible negative effect of CO_2 which was present in Air.
3. Operation at H_2/Air results in less water production and lower water content, which is critical for AMFC.

P. Khadke, U. Krewer, Electrochem. Com. 51 (2015) 117.

Operation at H_2/O_2 revealed 2 arcs:

- HF arc can be attributed to HOR and restricted ionic transport in electrodes,
- LF to ORR and possible diffusion limitation in electrode.

Operation at H_2/Air resulted in at least 2 arcs and LF inductance at low current, which might be due to 2-electron ORR

An increase in operating current led to a decrease in EIS response and presence only one loop at H_2/O_2, while for air case LF loop more pronounced, which indicates on its mass transfer limitations origin.