H2NEW: Hydrogen (H2) from Next-generation Electrolyzers of Water

H2NEW LTE: Manufacturing, Scale-Up, and Integration

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DOE Hydrogen Program

2022 Annual Merit Review and Peer Evaluation Meeting

Project ID # P196C
H2NEW Task 3a,b: Manufacturing, Scale-Up, and Integration
Overview

Timeline and Budget

• Start date (launch): October 1, 2020
• Awarded through September 30, 2025
• FY22 DOE funding: $1.75M
• Annual budget adjustments anticipated

Barriers
• Durability
• Cost

Consortium Task Team

Deputy Director:
Adam Weber (LBNL)
Task Liaisons:
Michael Ulsh (NREL)
Alexey Serov (ORNL)
Subtask Leads:
Debbie Myers (ANL)
Scott Mauger (NREL)
Mike Tucker (LBNL)
Jason Lee (LBNL)
Svitlana Pylypenko (CSM)
Iryna Zenyuk (UCI)
Shawn Litster (CMU)
Project Goals

Goal: H2NEW will address components, materials integration, and manufacturing R&D to enable manufacturable electrolyzers that meet required cost, durability, and performance targets, simultaneously, in order to enable $2/kg hydrogen.

H2NEW has a clear target of establishing and utilizing experimental, analytical, and modeling tools needed to provide the scientific understanding of electrolysis cell performance, cost, and durability tradeoffs of electrolysis systems under predicted future operating modes.
### Electrolyzer Stack Goals by 2025

<table>
<thead>
<tr>
<th></th>
<th>LTE PEM</th>
<th>HTE</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Capital Cost</strong></td>
<td>$100/kW</td>
<td>$100/kW</td>
</tr>
<tr>
<td><strong>Electrical Efficiency (LHV)</strong></td>
<td>70% at 3 A/cm²</td>
<td>98% at 1.5 A/cm²</td>
</tr>
<tr>
<td><strong>Lifetime</strong></td>
<td>80,000 hr</td>
<td>60,000 hr</td>
</tr>
</tbody>
</table>

- Task 3 specifically focuses on manufacturing cost reductions through enabling high throughput fabrication techniques:
  - Understanding inks
  - Catalyst layer optimization and fabrication
  - PTL Design and Optimization
- MEAs, PTLs and other components developed within Task 3 crosscut with Tasks 2 and 3
Task 3a: MEA fabrication, Interface engineering

i. Inks
   • Constituent interactions in and mixing of the ink predefine the micro- and macro-scale behaviors
   • Ink morphology: agglomeration, stability, level of adsorption of ionomer

ii. Electrodes
   • Coatability: rheology, wettability
   • Electrode Morphology: porosity/distribution of ionomer

iii. Cell Integration and Interfaces

Task 3b: Components

i. Porous Transport Layers
   • Develop understanding of structure and function, aid in design of new structures

ii. Recombination Layers
   • Model impact; develop understanding of structure and function, aid in design of new structures
### Approach: Year 2 Milestones

<table>
<thead>
<tr>
<th>Milestone Name/Description</th>
<th>Due Date</th>
<th>Type</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Targeting cost gains from scaling up processes: Using an automated, scalable coating</td>
<td>3/30/2022</td>
<td>QPM</td>
<td>Completed (see slide 15)</td>
</tr>
<tr>
<td>manufacturing process for MEAs, match or exceed performance of baseline MEA (within 20 mV at</td>
<td></td>
<td></td>
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<tr>
<td>current densities up to 2 A/cm²) and project potential cost reductions through scaleup.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(NREL, LBNL, ORNL)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quantifying impact on degradation of high throughput scaled up processes. Determine impact of</td>
<td>6/30/2022</td>
<td>QPM/GPRA</td>
<td>On-going (see slide 16)</td>
</tr>
<tr>
<td>anode casting method and parameters, as compared to the baseline spray-coated anode, on performance degradation rates using proposed catalyst ASTs (e.g., triangle cycling from 1.45 to 2 V and 0 to 2 V (1 min duration)), targeting a degradation rate similar to the baseline anode. (NREL, ORNL, ANL, LBNL, LANL)</td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>
Accomplishment: Impact of Iridium Surface: Ink Interactions

- Examine interactions in solvent with different surfaces: Iridium metal (JM), Iridium hydroxide (AA), and Iridium oxide (TKK)
- ITC for binding strength
  - Stronger binding in the order: IrOH AA > Ir JM > IrO2 TKK
  - Binding is entropically driven and so hydrophobic interactions dominate for all surfaces
- Different hydroxides also exhibit differences
  - Particle size in 2:1:1 nPA:H2O:EtOH
    - Without Nafion: AA IrO2 > AA IrOH > TKK IrO2
      - Agrees with ITC binding
    - With Nafion: AA IrOH > AA IrO2 > TKK IrO2
      - Nafion coats and changes interactions leading to different aggregated particle sizes
  - X-ray scattering shows only dependence on metal versus oxide

0.16 wt% catalyst inks
Accomplishment: Impact of Iridium Surface and Solvent and Sonication

- **Sonication Method**
  - Probe tip (30 minutes) in an ice bath
  - Bath (1 hour) with water recirculating at 10°C

- **Different catalysts show different aggregation behavior that somewhat depends on solvent ratio and sonication method**

- **Solvent ratio**
  - Ethanol makes the aggregate sizes decrease
  - Ethanol helps disperse the ionomer more homogenously based on previous studies

![Graphs showing average aggregate diameter](image1)

![Graphs showing average aggregate diameter](image2)

- Data collected via dynamic light scattering

*0.16 wt% catalyst inks*
Accomplishment: Dispersion media effect

- Studied 3M 725 EW ionomer at 10 wt.% solids in water:IPA mixture

- Results (with increasing IPA%):
  - Rheology: viscosity increases, though different scaling with wt.%
  - USAXS: trend in conformation agrees with rheology
  - USAXS: peak broadens, indicating greater polydispersity and agglomeration
  - Kratky plot: trend from globule-like toward more unfolded polymer structure

- Results consistent with prior data on Nafion (D2020)
Accomplishment: Ionomer EW effect

- Studied 3M ionomers at 10 wt.% solids in 25:75 water:IPA mixture
- With increasing EW, viscosity generally decreases
- For each EW, viscosity highest in IPA-rich ink
  - Transition from Newtonian to shear thinning behavior
- Kratky plot indicates structure trend from strongly unfolded to more globule-like with increasing EW
  - Opposite trend from rheology
  - Needs further study
Accomplishment: Anodic Inks Aging – Ir and IrO₂ Phase Separation (WAXS)

- Ir metal particles can reach 500-800nm
- Fraction of Ir metal in coating made by magnetic stirrer is smaller compared to Tube Drive
- Ir metal precipitates easier from inks re-dispersed by magnetic stirrer

See Backup Slides for experimental conditions
Magnetic stirrer re-dispersion (MAG) resulted in precipitation of large particles of IrO₂

Magnetic stirrer is not powerful enough for re-dispersion

See Backup Slides for experimental conditions
Accomplishment: Thickening of anode ink by aging

- Objective: Low viscosity of IrOx inks can be problematic for large-scale coating, and the catalyst particles are observed to crash out in ~a day, exacerbating coating issues. We want to further explore and understand parameter effects of the observation that anode ink “resting” can improve processability.

- Anode inks experiencing a multi-day dwell via simple rolling can increase in viscosity by several orders of magnitude

- However, this behavior is only observed for water-rich formulations
  - Observed for water mixtures with both IPA and nPA

![Graph showing the effect of solvent ratio on shear viscosity](image)
Accomplishment: Thickening of anode ink by aging

- Excess ionomer is required – no thickening is observed for very low I/C
- Behavior is observed for multiple ionomer types
- Result: Potential improvements to ink stability and processability are found in water-rich anode inks with excess ionomer
  - Ionomer adsorption and kinetics studies planned to understand thickening mechanism
  - Coating and performance impacts need to be verified
Accomplishment: R2R Process Comparison for Anode Coating

- Objective: verify that R2R coating methods can achieve comparable performance to FuGeMEA
  - Using baseline ink formulation and high-shear mixing
  - Compare performance of R2R coatings to spray-coated FuGeMEA (at 0.4 mg Ir/cm²)

Decal preparation
- Slot die coating: IrO₂ coating (0.39 mg Ir/cm²) on ETFE
- Gravure coating: IrO₂ coating (0.38 mg Ir/cm²) on ETFE
- Decal transfer
  140°C, 50 kg/cm², 3 min

- Result: Slot-die and gravure coated anodes showed comparable performance to FuGeMEA
Accomplishment: R2R Anode Loading Comparison

• Objective: evaluate R2R anode coating efficacy at different loadings
  – Study R2R gravure-coated anodes at 0.2 and 0.4 mg Ir/cm²
  – Compare performance of R2R coatings to spray-coated FuGeMEA at same loading

• Result:
  – Whereas R2R anode showed comparable performance to FuGeMEA at 0.4 loading, the R2R anode performance at 0.2 loading was much worse
  – Optical microscopy (transmission) showed poor micro-scale uniformity of the lower loaded R2R anode
  – Need additional studies to improve the uniformity of low-loaded anodes via R2R processes
Accomplishment: CL/PTL Interface Modification via Laser Ablation

- Laser ablation melts titanium phase altering interfacial morphology of PTLs

  - Laser Ablation
  - Laser Ablated PTL

- Parallel patterned PTL
  - Performance improvement with narrow path spacing
    - Channel structure at the interface causes severe deformation and accumulation of gas

- Cross patterned PTL
  - Performance improvement with wider path spacing
    - Wider path spacing flattens titanium phase providing enhanced contact and minimizes deformation

- Result: Laser ablated PTL outperforms baseline at both baseline and ultra-low loadings (0.4 and 0.055 mg/cm²)
Accomplishment: PTL Bulk Modification via Laser Ablation

- Fabricated patterned pores at the PTL-flow field interface to facilitate gas removal
  - Pores are not ‘through-pores’
  - CL/PTL interface remains unaltered

- Bulk modification can be used to enhance mass transport without sacrificing interfacial properties
  - Ohmic and kinetics remain consistent between two PTLs
  - Mass transport improved with patterned pores
Accomplishment: Ti PTL Pore Structure Optimization

- Developed tapecasting and sintering protocol for Ti powder
- Selected Ti powder morphology and size, poreformer type and size

Tradeoff between mechanical strength and over-densification
Accomplishment: Ti PTL Pore Structure Optimization

- Produced and tested PTLs with range of poreformer size and loading
- Result: 60 v% Ti – 40v% 60µm poreformer outperforms baseline commercial PTL

Tunable pore size and structure

<table>
<thead>
<tr>
<th>10µm PMMA</th>
<th>30µm PMMA</th>
<th>40:60 Ti:PMMA</th>
<th>60µm PMMA</th>
</tr>
</thead>
</table>

Cell Performance

- Baseline
- T60-P40-60um-mark65
- T60-M60-10um-mark70
- T60-P40-30um-mark65
- T60-P40-10um-mark65

Conditions:
- 80°C
- Water flow in anode and fully humidified H₂ in cathode
- N117 membrane
- Anode: Tkk IrO₂ (0.4 mg/cm²)
- Cathode: Tkk10V50E Pt/C (0.1 mg/cm²)
- PTL thickness: 10 thou / gasket 10 thou
- GDL: Toray 120 / gasket 10 thou
Responses to Previous Year Reviewers’ Comments

- Not reviewed last year
Collaboration and Coordination

NREL Team Members: Carlos Baez-Cotto, Sunil Khandavalli, Scott Mauger, Jason Pfeilsticker, Elliot Padgett, Tobi Schuler, Guido Bender, Michael Ulsh [Ink characterization and studies, Electrode coating, In situ testing, MPL studies]

LBNL Team Members: Grace Lau, Jason Lee, Nemanja Danilovic, Julie Fornaciari, Michael Tucker, Adam Weber, Ahmet Kusoglu, Elizabeth Greenberg, Ashley Bird, Sarah Berlinger [Fundamental material interactions and interfaces studies, Electrode coating, PTL fabrication and surface modification, In situ studies]

ANL Team Members: C. Firat Cetinbas, Nancy Kariuki, Debbie Myers, Jaehyung Park [X-ray characterization studies for inks and electrodes]

ORNL Team Members: Erin Creel, Xiang Lyu, Alexey Serov, Dave Cullen, Haoran Yu, David Arregui-Mena [Ink characterization and studies, Electrode coating, Electron microscopy]

University Collaborators: Iryna Zenyuk, Yu Morimoto, Devashish Kulkarni (UCI) [Tomography]; Svitlana Pylypenko, Jayson Foster (CSM) [Electron microscopy and XPS]; Shawn Litster, Kara Ferner, Fausto Pasmay (CMU) [Tomography]
Remaining Challenges and Barriers

- Improve anode ink stability
- Understand and predict ink interactions
- Improve coating uniformity of low-loaded R2R electrodes
- Optimize MEA interfaces, especially catalyst layer-PTL
- Understand MPL coating and target properties/design
- Validate benefit of new concepts
  - Laser ablation/structuring of PTL
  - Multilayer coatings

Overall Goal: Understand component integration and scaling while maintaining or improving durability
Proposed Future Work

Task 3a: MEA fabrication, Interface engineering

i. Inks
   • Constituent interactions in and mixing of the ink predefine the micro- and macro-scale behaviors
   • Ink morphology: agglomeration, stability, level of adsorption of ionomer

ii. Electrodes
   • Coatability: rheology, wettability
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Task 3b: Components

i. Porous Transport Layers
   • Develop understanding of structure and function, aid in design of new structures

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   • Model impact; develop understanding of structure and function, aid in design of new structures

Any proposed future work is subject to change based on funding levels
Summary—Task 3

- The task 3 effort focuses on cell integration and scale-up aspects of the overall H2NEW goals
  - Efforts are highly integrated with Task 1 durability and Task 2 performance efforts
- Task 3 work areas include inks, electrodes, integration and interfaces, PTLs, and MPLs
  - Completed foundational studies of the impacts of and interactions between ink constituents
  - Completed studies to understand the efficacy of scalable coating methods compared to the spray-coated baseline fabrication
  - Coordinated across labs on ink and anode coating baselining
  - Explored laser modification of PTL surfaces and control of PTL properties via processing routes
- Key findings to date include
  - Interactions between ink constituents as well as levels of agglomeration are highly dependent on formulation
  - R2R coatings can perform comparably to spray-coated baseline at FuGeMEA loading of 0.4 mg Ir/cm2, but further work required to achieve uniform coatings at lower loading
  - Laser ablation of PTL surface can improve performance and mass transport
  - Anode ink stability is a practical processing issue – formulation thickening can improve stability and processability
  - Engineering PTL porosity can result in performance improvements
Technical Back-up and Additional Information
Tech Transfer: Nafion Dispersion Variability Study

- Collaboration with Chemours to understand the impact of dispersion variability
- Characterized 4 lots of D2020 and D2021 dispersions, and resulting catalyst inks, with variations within current manufacturing tolerances
- Result: For dilute inks
  - For each ionomer content, no huge differences across the dispersions
  - The higher I:Cat ratio ink generally had higher
    - Zavg (more adsorption?)
    - Zeta potential (more stabilization)
Tech Transfer: Nafion Dispersion Variability Study

- Result: For concentrated inks
  - TGA: Not a large difference in ionomer wt.%
  - Rheology: The dispersions were more viscous than catalyst inks; inks with higher I:Cat ratio were slightly more viscous
  - Laser Diffraction: D2021 dispersions had larger particles than D2020
  - The D2021 lot 1 dispersion had the highest viscosity and volume of large particles
Accomplishment: Ink studies – Cross-lab Baselining

- Baseline ink formulation has been characterized
- Inks are Newtonian and the ink viscosities are reasonably consistent between the labs

**Ink Rheology**

![Ink Rheology Diagram]

- Ink rheology, thus agglomerated structure, is sensitive to mixing method and mixing duration
- Mixing parameter needs to be further optimized to maximize catalyst dispersion

**Mixing Effects**

![Mixing Effects Diagram]
Accomplishment: Baseline Anode Validation

- Objective: validate consistent fabrication of doctor blade-coated anode decals prepared at NREL, ORNL, and LBNL using the baseline catalyst ink formulation
  - Compare performance of doctor blade-coated decals to spray-coated FuGeMEA (at 0.4 mg Ir/cm²)

Baseline ink formulation

<table>
<thead>
<tr>
<th>Baseline ink</th>
<th>wt.%</th>
<th>Mass (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IrO₂</td>
<td>23.81</td>
<td>3.57</td>
</tr>
<tr>
<td>Water</td>
<td>27.62</td>
<td>4.14</td>
</tr>
<tr>
<td>nPA</td>
<td>24.76</td>
<td>3.72</td>
</tr>
<tr>
<td>Nafion D2020</td>
<td>23.81</td>
<td>3.57</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
<td>15</td>
</tr>
</tbody>
</table>

- High shear mixer (Turrax): 10,000 rpm for 15min

Coating preparation: doctor blade coating

- IrO₂ coating onto PTFE decal
- Transfer to N115
- Standard FuGeMEA sprayed cathode

- Result: Reasonable agreement in performance across labs, establishing basis for collaboration and comparison in future studies
Accomplishment: Impact of Solvent on CCM Structure and Performance

- Larger aggregates lead to larger overpotentials
- Largest aggregate lead to a more dense layer (porosity of 20%) and a higher through-plane tortuosity.

<table>
<thead>
<tr>
<th>Solvent Ratio</th>
<th>Porosity (through-plane)</th>
<th>Porosity (in-plane)</th>
<th>Tortuosity (through-plane)</th>
<th>Tortuosity (in-plane)</th>
<th>Average Pore radius (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:1:1</td>
<td>40%</td>
<td>40%</td>
<td>1.45</td>
<td>1.16</td>
<td>24.7</td>
</tr>
<tr>
<td>1:1:0</td>
<td>40%</td>
<td>40%</td>
<td>1.1</td>
<td>1.09</td>
<td>25.6</td>
</tr>
<tr>
<td>3:1:0</td>
<td>20%</td>
<td>20%</td>
<td>1.89</td>
<td>1.15</td>
<td>6.913 &amp; 23.5</td>
</tr>
</tbody>
</table>

Mass transport overpotential contributes most to the cell overpotential
- Different pathways for the water and oxygen to transport can lead to different overpotentials

FIB-SEM and porosity calculations done at UC Irvine by D. S. Kulkarni, H. Wang, I. Zenyuk

0.16 wt% catalyst inks, CCM ultrasonic spray-coated
Accomplishment: Small-scale Anode Coating Studies

- **Objective:** study doctor blade-coated anode decal and direct coating
  - Using baseline ink formulation and high-shear mixing
  - Compare performance of doctor blade-coated decals to spray-coated FuGeMEA (at 0.4 mg Ir/cm²)

- **Result:** Blade-coated decals and direct coatings had comparable iR-free performance to FuGeMEA
Accomplishment: Anodic Inks Aging Studies – Design of Experiment

- **“H2NEW Baseline” Recipe**

<table>
<thead>
<tr>
<th>Component</th>
<th>Mass Percent (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IrO2</td>
<td>23.81</td>
</tr>
<tr>
<td>Water</td>
<td>27.62</td>
</tr>
<tr>
<td>nPA</td>
<td>24.76</td>
</tr>
<tr>
<td>Nafion D2020</td>
<td>23.81</td>
</tr>
<tr>
<td><strong>Total Solids</strong></td>
<td><strong>28.81</strong></td>
</tr>
<tr>
<td>I/C</td>
<td>0.21</td>
</tr>
</tbody>
</table>

- **Substrate**: 123 um (5 mil) skived PTFE strips
- **Baker bar straddling the PTFE** – 0-21 days: 150 um bar

- **Mixing**: 9,000 rpm for 15 min. with IKA Tube Drive

Inks initially dispersed by IKA Tube Drive.

- **Study I**: re-dispersion by a) Tube Drive and b) Magnetic Stirrer
- **Study II**: re-dispersion by Tube Drive
Accomplishment: Anodic Inks Aging Study - XPS Surface Characterization

Data is reproducible from area to area (100s micron analysis area)

<table>
<thead>
<tr>
<th>Area Ratios</th>
<th>F/Ir</th>
<th>CF_x/Ir</th>
<th>C/F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Day 0</td>
<td>51.8</td>
<td>5.4</td>
<td>0.11</td>
</tr>
<tr>
<td>Day 3</td>
<td>57.5</td>
<td>6.2</td>
<td>0.11</td>
</tr>
<tr>
<td>Day 14</td>
<td>61.1</td>
<td>6.6</td>
<td>0.11</td>
</tr>
</tbody>
</table>

Increase in relative amount of ionomer species compared to Ir – confirmed from elemental ratios of F/Ir (derived from F 1s and Ir 4f) as well as CF_x/Ir (derived from C 1s and Ir 4f)

Ratio of C/F is the same as expected – both signals come from ionomer

No visible changes to Ir states
Publications and Presentations

• Ulsh M., Mauger S.A., Khandavalli S., Park J., Baez-Cotto C., Pfeilsticker J., Kang Z., Bender G. “Towards addressing fundamental scale-up questions for low-temperature electrolysis electrodes.” Invited oral presentation I04-1364 at the Fall ESC Meeting (virtual), October 2021.

