
Anthony Hechanova
University of Nevada, Las Vegas, hechanova@unlv.nevada.edu

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High Temperature Heat Exchanger Project

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Quarterly Progress Report
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The UNLV Research Foundation
4505 Maryland Parkway
P. O. Box 452036
Las Vegas, NV 89154-2036

Anthony E. Hechanova, Ph.D.
Project Manager
(702) 895-1457
(702) 895-2354 (FAX)
hechanova@unlv.nevada.edu

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1.0 UNLV Design and Testing Group

1.1 HTHX Thermal Systems Design (PI: Yitung Chen, UNLV)

1.1.1 HTHX Thermal Systems Design Highlights

- Hydrodynamics and thermal numerical modeling coupled with sulfur trioxide decomposition for the one channel geometry with three different channel configurations were performed. The results obtained from the numerical modeling were compared with the baseline design under the same boundary and operation conditions. The case with diamond shaped channels has the highest percentage of sulfuric acid decomposition. The baseline channel geometry has the lowest pressure drop compared with other cases.
- The single plate model for a parametric study of the sulfuric acid decomposer with two hexagonal-shaped layers was created. A parametric study on inlet and outlet manifolds using the single plate model was completed. An improved manifold design was chosen based on the parametric study. The selected design has a uniform velocity distribution at the midsection of the channels and a reasonable pressure drop.
- Modification of Matlab codes for calculations of probabilistic failure criteria (Weibull distribution) and safety factor distributions using Coulomb-Mohr failure criteria was made.
- The calculations of the safety factor and the probability of failure for the one channel geometries with ribbed ground surface of the channel and with hexagonal layers were completed. According to the calculations, the channel geometries will not fail under the proposed operating conditions.
- A finite element model of the “Ball on Three Ball Test” for ceramic material was created to select an appropriate specimen thickness for future experimental testing. The solution using the finite element model for 4 mm plate thickness was completed.
- The numerical modeling of a bayonet-type heat exchanger and decomposer based on the SNL design is in progress. The numerical results will be benchmarked with the experimental data based on the lab scale experiment carried out by SNL.

1.1.2 HTHX Thermal Systems Design Technical Summary

Numerical Analyses with Chemical Reactions and Optimization Studies for Ceramatec Sulfuric Acid Decomposer

The sulfur trioxide decomposition for the one channel geometry with ribbed ground surface of the channel with platinum catalyst was investigated. The height of the ribs is 0.2 mm, the width is 0.3 mm, and distance between ribs is 0.7 mm (Figure 1). All of other dimensions, boundary and operation conditions are the same as the baseline design. The decomposition percentage of using the ribbed geometry does not increase significantly as compared with the baseline design. The main reason is because stagnation zones between the ribs slow down the diffusion of chemical reaction products into the main-stream direction. The diffusion process is the limiting factor of decomposition rate compared to the convection process. Pressure drop in the channel with chemical reactions is 1300 Pa (for the baseline design the pressure drop is 280 Pa).
The numerical modeling of sulfur trioxide decomposition for the one channel geometry with two hexagonal layers under two values of layer overlapping (50% and 100%) was performed (Figure 2 a, b). For 100% overlapping, the percentage of SO$_3$ decomposition is 0.7% (higher than in the baseline design 0.5%) and the pressure drop in the channel with chemical reaction is 14,000 Pa (baseline design – 280 Pa). For the 50% overlapping, the percentage of SO$_3$ decomposition is 0.7% and the pressure drop in the channel with chemical reaction is 2700 Pa. According to the numerical results, the value of the layers overlapping doesn’t impact the percentage of SO$_3$ decomposition significantly. The pressure drop is significantly dependent on the hexagonal layer overlapping ratio.

The numerical modeling of sulfur trioxide decomposition for the one channel geometry with two diamond-shaped layers was performed (Figure 3). The percentage of SO$_3$ decomposition is 0.77% and the pressure drop in the channel with the chemical reaction is 5100 Pa. The results of the numerical modeling were compared with results of calculations for the different channels of other shapes (straight, hexagonal, and ribbed channels) for the same boundary and operation conditions (Table 1). The percentage of decomposition for the diamond shaped channels is higher than that in the other channel shapes. The main reason is because the surface area of chemical reaction for the diamond-shaped channels is larger than in the other geometries. The straightforward channel geometry has minimal pressure drop (280 Pa) compared with other cases.
(a) 100% overlapping  
(b) 50% overlapping

Figure 2. Hexagonal channels.

Figure 3. Diamond shaped channels.
Table 1. Numerical results of SO$_3$ decomposition percentage based on the different channels and geometries.

<table>
<thead>
<tr>
<th>Name of case</th>
<th>Area of chemical reaction, m$^2$</th>
<th>Volume of reacting flow, m$^3$</th>
<th>Area/Volume, m$^2$/m$^3$</th>
<th>Percentage of SO$_3$ decomposition, %</th>
<th>Pressure drop, Pa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Straightforward channels</td>
<td>8.864-$10^{-5}$</td>
<td>1.409-$10^{-8}$</td>
<td>6291</td>
<td>0.515</td>
<td>275</td>
</tr>
<tr>
<td>Ribs (0.1 mm)</td>
<td>9.320-$10^{-5}$</td>
<td>1.319-$10^{-8}$</td>
<td>7065</td>
<td>0.510</td>
<td>512</td>
</tr>
<tr>
<td>Ribs (0.2 mm)</td>
<td>9.756-$10^{-5}$</td>
<td>1.234-$10^{-8}$</td>
<td>7906</td>
<td>0.529</td>
<td>1275</td>
</tr>
<tr>
<td>Hexagons (100% overlap)</td>
<td>1.359-$10^{-4}$</td>
<td>1.903-$10^{-8}$</td>
<td>7141</td>
<td>0.703</td>
<td>13737</td>
</tr>
<tr>
<td>Hexagons (50% overlap)</td>
<td>1.330-$10^{-4}$</td>
<td>1.903-$10^{-8}$</td>
<td>6989</td>
<td>0.695</td>
<td>2733</td>
</tr>
<tr>
<td>Diamonds</td>
<td>1.480-$10^{-4}$</td>
<td>1.736-$10^{-8}$</td>
<td>8525</td>
<td>0.767</td>
<td>5106</td>
</tr>
</tbody>
</table>

The sulfur trioxide decomposition for the one channel geometry with straight channels for the different operation conditions and channel length compared with baseline design were studied to understand the effect of decomposition percentage when the residence time is increased. The length of the channels is 0.523 m (10 times longer than the baseline design), the operation pressure is 75 atm (5 times higher than the baseline conditions), and the mass flow rate for reacting and product flows is 6.3-$10^{-7}$ kg/s (10 times higher the baseline conditions). Figure 4 shows that SO$_3$ mass concentration is reduced in the reacting flow channel. On the other hand, Figure 5 indicates that mass concentration of SO$_2$ respectively increases along the reacting flow direction. The percentage of SO$_3$ decomposition for the case is 89% - much higher than that in the baseline design (0.5%). One of the main reasons is due to the residence time (7.7 sec) being much higher than in baseline case (0.02 sec). The other reason for this high percentage decomposition is that the total surface reaction area is 10 times higher than in baseline design. The pressure drop in the channel with chemical reaction is 45 Pa (baseline design – 280 Pa).

The single plate model for parametric study of the decomposer with two hexagonal-shaped layers was created. Two sizes of hexagons (7 mm and 2 mm length) were investigated. The value of layer overlapping was 50% for both of the cases. According to previous investigations, this value of overlapping provides minimal pressure drop in the channels. The velocity distribution for the case with 2 mm hexagons is more uniform when compared with the 7 mm case. The pressure drop for the case with 7 mm hexagons is 20 kPa while it is 22 kPa for the case with 2 mm hexagons.

A parametric study on inlet and outlet manifolds for the case with 2 mm hexagons was completed. An improved manifold design was chosen (Figure 6). For the selected design, the velocity distribution at the midsection of the channels is uniform (Figures 7 and 8) and the pressure drop for the whole plate is 7.5 kPa. The obtained velocity distribution and pressure drop are satisfactory.
Figure 4 - Mass fraction of $SO_3$

Figure 5 - Mass fraction of $SO_2$

Figure 6. Single plate model - hexagonal shaped channels, improved design.
Stress Analysis and Optimization of Ceramatec HTHX

Modification of Matlab codes for calculation of probabilistic failure criteria (Weibull distribution) and safety factor distributions using Coulomb-Mohr failure criteria was made. A subroutine that optimizes processing of large size matrices was added which resulted in a significant decrease in calculation time (from 40 min to 5 min).

The calculations of the safety factor and the probability of failure for the one channel geometry with a ribbed surface were completed. The ribs are 0.2 mm in height and 0.3 mm in width. The distance between ribs is 0.7 mm (Figure 1). Figure 9 shows the distribution of the nodal factor of safety. For this geometry, the minimum safety factor is 11 and the overall safety factor is 170. The probability of failure is equal to zero in the three principal directions.

The calculations of the safety factor and the probability of failure for the one channel geometry with hexagonal layers with 50% overlapping were performed. The length of the hexagons is 2 mm. Figure 10 shows the distribution of the nodal factor of safety. For this geometry, the minimum safety factor is 4.4 and the overall safety factor is 3500. The probability of failure is equal to zero in the three principal directions.
Figure 9. Safety factor distribution for the ribbed channel case.

Figure 10. Safety factor distribution for the hexagonal channel case.

The results of the stress analysis show that the ribs and especially hexagon layers have increased stresses in the SiC material as compared with baseline design (straight channels). However, all the considered channel geometries will not fail under the proposed operating condition. The
results also show that both approaches (Weibull and Mohr criteria) indicate the two designs will not fail.

A literature review of the testing methods for ceramic materials was completed.

A finite element model of the “Ball on Three Ball Test” for ceramic material was created to select an appropriate specimen thickness for future experimental testing. A mesh independence study of the model was completed and appropriate mesh for the calculations was chosen (Figure 11). The solution using the finite element model for a 4 mm plate thickness gave the same stress range as analytical solutions from literature; therefore the developed model was deemed reliable. The distribution of first principal stress is shown in Figure 12.

\[\text{Figure 11. Mesh for the “Ball on Three Ball Test” model.}\]

**Numerical analysis of bayonet HTHX and decomposer based on SNL design**

A literature survey was initiated. The SNL reports entitled “Preliminary Design for the Sulfuric Acid Section of the Integrated Lab Scale Experiment” and “Operational Characteristics and Performance of a Pressurized and Integrated H\textsubscript{2}SO\textsubscript{4} Decomposition Section” were received and reviewed.

**Numerical analysis of shell and tube HTHX and decomposer**

A literature survey was initiated.
1.2 Scaled HTHX Tests (PI: Samir Moujaes, UNLV)

Hydrodynamic tests using an isothermal single-chamber test section with 2 cSt and 5 cSt silicone oils were completed. The flow meter has a 2% uncertainty after the in-loop calibration. The manometer has 5-10% uncertainty depending on the flow rate. The pressure taps were located 5 mm before and after the fin area. The friction factors were calculated using the hydraulic diameter, length between the two pressure taps, and the average velocity between fins. The Reynolds number had an uncertainty of 4%, and the friction factor has an uncertainty of 7-11%. The experiments were performed using Reynolds numbers between 50 and 250 to simulate the prototype heat exchanger flow (Figure 13).
Thermal tests on a single-chamber test section with 5 cSt silicone oils were completed. The model to prototype dimension ratio is 2:1. The test section was made of one piece of Alloy 6061 (fin) and one piece of acrylic sheet. The heating source of uniform heat flux came from an electric heating pad under the fin area. The heat flux was controlled by a variable voltage controller. The test section was wrapped with fiberglass insulation blanks (k=0.032 W/m°C). There were insulation parts inside the test section between the inlet and outlet sections and the fin section to reduce axial heat transfer and to ensure heat transfer mainly in the fin area. CFD simulation and thermocouple readings verified that the heating from the entrance region caused about 5% error. The error caused by T-type thermocouples was 5%. Reynolds numbers varied from 50 to 110. The flow rate had 2% error. The Reynolds number had an uncertainty of 4%, and the overall heat transfer coefficient’s (U) (one-sided heat transfer for this case) uncertainty was 11%. Using \( U \) instead of heat transfer coefficient (\( h \)), the Nusselt number had an uncertainty of 11%. The \( j \) number, \( StPr^{2/3} \), having an uncertainty of 12%, is larger than the predicted. The plots of overall heat transfer coefficient and \( j \) number with Reynolds number are shown in Figures 14 and 15. No hydrodynamic data was obtained when the heat transfer experiment for the silicone oil was made (e.g., frictional pressure drop calculations). It was difficult to position the test section horizontally with the insulation layers, and the pressure readings heavily depend on the position.

Figure 13. Hydrodynamic data for liquid test sections of 2 cSt and 5 cSt silicone oil, isothermally at 25°C.
Thermal tests on a single-chamber test section with air are in process. The test sections are made of Alloy 6061. They are heated on either one side or both sides by electric heating pads. Because of the low specific heat capacity of air, the test sections are heated to higher temperatures than the liquid test section but with a lower heat transfer power. The higher temperature of the test section led to a large uncertainty on the thermocouple reading of the air temperature. CFD simulations were not in agreement with the experimental data which were probably due to these large uncertainties. The test section needs to be modified before the data is deemed to be reliable.
2.0 UNLV Materials Selection and Characterization (PI: Ajit Roy, UNLV)

2.1 Introduction

The selection of structural materials for heat-exchangers to generate hydrogen using nuclear power is a serious challenge to researchers. This challenge stems from the fact that significantly high temperature, approaching 950°C, will be used in sulfuric acid decomposition associated with the sulfur-iodine (S-I) cycle. In view of this rationale, the heat-exchanger materials must possess sufficiently high tensile strength to ensure the desired structural stability under the operating conditions. Three nickel (Ni)-base alloys, namely Alloys C-22, C-276 and Waspaloy, and a iron-nickel-chromium (Fe-Ni-Cr) alloy, known as Alloy 800H were identified and tested for evaluation of their tensile properties at temperatures ranging between ambient and 1000°C using the newly-installed Instron Model 8862 testing equipment. Two new alloys, namely Alloys 617 and 718, were recently added to the test matrix and their chemical compositions are given in Table 2. The tensile properties were determined by using smooth cylindrical specimens machined from solution-annealed materials. The resultant data and their analyses are summarized below.

Table 2. Chemical compositions of tested materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>C</th>
<th>Fe</th>
<th>Co</th>
<th>W</th>
<th>Si</th>
<th>Mn</th>
<th>V</th>
<th>P</th>
<th>S</th>
<th>E</th>
<th>Zr</th>
<th>Al</th>
<th>Ti</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy 617</td>
<td>44.5</td>
<td>20.0</td>
<td>8.0</td>
<td>0.05</td>
<td>3.0</td>
<td>10.0</td>
<td>--</td>
<td>1.0</td>
<td>--</td>
<td>0.015</td>
<td>--</td>
<td>0.6</td>
<td>0.8</td>
<td>10</td>
<td>0.5</td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td>Alloy 718</td>
<td>53.64</td>
<td>18.40</td>
<td>3.06</td>
<td>0.03</td>
<td>17.46</td>
<td>0.23</td>
<td>--</td>
<td>0.6</td>
<td>0.09</td>
<td>--</td>
<td>0.011</td>
<td>0.0002</td>
<td>0.0002</td>
<td>5.00</td>
<td>0.52</td>
<td>1.04</td>
<td>0.14</td>
</tr>
</tbody>
</table>

2.2 Results

The tensile properties of Alloys C-22, C-276, 800H and Waspaloy were presented in the previous quarterly report. The tensile data of Inconel 718 are presented in the current report. The engineering stress-strain (s-e) diagrams for this alloy are superimposed in Figure 16 to compare the tensile properties at different temperatures. An evaluation of this figure indicates that the magnitude of the yield strength (YS), ultimate tensile strength (UTS) and failure stress was gradually reduced with increasing temperature, as expected. It is also interesting to note that all three parameters showed significant drop beyond 600°C. Further, the YS and UTS could not be differentiated at temperatures beyond 800°C.

For Alloy 718, the magnitude of failure strain was reduced at 100°C, followed by its enhancement above this temperature. Such phenomenon of reduction in failure strain at this temperature is generally attributed to work hardening associated with the diffusion of solute elements ahead of imperfections in the metal lattice, such as dislocations near the grain boundaries. Thus, the dislocation mobility would be impeded, causing reduced plastic flow at
this temperature. This phenomenon is generally termed dynamic strain ageing (DSA) behavior of metallic materials. Beyond this critical temperature, the mobility of dislocations is enhanced, thus causing increased failure strain.

Transmission Electron Microscopy (TEM) was used to characterize dislocations in Waspaloy in the temperature regime of 200°C - 400°C. The variation in dislocation density ($\rho$) with temperature is illustrated in Figure 17. These data indicate that a maximum dislocation density was observed at 300°C, which is the critical temperature above which the dislocation mobility was enhanced.

The fractographic evaluation of the broken tensile specimens by scanning electron microscopy (SEM) revealed predominantly dimpled microstructure in Alloy 718, as shown in Figure 18, indicating ductile failure. However, above 600°C, some brittle failures were seen in the SEM micrographs.

### 2.3 Plans for the Next Quarter

- Tensile properties evaluation of Alloy 617 at different temperatures
- Stress corrosion cracking studies using cylindrical, DCB, C-ring and U-bend specimens
- General corrosion study using coupons
- Fracture toughness evaluation using compact tension (CT) specimens in the Instron device
- Crack growth study of CT specimens by DC potential drop (DCPD) method
- Dynamic strain ageing study by TEM
- Fractographic evaluation by SEM

<table>
<thead>
<tr>
<th>Material</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>C</th>
<th>Fe</th>
<th>Co</th>
<th>W</th>
<th>Si</th>
<th>Mn</th>
<th>V</th>
<th>P</th>
<th>S</th>
<th>B</th>
<th>Zr</th>
<th>Al</th>
<th>Ti</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy C-22</td>
<td>Bal</td>
<td>20.0 to 22.5</td>
<td>12.5 to 14.5</td>
<td>0.01 (max)</td>
<td>2.0 to 6.0</td>
<td>2.5 (max)</td>
<td>2.5 to 3.5</td>
<td>0.08 (max)</td>
<td>0.5 (max)</td>
<td>0.35 (max)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Alloy C-276</td>
<td>Bal</td>
<td>14.5 to 16.5</td>
<td>15.0 to 17.0</td>
<td>0.01 (max)</td>
<td>4.0 to 7.0</td>
<td>2.5 (max)</td>
<td>3.0 to 4.5</td>
<td>0.08 (max)</td>
<td>1.0 (max)</td>
<td>0.35 (max)</td>
<td>0.02 (max)</td>
<td>0.01 (max)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Waspaloy</td>
<td>Bal</td>
<td>18.0 to 21.0</td>
<td>3.5 to 5.0</td>
<td>0.02 (max)</td>
<td>2.0 (max)</td>
<td>12.0 to 15.0</td>
<td>-</td>
<td>0.75 (max)</td>
<td>1.0 (max)</td>
<td>-</td>
<td>0.03 (max)</td>
<td>0.03 (max)</td>
<td>0.003 to 0.01</td>
<td>0.02 to 0.12</td>
<td>1.2 to 1.6</td>
<td>2.75 to 3.25</td>
<td>0.5 (max)</td>
</tr>
<tr>
<td>Alloy 800H</td>
<td>31.99</td>
<td>19.67</td>
<td>-</td>
<td>0.08</td>
<td>4.50</td>
<td>0.4</td>
<td>-</td>
<td>0.24</td>
<td>0.75</td>
<td>-</td>
<td>-</td>
<td>0.001</td>
<td>-</td>
<td>0.44</td>
<td>0.33</td>
<td>0.26</td>
<td></td>
</tr>
</tbody>
</table>
Figure 16. s-e Diagram vs. Temperature of Inconel 718

Figure 17. $\rho$ vs. Temperature for Waspaloy.
Figure 18. SEM Micrograph of Inconel 718 at 400°C.
3.0 Materials, Design and Modeling for C/SiC Ceramic Heat Exchangers, (PI: Per Peterson, UCB)

3.1 Materials, Design and Modeling for C/SiC Ceramic Heat Exchangers

Highlights

- The subcontract to the ceramic vendor COI was completed. A prototype heat exchanger was fabricated, demonstrating the feasibility of all steps. Further process optimization is required, particularly in the area of plate lamination methods, which will be the focus of continued work with COI.
- A report on fluid flow distribution and thermal stress analysis for compact heat exchangers was completed, based upon the use of a porous media approximation. Further work will be performed to develop better approaches to estimate the effective porous media properties based on data obtained from unit-cell calculations.
- Researcher Dr. Jens Schmidt from the German Aerospace Center (DLR) arrived in Berkeley for a 3-month visit to collaborate on the design of liquid-silicon infiltrated ceramics for application in the S-I hydrogen production process.

3.2 Technical Progress Summary

3.2.1 PIP C-C/Si-C composite and other composite material study

The subcontract to ceramic vendor COI was completed and the fabrication of a prototype cross-flow heat exchanger using the PIP method was achieved. The fabrication method uses Teflon molds, as shown in Figure 19, to produce plates with complex and small flow passages embossed in their surfaces, using a paste-like mixture of chopped carbon fibers, silicon carbide powder, and SiC precursor polymer liquid. Plate fabrication using the molds, as shown in Figure 20, demonstrated that high-quality fins can be created, although the fact that some fins showed flaws from incomplete mold filling, and some porosity, shows that further process optimization is required. Following lamination, 5 infiltration and pyrolysis steps were performed, creating a monolithic heat exchanger as shown in Figure 21.

A variety of tests were performed to examine various plate lamination methods. In general, it was found that the green plates were difficult to laminate due to their very smooth surfaces, which resisted bonding. Conversely, pyrolyzed plates proved easy to bond due to the porosity created during pyrolyzation, but warping of the pyrolyzed plates required grinding to flatten the plates, a process that does not extrapolate to larger plates. Based on these observations, further process optimization is also required in plate lamination, with a candidate method being to assemble and pyrolyze a plate stack under compressive pressure but without bonding, and then to infiltrate and pyrolyze to achieve bonding. At the same time, other process optimization activity will occur, in particular focused on further improvement of the paste mixing process to reduce porosity and void generation following pyrolysis.
Figure 19. Teflon molds used to fabricate ceramic cross-flow heat exchanger with millimeter-scale flow channels.

Figure 20. Plate formed using Teflon mold.

Once FY 06 continuation funding is received, UC Berkeley will work with COI to start work focused on further process optimization to reduce residual porosity and to improve lamination methods, and will fabricate a heat exchanger test article with a closed flow path that can be used to demonstrate CVD SiC and pyrolytic carbon coating of interior heat exchanger flow channels.
3.2.2 Compact heat exchanger thermal design study

UC Berkeley completed initial work to develop a thermal and fluid mechanics model for compact ceramic and metal heat exchangers based on the porous media approximation. This approximation is valid when the flow structures in the heat exchanger are small compared to the overall heat exchanger size, and when these flow structures are repeated in such a way that they can be represented as repeating unit cells. Offset strip fin heat exchangers fall into this category. Under this approximation, fluid flow is modeled using effective, anisotropic permeability values estimated from unit cell calculations. Based on the calculated flow distribution of the two fluids, three energy equations can then be solved (two equations for the two fluid phases, and one equation for the solid phase of the heat exchanger structure) to determine the steady state and/or transient temperature distribution in the heat exchanger. The temperature distribution in the solid heat exchanger phase can then be used in thermal stress analysis to estimate global and local stresses, again using the porous media approximation.

The porous media model involves modeling the flow of fluid through the narrow and tortuous passages of the fin section of the IHX as one would model other flows in viscous dominated laminar flows such as those seen in flow through porous media. This treatment greatly simplifies the fluid mechanics modeling in these offset strip fin flow channels where the flow velocity will be nearly linearly proportional to the gradient of flow potential. Of course, this means that locally averaged properties will be found for these flow passages such as porosity, permeability and convection coefficients. The idea behind this approach is to simplify the advective thermal transport equations in order to find the global steady state and transient temperature distribution in the IHX from which a better stress analysis can be performed using the unit-cell analysis method discussed before.
In the reported work, two general approaches were applied for the porous media thermal model. In both approaches conduction in both fluid phases is ignored so that the only temperature gradient that arises in the fluids is found in the flow direction and both approaches rely on an energy balance on a representative volume as can be seen within the green lines of Figure 22 below. The difference between these two approaches lies in how the temperature distribution is modeled in the solid phase. Detailed results were reported, and further work is recommended to better develop this modeling method for transient fluid mechanics and heat transfer in compact heat exchangers.

Figure 22. The unit cell used for local volume averaged mechanical properties and control volume (green) over which momentum and energy balances are performed to derive effective properties for the porous media model.
4.0 Corrosion Studies of Candidate Structural Materials in HIₓ Environment as Functions of Metallurgical Variables (PI: Bunsen Wong, General Atomics)

4.1 Immersion Testing of Materials in HIₓ-H₃PO₄ (Iodine Separation)

Long-term corrosion testing of Ta and its alloys in the iodine separation environment was completed. They all show very low corrosion rate after more than 1000 h of testing (Table 3). Ta, Ta-W alloys and SiC are the only materials that do not exhibit any sign of corrosion in this environment (Figures 23–25). Testing also began on stainless steel specimens coated with Ta in the HIₓ-H₃PO₄ acid mixture. Figures 26 and 27 show a washer and a Swagelok fitting that were electroplated with Ta. After almost 300 h of testing, no sign of corrosion can be observed in either specimen. This shows Ta coated parts can be a viable HX material of construction solution. Further testing of Ta coated specimens is underway.

Table 3. Corrosion rate of qualified materials tested in HIₓ-H₃PO₄ acid mixture at 140 °C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Hours</th>
<th>Corr. rate (mpy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta</td>
<td>1209</td>
<td>0.113</td>
</tr>
<tr>
<td>Ta-2.5W</td>
<td>1080</td>
<td>0.029</td>
</tr>
<tr>
<td>Ta-10W</td>
<td>1209</td>
<td>0.018</td>
</tr>
<tr>
<td>SiC</td>
<td>640</td>
<td>0.239</td>
</tr>
<tr>
<td>Ta-10W*</td>
<td>874</td>
<td>0.011</td>
</tr>
</tbody>
</table>

*with 0.2 M% H₂SO₄ in HIₓ

Figure 23. Ta coupon tested in HIₓ-H₃PO₄ at 140 °C for 1209 h.
Figure 24. Ta-10W coupon tested in HI_x-H_3PO_4 at 140 °C for 1209 h.

Figure 25. SiC coupon tested in HI_x-H_3PO_4 at 140 °C for 640 h.

Figure 26. A stainless washer that was plated with a Ta layer and tested in HI_x-H_3PO_4 acid mixture at 140 °C for 294 h.
Figure 27. A swagelok fitting that was plated with a Ta layer and tested in $HI_X$-$H_3PO_4$ acid mixture at 140°C for 294 h.

Testing of specimen in the acid complex with trace of $H_2SO_4$ is also ongoing. This replicates the flow sheet composition of the iodine separator. Figure 28 shows a Ta-10W coupon tested in the iodine separation environment with 0.2 wt% of $H_2SO_4$ in $HI_X$. The result is similar to the specimen tested without $H_2SO_4$.

Figure 28. Ta-10W coupon tested in $HI_X$-$H_3PO_4$ acid mixture with 0.2 M% of $H_2SO_4$ at 140°C for 874 h (The dark mark in the first two pictures is not any corrosion related feature but is the reflection of the camera).

Also, initial testing of Ta-2.5W in the iodine separation test system with flowing acid was completed. A section of a Ta-2.5W tube was cut in half and placed inside the test capsule that contains the $HI_X$-$H_3PO_4$ acid mixture. After more than 350 h of testing, there is no sign of corrosion in the test specimen (Figure 29) and the behavior observed so far is similar to that seen in the static environment.
The construction of a test system to test valves and other components for HI\textsubscript{x} is ongoing. It will be completed by 10/15/06.

4.2 Immersion Testing of Materials in boiling H\textsubscript{3}PO\textsubscript{4} (H\textsubscript{3}PO\textsubscript{4} Concentration) (ongoing)

The testing of heat exchanger candidate materials in concentrated H\textsubscript{3}PO\textsubscript{4} is ongoing. In order to accelerate specimen testing in the boiling H\textsubscript{3}PO\textsubscript{4} environment, an iodine separation test system was successfully converted into a H\textsubscript{3}PO\textsubscript{4} test system.

A Ta-2.5W coupon was tested in 95wt% for H\textsubscript{3}PO\textsubscript{4} 980 h (Figure 30). There is no sign of severe corrosion but discoloration can be observed in part of the specimen. The corrosion rate is relatively low. The specimen will complete the 1000 h test and be sent to UNLV for analysis.

![Figure 29. A section of a Ta-10W tube that was tested in flowing HI\textsubscript{x}-H\textsubscript{3}PO\textsubscript{4} acid at 130°C for 384 h.](image)

![Figure 30. Ta-2.5W coupon tested in 95 wt% boiling H\textsubscript{3}PO\textsubscript{4} at 240°C for 980 h.](image)
Also the corrosion effect due to the presence of HI and iodine in H$_3$PO$_4$ was explored. Figure 31 shows a Ta-10W coupon that was tested in boiling H$_3$PO$_4$ distillation liquid [87H$_3$PO$_4$ – 3HI – 9H$_2$O – 1I$_2$ (wt%)] for over 1000 h. The result is similar to that tested in concentrated H$_3$PO$_4$ and no accelerated corrosion due to the presence of HI and I$_2$ was observed.

![Figure 31. Ta-10W coupon tested in boiling HI distillation solution [87H$_3$PO$_4$ – 3HI – 9H$_2$O – 1I$_2$ (wt%)] at 200°C for 1050 h.](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Hours</th>
<th>Corr. rate (mpy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta-2.5W*</td>
<td>980</td>
<td>0.541</td>
</tr>
<tr>
<td>Ta-10W**</td>
<td>1072</td>
<td>2.583</td>
</tr>
</tbody>
</table>

*95wt% H$_3$PO$_4$ at 240°C,  
** 87H$_3$PO$_4$ - 3HI- 9H$_2$O - 1I$_2$ (wt%) at 200°C

### 4.3 Testing of Materials in HI + I$_2$ + H$_2$ (HI gaseous decomposition)

Long-term testing of Hastelloy B2 in both the HI gaseous decomposition and the iodine condenser environments was completed (Figures 32 and 33). It has the lowest corrosion rate among the different materials tested so far (Table 5) and is definitely a good HX candidate for the decomposer. Long-term testing of Hastelloy C-22 and C-276 in the decomposition environment is ongoing (Figures 34 and 35) and they also have good corrosion characteristics in this environment. In addition to Hastelloys, Monel (MW400) has also been screened for use in the decomposer (Figures 36 and 37). Its corrosion rate in the decomposer environment is much higher even though it has similar corrosion rate as B2 in the iodine condenser setting.

Investigation was initiated into the stress corrosion effect on various Hastelloys in the HI decomposition environment. C-ring and U bend specimens of C-22 and C-276 were tested for more than 500 h and no cracking was observed (Figures 38–41). Testing is continuing.
Table 5. Corrosion rate of materials tested in the HI gaseous decomposition (450°C) and iodine condenser environment (160°C).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Hours</th>
<th>Corr. rate (mpy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B2</td>
<td>1172</td>
<td>2.549</td>
</tr>
<tr>
<td>B2*</td>
<td>1172</td>
<td>0.823</td>
</tr>
<tr>
<td>C-22</td>
<td>586</td>
<td>4.483</td>
</tr>
<tr>
<td>C-276</td>
<td>836</td>
<td>3.972</td>
</tr>
<tr>
<td>Monel</td>
<td>576</td>
<td>33.969</td>
</tr>
<tr>
<td>Monel*</td>
<td>640</td>
<td>0.891</td>
</tr>
</tbody>
</table>

*iiodine condenser

Figure 32. B-2 coupon tested in the gaseous HI decomposition environment for 1172 h.

Figure 33. B-2 coupon tested in the iodine condenser environment for 1172 h.
Figure 34. C-22 coupon tested in the gaseous HI decomposition environment for 586 h.

Figure 35. C-276 coupon tested in the gaseous HI decomposition environment for 836 h.

Figure 36. Monel coupon tested in the gaseous HI decomposition environment for 576 h.
Figure 37. Monel coupon tested in the gaseous iodine condenser environment for 576 h.

Figure 38. C-22 C-ring tested in the HI gaseous decomposition environment for 576 h.
Figure 39. C-22 U-bend tested in the HI gaseous decomposition environment for 756 h.
Figure 40. C-276 C-ring tested in the HI gaseous decomposition environment for 576 h.

Figure 41. C-276 U-bend tested in the HI gaseous decomposition environment for 576 h.
5.0 The Development of Self Catalytic Materials for Thermochemical Water Splitting Using the Sulfur-Iodine Process (PI: Ronald Ballinger, MIT)

The Sulfur-Iodine process, as it is currently envisioned, will require that the H$_2$SO$_4$ decomposition reaction be accomplished over the temperature range from 450-850°C. After decomposition the reaction

\[ \text{SO}_3 \rightarrow \text{SO}_2 + \frac{1}{2} \text{O}_2 \]

must be promoted using a suitable catalyst. The objective of this task is to develop a heat exchanger that will also be able to serve as a catalyst for the above reaction.

The general approach for the development process is to focus on structural alloy systems that would normally be considered for the heat exchanger. The alloy should also be one that shows promise as a material that would also be corrosion resistant in the environment that the acid decomposition reaction takes place in. These alloys would be then modified via the addition of a catalytic element which would promote the SO$_3$$\rightarrow$SO$_2$ reaction. The program is focusing on alloy 800HT and alloy 617 to which Pt was added to the base chemistry. Several alloy chemistries were produced, first in small “button” quantity form, and then, during FY06, in larger heat size form that will then be fabricated into useful shapes for characterization and analysis-both metallurgically/mechanically and for catalyst effectiveness determination. Lastly, depending on the results of the initial development process, material will be used to fabricate a small heat exchanger for actual testing in FY07.

5.1 Material Chemistry Identification, Alloy Procurement and Metallurgical Characterization

5.1.1 Initial Chemistry Identification and Characterization

A series of alloy 800HT plus Pt and alloy 617 plus Pt alloys in “button” form were melted and characterized from a metallurgical standpoint. As a result of this characterization, the chemistry of the larger heats was defined. The larger heat chemistries will consist of 1 wt% Pt added to base chemistries for alloy 800H.

5.1.2 Larger Size Quantity Production

At the most recent heat exchanger program review meeting it was decided that the overall program would be refocused. As a part of this refocus, the catalytic alloy development tasks will be redefined to focus on the detailed characterization of the Pt-added alloys. The procurement and testing of a test article heat exchanger using the new alloys is being put on hold.

New Alloys

As a part of the refocusing of the program, the new alloy characterization task will focus on a detailed characterization of the Pt-added alloys. While the test article production task (put on hold) would have required the production of larger (several 10s of kg) heats of material, detailed
catalytic characterization will require much smaller amounts of material. In this case, the project can expand the number of Pt-added alloy combinations to better characterize the system. The proposed new work plan will focus on the following alloy compositions:

- Alloy 800H + 1wt% Pt
- Alloy 800H + 2wt% Pt
- Alloy 800H + 5wt% Pt
- Alloy 617 + 1wt% Pt
- Alloy 617 + 2wt% Pt

The above alloys are being procured in amounts necessary to perform detailed catalytic characterization and a limited amount of mechanical properties determination.

5.2 Catalyst Effectiveness Determination

5.2.1 Facility Construction

The catalyst facility is in operation. The GC unit is in the process of being recalibrated in anticipation of the work on the new heats of material.

5.2.2: Catalyst Proof of Principal

The results of this task have shown proof of principal and have shown that the Pt-added alloys are catalytic.

5.3 Mechanical Properties Determination

This task is currently on schedule with the research plan. However, this task will be redesigned based on the limited alloy mass that will not be procured.

5.4 Future Project Direction

The following is the revised program path forward:

1. Reduce the size of the larger heats to the minimum size necessary to meet the following requirements: (1) assure “commercial-like” wrought material properties and (2) assure enough material to allow microstructural, catalytic, and minimal mechanical properties characterization, and (3) allow for enough material for INL participation in the characterization process.
2. Add a more complete electrochemical characterization task. Initial indications are that the hydrogen exchange current density for the Pt-added materials is very high-close to that of pure Pt-and that this property will make the new alloys useful for electrolytic hydrogen production.
6.0 Development of an Efficient Ceramic High Temperature Heat Exchanger (PI: Merrill Wilson, Ceramatec, Inc.)

6.1 Program Highlights

- Experiments to determine the effect of temperature and process fluid composition on the corrosion of non-oxide ceramic materials (silicon carbide and silicon nitride) were initiated.
- Experiments to determine the thermomechanical properties and corrosion resistance of materials for cooling oxygen obtained from water-splitting processes were initiated.
- Experimental flow tests were used to validate the FLUENT CFD models for flow/thermal coupons. The experiments were done using 3 pressure measurement techniques, each with very good agreement: manual single pressure transducer (within 5%), Tekscan pressure mats (within 10%) and Scanivalve multi-transducer (within 5%).
- Parametric flow analyses have begun to optimize the design of the flow channels in the decomposer. Preliminary results indicate improved performance can be obtained using undulating offset flow channels at a nominal increase in pressure drop. These analyses are continuing and undergoing refinement.
- A preliminary process flow sheet for the oxygen chiller (electrolysis process) indicates that the oxygen can be chilled for commercial applications while raising steam to augment electrolysis feed stream.

6.2 Technical Summary

Task 6.2.1 Temperature Effects

Corrosion experiments to determine the effect of temperature and process fluid composition on the corrosion of non-oxide ceramic materials (silicon carbide and silicon nitride) were initiated. The experimental test plan for determining these effects is shown in Table 6. Experiment #2 is in progress and is designed to investigate the effect of higher concentrations of sulfuric acid than had been used previously. Since the initial screening experiment also had a lower concentration of oxygen than the process flow sheets indicate will be present in the sulfuric acid decomposition section an oxygen pump was purchased and installed in the experimental apparatus. A third experiment at 900°C, Experiment #3, will be conducted in order to isolate the effect of oxygen concentration on the corrosion rate; subsequent experiments, however, will be conducted only with the higher oxygen concentration. In addition, to performing corrosion experiments at two different concentrations of sulfuric acid, experiments will be performed at three temperatures to determine the activation energy for the corrosion process.
Table 6

<table>
<thead>
<tr>
<th>Exp</th>
<th>Temperature (°C)</th>
<th>mole fraction (ambient)</th>
<th>H2O</th>
<th>H2SO4</th>
<th>O2</th>
<th>N2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>900</td>
<td>60</td>
<td>30</td>
<td>2</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>8</td>
<td>30</td>
<td>60</td>
<td>9.5</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>8</td>
<td>30</td>
<td>60</td>
<td>2</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>950</td>
<td>60</td>
<td>30</td>
<td>9.5</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>8</td>
<td>30</td>
<td>60</td>
<td>9.5</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>850</td>
<td>60</td>
<td>30</td>
<td>9.5</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>8</td>
<td>30</td>
<td>60</td>
<td>9.5</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>8+</td>
<td>450</td>
<td>30-80</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The formation of a silicon dioxide (silica, SiO₂) layer on corrosion samples was confirmed by Prof. Allen Johnson (UNLV) by x-ray photoelectron spectroscopy (XPS). A layer of silica on the surface of the materials may act to blunt surface flaws and lead to an apparent increase in strength, as measured. Additionally, Prof. Johnson found that the surface of silicon carbide samples were slightly rich in carbon after the first corrosion experiment, whereas the surfaces of silicon nitride samples were not.

To determine the effect of corrosion on the strength, hence reliability, of the Ceramatec, Inc. silicon carbide, the strength of the material, the strength after corrosion, and the strength at the temperature of the corrosion experiment was measured. The results are shown in Table 7. The results indicate that the strength of the silicon carbide is not sensitive to test temperature and it is improved by oxidation. Additional experiments are planned to determine the effect of temperature on strength and whether the oxidation during corrosion testing is accelerated by the presence of sulfuric acid.

Table 7

<table>
<thead>
<tr>
<th>Condition</th>
<th>Test Temperature</th>
<th>Strength (MPa)</th>
<th>Std. (MPa)</th>
<th>Dev.</th>
<th># samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>untreated</td>
<td>25°C</td>
<td>409</td>
<td>34</td>
<td></td>
<td>9</td>
</tr>
<tr>
<td>untreated</td>
<td>900°C</td>
<td>409</td>
<td>107</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>after experiment 1</td>
<td>25°C</td>
<td>521</td>
<td>89</td>
<td></td>
<td>13</td>
</tr>
<tr>
<td>after oxidation @ 900°C in air</td>
<td>25°C</td>
<td>ongoing</td>
<td>--</td>
<td></td>
<td>--</td>
</tr>
</tbody>
</table>

Task 6.2.2 Full-Size Design

Several advanced microchannel designs were considered. These will first be analyzed at the coupon scale and those that seem most promising will be fabricated and tested. These results will lead to a revised full-size heat exchanger wafer design.
Task 6.2.3 Full-Size Design Analysis

Flow model validation analyses were performed on straight through channels of various configurations matching those fabricated for flow testing. These analyses were found to be within 5% of measurements using traditional pressure sensors and within 10% for the advanced (less accurate) Tekscan pressure sensors – see below.

The advanced microchannel features were classified for design optimization at the coupon level. The overall design should maximize the heat transferred (to the decomposing sulfuric acid) and minimize the pressure drops in the flows. Conceptually, these advanced designs are an arrangement of offset polygons that form an interconnected network of flow channels. The offset features interrupt the straight laminar flow patterns and cause the flow streams to undulate in the x, y and z directions. These undulations enhance the heat transfer by creating repetitive “entrance regions” along the flow axis. This performance increase comes at the cost of increased pressure drop. This analysis effort will predict (and optimize) the heat transfer performance as a function of pressure drop (mechanical work). During this last quarter, simulations and analyses of the offset hexagonal channels began.

As a metric in optimizing the microchannels, the chemically reacting flows were also modeled. These models assumed chemical kinetics at the walls of the microchannels, attempting to capture the affects of the catalysts. These analyses, as modeled, showed only slight conversion of SO$_3$ to SO$_2$ and O$_2$ (about 0.5%). Parametric analyses showed that by increasing the residence time (longer channels, lower flow rates and higher pressures) and by increasing the surface to volume ratio (lateral ridges) this conversion could be increased. All these effects are qualitatively correct. However, the kinetic data used for these analyses was based on published Japanese results for catalyzed glass wool within a quartz tube, a significantly different test condition. Upon further investigation, it was found that the catalysis area as computed by FLUENT was that of the planar walls only. These assumptions neglect the high surface possibilities when the walls are coated with micro-spheres of catalyst on either the nominal dense walls or the preferred porous walls. Incorporating these high surface area catalysts (and supports) more closely mimic the test conditions of the Japanese experiments.

Task 6.2.4 Component Fabrication

Several additional batches of flow/thermal coupons were completed. These include hexagonal channel features which will be flow tested in order to determine the flow distribution and to validate the flow models of UNLV. This completes the component fabrication as required for FY06.

Efforts continued on selecting a suitable method for joining heat exchanger plates into stacks. Methods are being evaluated for leak tightness, mechanical durability, and ease of fabrication. The methods being evaluated are: reaction-bonding, pyrolysis of preceramic precursors, and a modified diffusion bonding approach. Each method is still under development, but the modified diffusion bonding method appears to provide the most leak tight joints. Unfortunately, the processing temperature for this method of joining is extremely high (>2000°C) and therefore the
alternative approaches are still being explored. Additionally, work has begun on developing a ceramic to metal joint for joining ceramic inlet and outlet ports to metal pipes and manifolds.

**Task 6.2.5 Validation Testing**

Additional series of flow tests were completed in the third quarter and compared to Valery Ponyavin’s flow models. These flow measurements were completed using three pressure measuring techniques.

The first technique uses 18 pressure taps that can be manually connected to a single pressure transducer. This method was found to be within 5% of the FLUENT CFD modeling (Figure 42). It was also found that the manual sequential connecting of the individual ports was slow and tedious, not permitting transient flow measurements.

The second method utilized an electronic pressure sensitive mat (Tekscan). Within these pressure sensitive mats is an array of elements that change resistivity as a function of load. By capping the pressure ports with these pressure sensitive elements, dynamic readings of the pressure field could be measured. This method was found to be within 10% of the FLUENT models (Figure 43).

The third method utilizes an instrument that adapts the benefits of each of the previous method into a single instrument (Scanivalve). By using high resolution, traditional pressure sensors, the flow measurements and higher accuracy was attained; by using an array of sensors, manual switching could be avoided and dynamic readings could be acquired. This instrument also demonstrated a very good agreement of 5% with the FLUENT Models (Figure 44).

![Figure 42. Comparison of Flow Coupon Data with FLUENT Model – Single Pressure Transducer](image-url)
A methodology for measuring surface temperatures of heat transfer coupons was demonstrated for moderate temperatures (up to about 250°C). Using an IR camera and an IR transmitting lens (ZnSe), a thermal map can be measured for an “enclosed” system. Figure 45 shows the heating of two flow/heat transfer coupons on a hot plate as seen through the ZnSe window. Using this concept, an enclosure was designed such that the flow coupons could be tested in counter-flow (or co-flow) configurations. This test fixture includes instrumented gas ports to permit the measurement of temperatures and flow rates of the respective flow paths. Additionally, there will be two reference temperature nodes for calibrating the IR images/data of the heat exchanger surfaces (Figure 46).
6.2.6 HX Materials Screening

Alumina (Al$_2$O$_3$) samples were exposed to the conditions of Experiment #1 (Table 8) for 1000 hours. The weight gain and strength were measured after exposure. The strength of alumina was not affected by the exposure, see Figure 47, and a weight gain of 1.5 $\mu$g/mm$^2$ was measured after 1000 h. Samples were sent to Prof. Johnson at UNLV for microstructural and surface analysis. The next samples to be exposed will be alumina in high oxygen/steam environments.
Figure 47. The strength of alumina samples as a function of time of exposure.

6.2.7 Conceptual Designs

A process flow model of an oxygen chilling heat exchanger was developed for the electrolysis process. This cooling loop utilizes water as the coolant in a counter flow condition. With a molar flow ratio (oxygen:water) of three, water is first vaporized then superheated to cool the oxygen. The chilled oxygen can thus become a marketable product and the superheated steam becomes part of the electrolysis feed stream. A simplified process flow sheet is found in Figure 48 and shows the heat duty required for the vaporizer/boiler and superheater respectively. This flowsheet will serve as a conceptual basis for which heat exchanger designs can be conceptualized.

Figure 48. Process Flowsheet for Oxygen Chiller within the Electrolysis Process.
7.0 Efficiency Improvement and Cost Reduction of Solid Oxide Electrolysis Cells through Improved Electrodes and Electrolytes (PI: Clemens Heske, UNLV)

7.1 Introduction

The University of Nevada, Las Vegas (UNLV) and Argonne National Laboratory (ANL) have teamed up to address the underlying materials issues that affect the efficiency and cost-competitiveness of solid-oxide electrolysis cells (SOECs) for hydrogen production by high-temperature steam electrolysis. The project investigates structure-property-performance relationships for oxygen electrodes and electrolytes, as well as the fabrication of thin-film electrolytes using atomic layer deposition (ALD). The findings from this project will help with the design of higher efficiency, more durable, and less costly SOEC systems. The project draws on the unique combination of surface science and interface characterization capability at UNLV and leading-edge experience in fuel cell technology, electrochemical characterization, and ALD technology at ANL.

7.2 Research Accomplishments at UNLV

In the past quarter, focus was on a detailed analysis of (La,Ca)MnO₃ electrode films that were prepared by ANL using pulsed laser deposition (PLD). The analysis was performed using X-ray photoelectron spectroscopy on the surface science instrument at UNLV. Figure 49 shows XPS survey spectra of three samples. The films were grown on two different substrates [YSZ(100) and MgO, respectively]. Furthermore, one sample with YSZ substrate was conditioned (“cond”) by subjecting the electrode/electrolyte sample to DC current for several hours at 800° C in the electrochemical in-situ set-up at ANL. As expected, all samples show characteristic signatures of La, Ca, Mn, and O core levels and Auger transitions. Furthermore, significant C and O contaminations were found on the surface. This is not unexpected, since the surfaces were exposed to air after preparation and during additional tests at ANL. For future experimental rounds, samples will be sealed under inert conditions immediately after preparation and only removed from their container in the inert atmosphere of the glove box of the Andere ESCA and directly transferred into ultra-high vacuum without air exposure.

Closer inspection of the spectra in Figure 49 reveals a Bi contamination on the “YSZ cond” and “Mgo” samples, which is ascribed to the contact paste used in electrochemical investigations at ANL. Furthermore, “YSZ cond” shows a small Zr 3d signal due to a scratch on the sample surface which, in a small localized region of the sample, exposes the YSZ substrate.

First stoichiometric information can be directly taken from a comparison of the three spectra in Figure 49. For example, the Mn 2p signal of the sample grown on the MgO substrate is significantly smaller than on the two other samples. Furthermore, the La 3d and La 4d signals of the “YSZ cond” sample are larger than on the non-conditioned samples. Finally, the O 1s signal is significantly increased after conditioning.
To quantify this information, the relative composition of the various elements was compiled, taking both the inelastic mean free path dependence of the emitted photoelectrons as well as the photoionization cross section and an approximate analyzer transmission function into account. The derived numbers are listed in Table 8. Note that the composition numbers are strongly affected by the surface contamination layer, as can be seen in the high relative fraction of C on the surface. Furthermore, the presence of Bi on two of the samples (albeit localized to a small area) also needs to be taken into account. Finally, two different oxygen species are observed (see discussion of Figure 51 below), which are listed as “peak 1” and “peak 2” in Table 8. More precise information is expected once the sample handling is optimized to avoid air exposure and residual material from other tests.

In order to derive quantitative information about the relative abundance of the metal components in the LCM films, the relative stoichiometry of La, Mn, and Ca was computed, irrespective of Table 8. Relative chemical composition of the probed (La,Ca)MnO$_3$ electrode film surfaces, as derived from detail spectra of the prominent lines in Fig. 49. Note that this composition is strongly affected by the surface contamination layer, as can be seen in the high relative fraction of C on the surface. Furthermore, the presence of Bi on two of the samples (albeit localized to a small area) also needs to be taken into account. Finally, two different oxygen species are observed (see discussion of Figure 51 below), which are listed as “peak 1” and “peak 2” in Table 8. More precise information is expected once the sample handling is optimized to avoid air exposure and residual material from other tests.

Table 8. Relative chemical composition of the probed (La,Ca)MnO$_3$ electrode film surfaces, as derived from detail spectra of the prominent lines in Fig. 49. Note that this composition is strongly affected by the surface contamination layer, as can be seen in the high relative fraction of C on the surface.

<table>
<thead>
<tr>
<th>LCM film on</th>
<th>La</th>
<th>Mn</th>
<th>Ca</th>
<th>O, peak 1</th>
<th>O, peak 2</th>
<th>C</th>
<th>Bi</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>5.3%</td>
<td>2.0%</td>
<td>1.7%</td>
<td>16.3%</td>
<td>16.7%</td>
<td>52.4%</td>
<td>5.7%</td>
</tr>
<tr>
<td>YSZ not cond</td>
<td>2.6%</td>
<td>7.3%</td>
<td>3.3%</td>
<td>13.6%</td>
<td>21.6%</td>
<td>51.6%</td>
<td>0.0%</td>
</tr>
<tr>
<td>YSZ cond</td>
<td>13.1%</td>
<td>3.4%</td>
<td>2.8%</td>
<td>15.8%</td>
<td>18.7%</td>
<td>41.5%</td>
<td>4.7%</td>
</tr>
</tbody>
</table>

Figure 49. X-ray photoelectron spectroscopy survey spectra of three different (La,Ca)MnO$_3$ electrode films. The films were grown on two different substrates [YSZ(100) and MgO, respectively]. Furthermore, one sample with YSZ substrate was conditioned (“cond”) by subjecting the electrode/electrolyte sample to DC current for several hours at 800° C.
any other present elements. The results are shown in Table 9. They clearly corroborate the above-given qualitative discussion of the spectra in Figure 49. For the two LCM samples grown on YSZ, a significant reversal of the La/Mn ratio was found after conditioning. This is in direct agreement with the interpretation of the O K edge XAS spectra (not shown).

As an example of the above-mentioned detail spectra, Figure 50 shows the La 3d\(_{5/2}\) XPS spectra of the three LCM samples. All three spectra are very similar. Comparison with literature references [e.g., Y. Uwamino et al., J. Electron Spectroscopy and Related Phenomena 34, 67 (1984)] assigns these spectra to La\(_2\)O\(_3\), i.e., indicating a 3+ oxidation state of La. It should be noted that the second component is not due to a second, chemically different La species, but is rather ascribed to a charge-transfer satellite.

*Table 9. Relative abundance of metals in (La,Ca)MnO\(_3\) thin films, as derived from detail XPS spectra.*

<table>
<thead>
<tr>
<th>LCM film on</th>
<th>La</th>
<th>Mn</th>
<th>Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>59.3%</td>
<td>22.0%</td>
<td>18.8%</td>
</tr>
<tr>
<td>YSZ not cond</td>
<td>19.8%</td>
<td>55.4%</td>
<td>24.8%</td>
</tr>
<tr>
<td>YSZ cond</td>
<td>67.9%</td>
<td>17.5%</td>
<td>14.6%</td>
</tr>
</tbody>
</table>

*Figure 50. La 3d\(_{5/2}\) XPS detail spectra of the three LCM films, indicating a 3+ oxidation state of the La atoms in all three cases.*
As a second example, detail spectra of the O 1s core level are shown in Figure 51. The three O 1s spectra of the LCM films are shown normalized to the integrated C 1s intensity. All spectra show (at least) two distinct oxygen species, which is tentatively assigned to the metal oxides (low binding energy component, peak 1) and to adsorbed species such as water and OH-containing species (high binding energy component, peak 2). After conditioning of the LCM/YSZ sample, the intensity of peak 1 is increased, while the intensity of peak 2 is decreased. This is assigned to an enhanced metal oxide formation at the surface and a desorption of contamination species, respectively.

Figure 51. O 1s XPS detail spectra of the three LCM films. The spectra were normalized with respect to the C 1s signal (see Fig. 49). The two observed components are ascribed to the metal oxide species (low binding energy component, peak 1) and to adsorbed species such as water and OH-containing species (high binding energy component, peak 2). After conditioning of the LCM/YSZ sample, the intensity of peak 1 is increased, while the intensity of peak 2 is decreased. This is assigned to an enhanced metal oxide formation at the surface and a desorption of contamination species, respectively.

As a second example, detail spectra of the O 1s core level are shown in Figure 51. The three O 1s spectra of the LCM films are shown normalized to the integrated C 1s intensity. All spectra show (at least) two distinct oxygen species, which is tentatively assigned to the metal oxides (low binding energy peak) and oxygen of adsorbed species (high binding energy peak) such as water and OH species. From Figure 51 it is learned that the overall oxygen intensity of LCM on the YSZ substrate increases after conditioning, due to an increase in the low binding energy component (i.e., the metal oxide component in our interpretation). This is not completely unexpected, since annealing at high temperatures and in air should enhance the oxide formation at the surface. Furthermore, the high binding energy shoulder decreases, which is ascribed to an annealing-induced desorption of some of the adsorbed species (e.g., water).