The Effect of Teflon Emulsion on Hydrogen Electrode Properties and Performance in Nickel-Hydrogen Cells

Margot Wasz, Ph.D. and Albert Zimmerman, Ph.D.

Mail Stop M2-275
Energy Technology Dept./The Aerospace Corporation
P.O. Box 92957
Los Angeles, CA 90009-2957
Margot.L.Wasz@aero.org
Concern

• T30, the Teflon emulsion used in the manufacture of hydrogen electrodes used in nickel-hydrogen cells, will soon no longer be available
  – PFOA (perfluorooctanoic acid) and Triton X-100 surfactant is being phased out in North America and Europe due to environmental concerns
  – T30, an aqueous solution of Teflon containing both of these compounds, was removed from the commercial market in 2007
  – Teflon emulsions have a short shelf life due to Teflon particle settling and coagulation
Approach

• Establish a better understanding of the links between the properties of the Teflon emulsion, hydrogen electrode and cell performance
  – Materials characterization
  – Electrode characterization
  – Cell performance
• Put in place tools and methods of evaluation for more quickly evaluating candidate replacement emulsions when T30 is no longer available
  – TE3859, now in-use commercially as a replacement for T30, is expected to be removed from production by 2013 due to further restrictions on the use of PFOA during manufacturing
Historical Development of the Hydrogen Electrode

- Hydrogen electrodes composed of Teflon were developed for alkaline fuel cells in the 1960s
- When nickel-hydrogen cells were proposed as an alternative to nickel-cadmium cells for satellites, the same hydrogen electrode was tested and implemented
- Hydrogen electrode composition
  - Nickel screen current collector
  - GoreTex membrane on backside to retard water loss
  - Pt/Teflon active material to reversibly catalyze the conversion of water to hydroxide and hydrogen
- Hydrogen electrode processing parameters were optimized to provide the best performance in fuel cells
Operation of the Hydrogen Electrode

- **Charge**
  \[ \text{H}_2\text{O} + \text{e}^- \rightarrow \frac{1}{2} \text{H}_2 + (\text{OH})^- \]

- **Overcharge**
  \[ 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow 2(\text{OH})^- + \text{H}_2 \]

- **Discharge**
  \[ \frac{1}{2} \text{H}_2 + (\text{OH})^- \rightarrow \text{H}_2\text{O} + \text{e}^- \]

- **Reversal (positive precharge)**
  \[ 2(\text{OH})^- \rightarrow \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \]

- **Reversal (negative precharge)**
  \[ \frac{1}{2} \text{H}_2 + (\text{OH})^- \rightarrow \text{e}^- + \text{H}_2\text{O} \]
Reported Failure Modes Associated with Hydrogen Electrodes

• Alkaline Fuel Cell Applications
  – Excessive hydrophilic nature – flooding
  – Excessive hydrophobic nature – insufficient wetting
  – Flooding due to water vapor accumulation
    • More commonly a concern at higher temperatures
  – Recrystallization of Pt particles over life
    • Lowers reactivity and catalyst surface area
  – Oxidation and dissolution of platinum
  – Carbon dioxide poisoning - usually from impure reactant gases
  – Silicate build-up from asbestos wicks

• Battery Applications
  – Shorting due to Pt particle dislocation
Structure of the Hydrogen Electrode

• Materials Parameters of Interest
  – Conductivity
  – Surface Area
  – Pore size distribution
  – Density
  – KOH retention
  – Gas permeability
  – Cracking
  – Adhesion of the active material
  – Phase distribution of Pt and Teflon

*SEM Image of the top surface of a hydrogen electrode*
Processing Variables of Interest

• Mechanism for creating pores and surface area considered important for electrode performance…
  – Impact of the surfactant type
  – Impact of sintering temperature
  – Impact of other processing variables such as cooling rates, pressure levels, slurry composition
• …however, how much change can be accommodated without affecting performance or life is not known

SEM Image of the top surface of a hydrogen electrode with residue left in surface crater
Comparison of T30 with TE3859 Replacement Emulsions

• Analysis of Trace Components
  – FTIR analysis confirmed that T-30 contained volatiles consisting of phenol ethoxylates; octyl, nonyl and decyl phenol ethoxylates
  – FTIR analysis confirmed that TE3859 contained polyethylene glycol monomethyl ether
• Different volatility of new surfactants on likely to affect final surface area and pore size distribution for the same sintering temperatures
• Effect of different class of surfactants on electrode life is unknown
  – Ability to wash residues from electrodes also unknown

FT-IR spectra of the T-30 and TE-3859 residues of the centrifuged supernatant heated to 120°C
Plate Characterization for T30 and TE3958 Electrodes

• In 2006, Aerospace sampled 24 electrode plates, 50% produced with T30 and 50% produced with TE3859.

• Tests included:
  – Density, thickness
  – Adhesion, surface appearance
  – KOH wettability, gas permeability, bubble pressure
  – Pt solubility, hot KOH exposure
  – Inorganic and organic contaminants
  – SEM analysis for pore, Pt particle, Teflon distribution, and cracking characteristics
  – Oxygen and hydrogen overpotential measurements
Results of Plate Characterization for T30 and TE3958

- TE3859 electrodes were thinner and more dense, less wettable with KOH and had smoother surface
  - 20 – 50% less KOH held within pores
  - Less internal pore and void volume
  - Loss of much of the larger pores compared to T30 electrodes
  - Loss of much of the macroscopic cracking compared to T30 electrodes
  - Slightly more organic contaminants
- Slightly poorer Pt catalyst adhesion in TE3859 electrodes
  - Adhesion degraded slightly more by hot KOH exposure
- Small changes in averaged charge and discharge voltages
  - Higher H$_2$ evolution (recharge) voltage for TE-3859 (about 10mV at C/2)
  - Similar H$_2$ recombination (discharge) voltages
  - Lower O$_2$ recombination potential for TE-3859 (about 20mV at C/2)
  - Higher O$_2$ evolution potential for TE-3859 (about 10mV at C/2)
Impact of Normal Processing Variables

• Difficult to interpret electrode test results because the normal variation of these parameters for T30 were unknown
  – Aerospace then studied 10 samples each of T30 and TE3859 electrodes where the post-sintering cool-down was varied between the allowable minimum and maximum rates

• Tests performed included:
  – Density, thickness, adhesion to substrate, surface appearance
  – KOH wettability and gas permeability

• Results found:
  – Cooling rate affected electrode density and active material adhesion
  – Range found overlapped the range seen in the prior T30 & TE3859 tests
  – Gas permeability affected by degree of compression of the Gortex layer
Cell Testing with T30 and TE3859

• Four 90Ah cells received from EP for evaluation
  – RNH90, double zircar separator, wall wick, 31% KOH, and strain gages
  – Two made with T30 (cells 1, 4) and two with TE3859 (cells 2 & 3)
• Capacity measured at -10, 0, 10°C
  – Charge at C/10 (9A) for 16 hours followed by a C/2 (45A) discharge to 1.0V
• Voltages were slightly higher in TE3859 cells during charge and discharge

<table>
<thead>
<tr>
<th></th>
<th>T30 (Cell 1)</th>
<th>T30 (Cell 4)</th>
<th>TE3859 (Cell 2)</th>
<th>TE3859 (Cell 3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacity (Ah)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-10°C</td>
<td>104.2</td>
<td>105.5</td>
<td>105.4</td>
<td>104.8</td>
</tr>
<tr>
<td>0°C</td>
<td>106.8</td>
<td>107.0</td>
<td>107.3</td>
<td>107.5</td>
</tr>
<tr>
<td>10°C</td>
<td>98.3</td>
<td>97.9</td>
<td>98.4</td>
<td>98.4</td>
</tr>
<tr>
<td>EOC Voltage</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-10°C</td>
<td>1.604</td>
<td>1.603</td>
<td>1.606</td>
<td>1.605</td>
</tr>
<tr>
<td>0°C</td>
<td>1.561</td>
<td>1.560</td>
<td>1.561</td>
<td>1.562</td>
</tr>
<tr>
<td>10°C</td>
<td>1.519</td>
<td>1.519</td>
<td>1.520</td>
<td>1.520</td>
</tr>
</tbody>
</table>
Initial Capacity Cycling of Four Cells at -10°C: Voltage

Initial Cell Cycling at -10degC

- OCV
Initial Capacity Cycling of Four Cells at -10°C: Pressure
Cell-Level Testing of Cells made with T30 and TE3859

• Problem: How to test NiH₂ cells to best compare the capability of the different hydrogen electrodes?
  – The nickel electrode is usually the life-limiting electrode when cycling NiH₂ cells

• Typically, life tests and stress tests defined for NiH₂ cells are designed to stress the nickel electrode
  – Higher depth of discharge
  – Increased temperature
  – Increased amount or rate of overcharge
  – Increased frequency of cycles (throughput)

• Stress factors appropriate to the H₂ electrode were proposed
  – Increased rates for charge and discharge
  – Reduced temperatures to evaluate liquid and gas transport processes
  – Overcharge to evaluate O₂ recombination tolerance
Hydrogen Electrode Stress Test Cycle

- Low temperature operation: -10°C at end of charge
  - Enables operation with minimal overcharge to stress the nickel electrodes
  - Worst case for transport processes
  - Relatively abrupt onset for oxygen evolution at full charge
- 90-minute cycle profile
  - 30 minutes discharge, 60 minutes recharge
- 40% DOD with periodic high rate discharge pulses
  - Three cycles of 8 minutes discharge at 0.5C followed by 2 minutes at 2C for a 40 DOD
  - High rate pulses expected to stress the H₂ electrode transport capabilities
  - Pulse periodicity expected to allow H₂ pressure dependence to be studied
- High peak recharge rate (C-rate)
  - Current taper at a peak cell charge voltage limit
  - One set of cells run at 1.02 RCF, other set at a 1.04 RCF target (1.03 – 1.05 actual)
    - Lower RCF cells go to open circuit conditions while the second set of cells obtain their higher RCF during the 60 minute charge
P/F Criteria and Parameters Trended

- Tests will run until cell voltage falls below 0.7 V during 2C discharge or 1.0 V at 0.5C
  - To date, over 1880 cycles had been applied

- Parameters trended for possible sensitivity to the type of emulsion used in the hydrogen electrodes
  - Voltages signatures during charge and discharge
  - EOCV and EODV
  - Current taper
  - Recharge ratios (RCF)
  - Thermal signatures
  - Pressure signatures
Stress Test Results to Date:  End of Discharge Voltage

EODV as a function of Cycle Number
(measured at the maximum pulse discharge rate)
Stress Test Results to Date: Current Taper (cells 3 & 4)

EOC-Current as a function of Cycle Number (cells 3 & 4)

- Power Outage
- Chiller anomaly
Stress Test Results to Date: End of Charge Voltage

EOCV as a function of Cycle Number

End of Charge Voltage (V)

Cycle Number

- T3C (cell 1)
- TE3859 (cell 2)
- TE3859 (cell 3)
- T3C (cell 4)
Stress Test Results to Date: Max Charge Voltage prior to Taper

Maximum Charge Voltage as a function of Cycle Number

- T30 (cell 1)
- TE3859 (cell 2)
- TE3859 (cell 3)
- T30 (cell 4)
Stress Test Results to Date: Recharge Fraction (RCF)
Stress Test Results to Date: End of Charge Temperature

End of Charge Temperature as a function of Cycle Number

-8
-8.5
-9
-9.5
-10
-10.5
-11
-11.5
-12

0 200 400 600 800 1000 1200 1400 1600 1800 2000
Cycle Number

T30 (cell 1)
TE3869 (cell 2)
TE3869 (cell 3)
T30 (cell 4)
Stress Test Results to Date: End of Discharge Temperature

End of Discharge Temperature as a function of Cycle Number

- Temperature (°C)
- Cycle Number
- Cycle Number ranges from 0 to 2000
- Different lines represent different cell numbers and configurations.
Stress Test Results to Date: End of Charge Pressure

End of Charge Pressure as a function of Cycle Number

![Graph showing End of Charge Pressure vs. Cycle Number with different lines for T30 (cell 1), TE3869 (cell 2), TE3869 (cell 3), and T30 (cell 4).]
Stress Test Results to Date: End of Discharge Pressure
Summary of Findings to Date

• Differences in surfactants used in electrodes expected to impact microstructure of electrodes produced due to differences in volatility, however, processing variables may have as strong of an impact
  – Expect to need to vary some processing parameters for follow-on replacement emulsion for T30
  – Need to develop the allowable range for critical parameters based on existing T30 production lots

• Different Teflon emulsions expected to show small impacts in charge and discharge voltages

• Low temperature, high pulse cycling of cells containing T30 electrodes and other cells containing TE3859 electrodes are presently showing greater end-of-discharge voltage losses in the cells containing the T30 electrodes
  – About 1850 cycles applied so far
Next Directions

• Continue four-cell low temperature cycling tests
• Continue baseline effort for existing T30 electrodes
• Study variation of processing parameter on hydrogen electrode material characteristics
  – Surface area, porosity
  – Hydrophobicity
  – KOH retention
• Study variation of processing parameter on hydrogen electrode material characteristics
  – Plate-level stress tests
• Evaluate candidate replacement emulsions when they become available
Acknowledgments

• The author is grateful for the assistance and contributions of the following personnel:
  – The Aerospace Corporation: Lindsay Berger, Boyd Carter, Myriam Easton, Tom Giants, Warren Hwang, Michael Quinzio, Larry Thaller, and Gloria To
  – Boeing: Ken Jennings
  – Eagle-Picher: Jeff Dermott

• The Aerospace Corporation is gratefully acknowledged for supporting this work as part of the Aerospace Mission Oriented Investigation and Experimentation (MOIE) program.

• All trademarks, service marks, and trade names are the property of their respective owners
Additional Data
Initial Capacity Cycling of Four Cells at 0°C
Initial Capacity Cycling of Four Cells at 10°C
Cycle 100 Curves for 1.02 RCF

Cycle 100: Cells cycled to 1.02 RCF
Cycle 1000 Curves for 1.02 RCF

Cycle 1000: Cells cycled to 1.02 RCF

Time (days)

Cell Voltage (V)

T30 (cell 1)
TE3659 (cell 2)
Cycle 1886 Curves for 1.02 RCF
Cycle 100 Curves for 1.03 – 1.05 RCF

Cycle 100: Cells cycled to 1.03 RCF

Cell Voltage (V)

Time (days)

TE3859 (cell 3)

T30 (cell 4)
Cycle 1000 Curves for 1.03 – 1.05 RCF
Cycle 1868 Curves for 1.03 – 1.05 RCF