

出國報告（出國類別：其他）

赴美參加第 **31** 屆 **Cocoa Beach** 先進陶瓷與
複合材料國際研討會暨第四屆固態氧化物
燃料電池材料與技術國際論壇

服務機關：行政院原子能委員會核能研究所
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摘 要

美國陶瓷學會第 31 屆 Cocoa Beach 先進陶瓷與複合材料國際研討會暨第 4 屆固態氧化物燃料電池材料與技術國際論壇，於 2007 年 1 月 21 至 27 日在在佛羅里達州代托那海灘(Daytona Beach)市舉行。核能研究所受大會邀請演講，由李堅雄博士代表宣讀論文，題目為”SOFC Development at INER”，介紹核能研究所 SOFC 研發近況與未來展望。

參加第 4 屆固態氧化物燃料電池材料與技術國際論壇之各國專家學者，有來自美國、日本、德國、韓國、芬蘭、丹麥、西班牙、羅馬尼亞、印度、伊朗、義大利、亞美尼亞、法國、巴西、英國、新加坡、澳洲、烏克蘭、加拿大、台灣、中國大陸等國家地區，共計有 108 篇口頭報告論文以及 28 篇海報論文發表。整個會議包括以下十五個分項主題：1 SOFC: Plenary；2 Performances of Cells and Stacks I；3 Performances of Cells and Stacks II；4 Seals；5 S3 Poster Session；6 Electrodes I；7 Electrodes II；8 Interconnects/Coatings；9 Novel Cell/Stack Design；10 Reactions/Material Transport/Electrode Poisoning；11 Oxide and Proton Conductors/Conduction Mechanisms；12 Fabrication of Cells/Stacks；13 Processing of Cell/Stack Materials；14 Fuel Processing/Reforming；15 Mechanical Behavior；16 Reliability/Degradation。

參加本次會議，可以更廣泛的瞭解國際上各國在固態氧化物燃料電池上的研發現況，收集國際研發資訊，協助核能研究所計畫推動及未來策略擬定；在會議期間分別與 GE Dr. Minh、FZJ Dr. Nabielek、及 PNNL Dr. Prabhakar Singh 討論：推動驗證大型 SOFC 系統之規劃構想、可能之執行策略、及未來合作研究之可行性。

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一、目的

高溫固態氧化物燃料電池(SOFC)，藉由電化學的反應及固態電解質傳導氧離子的功能，產生電流。SOFC 具有高能源轉換效率(40~60%)、低污染氣體排放、多元化靈活燃料使用之優點，可結合渦輪機發電系統及生質酒精，使用多元化之進氣燃料，提供分散式發電系統之基載電力，及紓解能源使用對環境所造成的影響。SOFC 技術研發現況是屬於市場發展之初期，其產品商業化所面臨之挑戰包括:高的製造成本、複雜的製造技術、零組件工業之投資、產品效能的衰減、使用期限的延長及可靠度。核能研究所積極推動 SOFC 發電系統市場商品化之研發，亟思積極瞭解先進國家技術開發現況與未來展望，因此參加第 31 屆 Cocoa Beach 先進陶瓷與複合材料國際研討會暨第 4 屆固態氧化物燃料電池材料與技術國際論壇，藉由論文發表以及議程參，以瞭解目前世界各國最新研發成果及重點方向。會議期間分別與美國 GE 公司之 Dr. Minh、德國 FZJ 之 Dr. Nabielek、及美國 PNNL 國家實驗室之 Dr. Prabhakar Singh 討論，提及在核能研究所規劃大型 SOFC 驗證系統之構想、策略、及未來合作研究之可行性。

二、過 程

本次出國公差時間自 95 年 1 月 20 日至 95 年 1 月 29 日共計 10 天，行程如下：

日期	工作重點
95/01/20	往程：台北—舊金山—亞特蘭大
95/01/21	往程：亞特蘭大—佛羅里達州代托那海灘市 登記註冊第 31 屆 Cocoa Beach 先進陶瓷與複合材料國際研討會暨第 4 屆 固態氧化物燃料電池材料與技術國際論壇
95/01/22~95/01/26	<ol style="list-style-type: none">1. 參加第 31 屆 Cocoa Beach 先進陶瓷與複合材料國際研討會暨第 4 屆 固態氧化物燃料電池材料與技術國際論壇2. 受大會邀請發表論文” SOFC Development at INER”3. 與國外專家學者交換研發經驗及商談合作研究事宜
95/01/27~95/01/29	返程：佛羅里達州代托那海灘市—亞特蘭大—洛杉磯—台北

三、心得

(一)、研發資訊

第 31 屆 Cocoa Beach 先進陶瓷與複合材料國際研討會暨第 4 屆固態氧化物燃料電池材料與技術國際論壇，於 2007 年 1 月 21 至 27 日，在佛羅里達州代托那海灘(Daytona Beach)市舉行。本次大會以固態氧化物燃料電池為最主要議程，本所受大會邀請演講，由李堅雄博士代表宣讀論文，題目為”SOFC Development at INER”，介紹本所 SOFC 研發近況與未來展望 (附件 1)，聽講人員踴躍，反應良好，大會並請本所明年參加會議，除了邀請演講外，亦能多發表些論文。於今年 3 月 10 日收到 International Journal of Applied Ceramic Technology (ACT)的主編來函，肯定本所研發成果之品質，希望我們能接受其邀請，將在會議發表之論文，可以刊登在 ACT 期刊，已回函同意。

參加本次會議，增進國際 SOFC 研發趨勢之瞭解及相關資訊之收集，茲將印象深刻之研發資訊含括：中低溫 SOFC-MEA 材料研發現況、德國 FZJ 降低 SOFC 電池堆性能衰減效應之研究、美國 PNNL 對 SOFC 連接板之金屬與合金材料腐蝕之研究、日本 AIST 開發中低溫 SOFC 之高活性材料($<650^{\circ}\text{C}$)及微管型 SOFC 模組、韓國科學技術研究院(KIST)研發 SOFC 之現況、丹麥 Risø 對固態氧化物電解電池(SOEC, solid oxide electrolysis cell)之研發、及美國西北大學以天然氣為燃料利用 SOFC 電池產生合成氣(syngas)的研究，分別摘要說明如下：

1. 中低溫 SOFC-MEA 材料研發現況

高效能且能運轉在中低溫度($500\sim 650^{\circ}\text{C}$)之 SOFC 電池材料，是目前研發之主流，茲將陰極材料、電解質材料、及陽極材料之研發分別說明如下。

(1) 陰極材料

PNNL 的 Dr. Simner 等人針對傳統與新型陰極材料深入的研究，探討其特性與最佳化條件的開發，他們利用一種乾式粉體複合技術，機械融合法(mechanofusion，圖 1)，將尺寸較小之離子電導或混合電導材料披覆在尺寸較大之電子電導材料之上，希望藉以提高發電密度與長期穩定性。該方法一是將 sub-micron 之鏽鋇鈷鐵氧化物(LSCF)披覆在原子尺度的銀粒子(Ag, $10\sim 50\mu\text{m}$)上，能夠使電池在 EIS Data 的表現上，Ohmic 電阻降低 27 倍(3.2 to $0.12\text{ ohm}\cdot\text{cm}^2$)，非 Ohmic 極化降低 4 倍(1.5 to $0.36\text{ ohm}\cdot\text{cm}^2$)，雖然在高溫使用與長期穩定性上仍有不足，但是利用銀在低溫陰極材料上的可行性得到證實；另一是將 SDC($<50\text{nm}$)粒子披覆在 LSM 粉末($1\sim 2\mu\text{m}$)上，其發電密度 $0.5\text{W}/\text{cm}^2 @ 250\text{hr}$ ，相較於一般粉末混合之 LSM-SDC 與單純 LSM 為陰極材料的 0.4 與 $0.3\text{ W}/\text{cm}^2 @ 250\text{hr}$

來得高(圖 2)。機械融合法是一經濟及可量化的製程，但是仍需考慮參數之最佳化，如 SDC 的比例與批覆的厚度、LSM 與 SDC 原料粉末的尺寸以及燒結溫度等等。

University of Florida 的 Dr. Camaratt 的研究指出， $\text{Bi}_2\text{Ru}_2\text{O}_7(\text{BRO7})-\text{Bi}_{1.6}\text{Er}_{0.4}\text{O}_3(\text{ESB20})$ 是中溫固態氧化物燃料電池應用上之潛力材料，陰極材料必須具有還原能力較陽極氧化速率慢的特點，因此陰極材料的選定是降低操作溫度的關鍵。利用超聲波(sonication)與沉降(sedimentation)的等固態反應法可得到不同尺寸之 BRO7 與 ESB20 粉末(圖 3)。研究結果指出，BRO-ESB 複合陰極材料若全以小粒徑組成者在 625°C 下可得最小之比面積電阻(ASR, area specific resistance) $0.1 \text{ ohm}\cdot\text{cm}^2$ (圖 4)；對厚度效應而言，較大之 BRO7 顆粒之複合粉末其比面積電阻隨著厚度增加而下降超過一個數量級(圖 5)。

Lawrence Berkeley National Lab 的研究人員利用陰極滲透(cathode infiltration)方式改善 MEA 在低溫操作的性能(圖 6)，此一概念與李茂傳博士實驗室近期提出之研發方向一致。他們在陰極支撐型電池以真空滲透的方式在陽極滲入 Ce 以及 Ru，藉此改善陽極高溫抗硫化性。

(2) 電解質材料

LSGM 電解質被証實可以在 600°C 還能達到高發電密度，針對此一電解質特性開發西北大學的研究人員 Y. Lin 提出了以 $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{2.7}-\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.1}\text{O}_{2.75}$ 複合物為陰極材料的研究成果。陰極材料含 70 wt% LSGM 並燒結溫度為 1100°C 時，於 650°C 測得最低的極化電阻為 $0.2 \text{ Ohm}\cdot\text{cm}^2$ ，並且在長時間測試下開路電壓(OCV)穩定而電流密度維持在 $0.5 \text{ A}/\text{cm}^2$ ，LSGM 粉末尺寸較小者有較小之極化電阻。具 LSGM 電解質與 LSCF-LSGM 複合陰極的單電池測試結果，在 650°C 氫氣環境下其發電功率密度為 $0.6 \text{ W}/\text{cm}^2$ 。

(3) 陽極材料

SOFCo-EFS Holdings LLC 以及 Trans Tech Inc. 的 Dr. Goettler 等人研究 Ruddlesden-Popper 層狀鎳基氧化物材料在中溫及高溫的使用情形(圖 7)。

賓州大學的研究人員利用在陽極與電解質間置入一功能層(functional layer)，研究不同厚度之功能層的效果，最佳之功能層厚度為 $10\mu\text{m}$ ，浸滲 40 wt% CeO_2 以增加電導性，同時摻雜 1 wt% Pd 以增加催化效能(圖 8)。

2. 德國 FZJ 降低 SOFC 電池堆性能衰減效應之研究 (附件 2)

平板陽極支撐型電池(anode support cell)由於有相當薄之 YSZ 電解質層使得其在低溫操作有很高的發電效率，德國 FZJ 在陽極支撐型膜電極組(membrane electrode assembly)的研發製程包含有熱壓 and/or 帶鑄法製備陽極基板、真空帶鑄法製備電解質、網印法製作陰極，這些製造方式與程序已標準化且可生產出在長期操作下穩定可靠與電化學表現良好的膜電極組。單電池尺寸有 5x5、10x10 以及 20x20cm²，電池堆最多可由 60 個單電池堆疊組合而成，並已測試超過 250 個電池堆組合。Dr. Heinz Nabelek 發表”FZJ 降低 SOFC 電池堆性能衰減效應之研究”論文，整體回顧 FZJ 從 1995 年到 2006 年間，研究 SOFC 長期運轉性能衰減之機制、其改善方向與成效。FZJ 就陰極、電解質、陽極、連接板、封裝材料、接觸面積、接觸電阻等方面，定性及定量探討造成 SOFC 性能衰減之原因(表 1)，其中最主要減少電池堆性能衰減的影響有三，分別為 Chromium poisoning、Sulfur poisoning 與 re-oxidation，這些技術資訊，對於我們正在從事之相關研究，頗具參考價值。

3. 美國 PNNL 對 SOFC 連接板之金屬與合金材料腐蝕之研究 (附件 3)

PNNL Dr. Singh 發表”SOFC 連接板之金屬與合金材料腐蝕”之研究，主要探討金屬連接板材料，在單極雙極或雙向氣氛下之以及模擬重組氣氛下的腐蝕行為(圖 9)。高溫抗氧化合金是 SOFC 連接板常用之材料，SOFC 操作運轉時，金屬連接板瞬間在陰極端暴露在空氣中而在陽極端暴露在氫氣或碳氫燃料之下，同時也與封裝材料接觸。因此除了在空氣端需抗環境氧化能力與在燃料端避免還原之外，亦需考量氫氣濃度梯度之下的穩定性與發電效率的弱化。他們發現在雙向暴露與單向暴露其氧化腐蝕行為表現不同；在 H₂||air 雙向暴露環境下，Fe-Cr 基合金材料會形成氧化鐵，這在 reformat || air 環境下不會發生，主因為氫氣濃度梯度較低。對 Ni-Cr 合金來說，雙向暴露傾向於增進附著能力。

4. 日本國立先進產業科學研究所(AIST)開發中低溫 SOFC 之高活性材料(<650°C)及微管型 SOFC 模組

日本 AIST 的 Dr. Yamaguchi 指出傳統 SOFC 的三大問題為：電池啟動-停止的議題 (startup-stop of Cell)、高溫操作的 durability、以及成本降低，並提出解決方案分為使用小尺寸的單元電池、開發新材料與新結構、以及改善單位體積的發電功率密度。開發微管型 SOFC(micro tubular SOFC)(圖 10)與電池堆組合最佳化；以及開發 Honeycomb type SOFC 與 Multi Microcell 製程與性質探討是 AIST 研發 SOFC 模組之兩大主軸。此創新的製程，利用擠型的觀念製作出陰極微管，密度為 700 cpsi(channels per square inch)，管壁厚

200 μm，以 Dip coating 鍍上電解質材料在 1573K 共燒，塗上陽極 slurry NiO-GDC 於更高溫度燒結(圖 11)。完成之結構為電池密度 1000 cpsi，陰極、電解質、陽極厚度分爲 160、10、20 μm，在 823K 時操作其體積發電功率密度爲 2W/cc(圖 12)。AIST 在 2005~2010 年的主要研發計劃包含有：1.開發低溫 SOFC 之高活性材料(<650°C)；2.研發三維尺度的製程技術；3.評估原型電池模組(prototype)與先進陶瓷反應器的應用。

5. 韓國科學技術研究院(KIST)研發 SOFC 之現況

韓國科學技術研究院(KIST)於 1992 年即開始 SOFC 方面的研究，目標在研發商業化之 SOFC 電池堆，應用在汽車之輔助電力 APU、住商分散式發電、及與渦輪機結合之發電站。KIST 發展研製之 ASC 單元電池 10X10 cm² 厚度 0.6mm 在 650°C，0.7V 時功率密度達 567mW/cm²，在 OCV 1.1V 經過 100 次的 thermal cycle 運轉，電池性能仍可維持。在電池堆方面，已建立 500W (10X10 cm²) 電池堆設計及組裝技術(包括連接板及玻璃封裝材料)，根據 PNNL Dr. Prabhakar Singh 的告知，韓國規劃投資四百萬美金進行國際合作 SOFC 研究，以加速其達到 SOFC 發電商業化之目標。圖 13 爲 KIST 的各種尺寸單電池。

6. 丹麥 Risø 對固態氧化物電解電池(SOEC, solid oxide electrolysis cell)之研發

Risø 的研究報告指出，再生能源(如風能、太陽能、儲氫)的利用最大的障礙在於轉換效率低以及能量儲存形式不適合等問題。可逆反應之固態氧化物燃料電池(SOFC, solid oxide fuel cell)，使用在高溫電解質材料(HT electrolyzer)上的固態氧化物膜(membrane)由於電解反映部分能量轉移，有效率的產氫，爲固態氧化物電解電池(SOEC, solid oxide electrolysis cell)。SOEC 可高溫電解水產出氫，產出的氫可供應於高效率 SOFC 使用(圖 14)。同時 SOEC 可將 CO₂ 分解成 CO+O₂，亦即高溫蒸氣與 CO₂ 可電解爲 H₂ 與 CO 混合氣(syngas)，並可產生其他含氫能量載體，如甲醇(methanol)與甲烷(methane)。研究人員針對高溫電解水蒸氣與二氧化碳產生氫氣與甲烷作探討，並評估出最佳狀態下假設電價爲 3.6 US\$/GJ，產氫成本 4.8 US\$/GJ，相當於利用每桶原油的成本 29 US\$/barrel crude oil；產甲烷成本預估爲 7.8 US\$/GJ，則相當於利用每桶原油的成本 48 US\$/barrel crude oil。SOEC 的經濟效益如圖 15、16 所示。SOEC 需克服的包含了氫氣電極(Ni+YSZ)在高溫高電流密度(4 A/cm²)下操作之穩定性、陽極 Redox tolerance 的改善等等。

7. 美國西北大學以天然氣爲燃料利用 SOFC 電池產生合成氣(syngas)的研究

美國西北大學的 Dr. Pillai 等人探討以天然氣(natural gas)爲燃料利用 SOFC 電池產生合成氣

(syngas)的研究。SOFC 可作為以天然氣為燃料之 syngas generator 乃由於其形成電化學部份氧化(EPOx, electrochemical partial oxidation)，其電化學反應產生汽電共生效應 (co-generation, electricity and syngas)，如此可有效率的利用天然氣降低成本並提升 SOFC 電池堆的應用價值。圖 17、18 為 syngas 實驗細節與電池組測試示意圖。研究指出，有 barrier layer 當作 catalyst 能使 syngas 的產出穩定，並且在 EPOx 情形之下汽電共生效應的發生被證實：syngas 產生量為 32 sccm/cm²，電力輸出為 0.9 W/cm²。Catalyst layer 與 Barrier layer 需尋找更穩定適用的材料使得 syngas 產出達到最佳化，替代的陽極材料也是改善的方式之一。

(二)、合作討論

此次受邀代表本所出國參加第 31 屆 Cocoa Beach 先進陶瓷與複合材料國際研討會暨第 4 屆固態氧化物燃料電池材料與技術國際論壇，主要目的在擴大國際交流與促進國際合作，並收集國際研發資訊協助本所 SOFC 計畫推動與未來策略擬定。建議事項與會談結論如下：

1. 經由本所以往主辦之 SOFC Workshop 所建立之人脈關係，在此次會議從受邀過程與議程中之個別會談，皆有實質的幫助。藉由參與國際性的研討會不僅可以瞭解最新的研發趨勢與現況，更能活化此項人脈網絡，達到國際交流合作的目的。對於本所 SOFC 計畫的研究發展來說，日後仍應積極規劃參與相關國際性的技術研討會議。

2. 會議期間分別與美國 GE 公司之 Dr. Minh、德國 FZJ 之 Dr. Nabielek、及美國 PNNL 國家實驗室之 Dr. Prabhakar Singh 討論，提及在核能研究所規劃大型 SOFC 驗證系統之構想、策略、及未來合作研究之可行性。

(1) Dr. Minh 認同本所長程 SOFC 研發規劃，發展 20~50kW SOFC 驗證系統亦是目前國際趨勢，由於 GE 參加 SECA 計畫研發之技術不能外流至其他國家，正式與 GE 之 SOFC 團隊合作是不可能，他願意以私人身份提供技術諮詢。

(2) Dr. Nabielek 表示 FZJ 本年度之計畫負荷已滿載，要商討明年本所與 FZJ 合作是有空間。Nabielek 在今年 6 月退休，目前已有一些研究機構請他做短期顧問，是否需要請 Nabielek 來所短期指導 SOFC 之研發工作，是值得評估。

(3) Dr. Prabhakar Singh 認同本所發展 SOFC 產品商業化之企圖心，及對臺灣工業界之價格降低量產技術亦有肯定。Prabhakar 有意願促成 PNNL 與核研所在 SOFC 技術合作研究，

及美國與台灣 SOFC 工業團隊合作量產技術。在會議期間 Prabhakar 撰寫 5 年的合作研發 25~50kW 發電系統之構想初稿，供本所參考，如有需要，亦願意來所討論合作研究之議題。

四、建議事項

參加第 4 屆固態氧化物燃料電池材料與技術國際論壇，藉由論文發表以及議程參與，不僅可以瞭解最新的研發趨勢與現況； International Journal of Applied Ceramic Technology (ACT)的主編來函，邀請在會議發表之論文，刊登在 ACT 期刊，更能展示本所研發成果，達到國際交流合作的目的。本所 SOFC 計畫的研究發展必須與國際接軌，日後仍應積極規劃參與相關國際性的研討會議，並鼓勵同仁在國際會議上多發表論文，達到國際交流並提升核研所所譽。

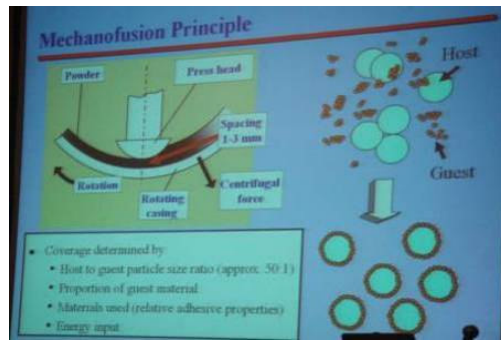


圖 1. 機械融合法(Mechanofusion)的原理

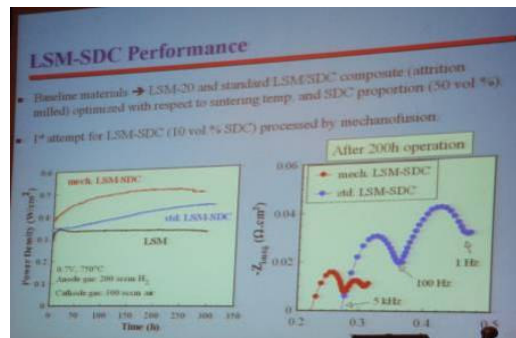


圖 2. 機械融合法處理 LSM-SDC 之電性表現

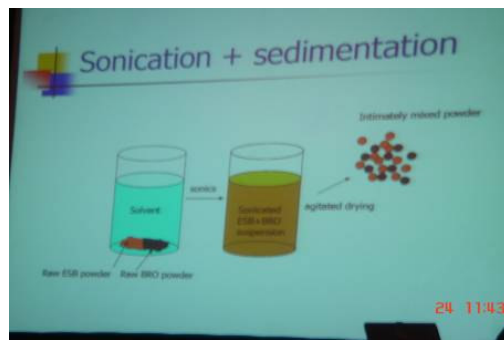


圖 3. 固態反應法: 超聲波與沉降法

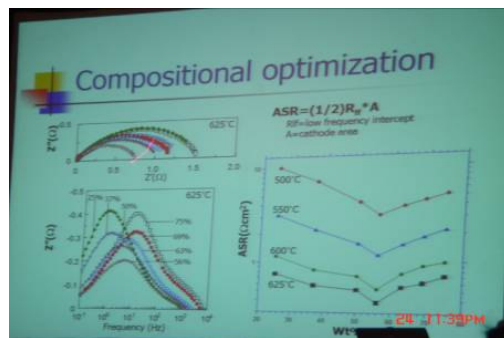


圖 4. 比面積電阻(ASR, area specific resistance)

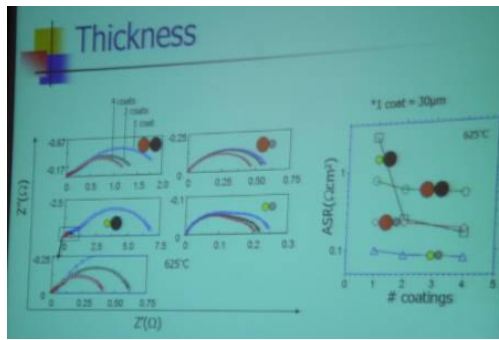


圖 5. 厚度對比面積電阻之影響

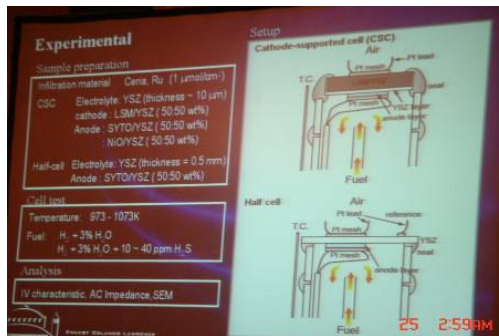


圖 6. 陰極滲透法實驗配置設計

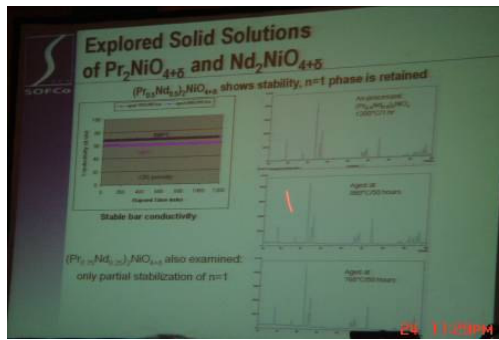


圖 7. Ruddlesden-Popper 層狀鎳基氧化物材料之相穩定評估

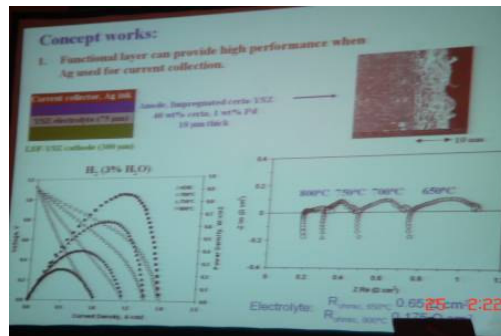


圖 8. Function layer 的概念與圖示

SOFC degradation		
Cathode side	Electrolyte	Anode side
Three phase boundary reduction by <ul style="list-style-type: none"> - Cr poisoning - Particle sintering Phase changes	Phase instabilities	Ni-agglomeration Ni-coarsening S poisoning Interdiffusion
Interdiffusion Contact degradation Resistivity Cr transport	Interdiffusion	Destruction by re-oxidation Contact loss by <ul style="list-style-type: none"> - by sintering - by seal swelling - temp. gradient Resistivity
Interconnect: <ul style="list-style-type: none"> - Cr evaporation - Corrosion cracking - Inner oxidation 		Interconnect: <ul style="list-style-type: none"> - Scale resistance - Embrittlement by carburization - Corrosion cracking
Ceramic glass sealant <ul style="list-style-type: none"> - Interaction with gaseous species/ contaminants - Interaction between components - Leakage or short circuit during thermal cycling - Degradation due to impurities in raw materials 		

表 1 Overview of the main SOFC stack degradation mechanisms

圖 9. 單極雙極或雙向氣氛下之以及模擬重組氣氛下的腐蝕行爲

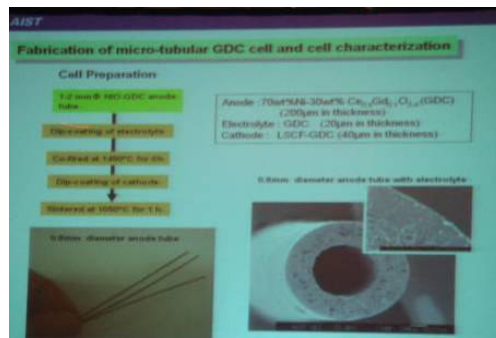


圖 10. 微管型 SOFC(micro tubular SOFC)

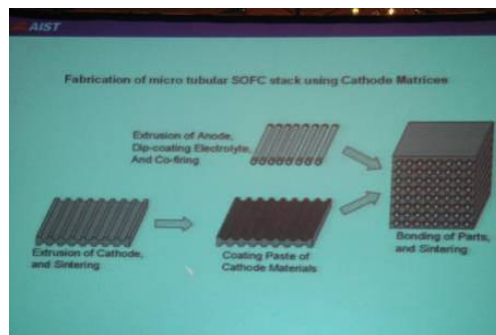


圖 11. Fabrication of Honeycomb-type Cells

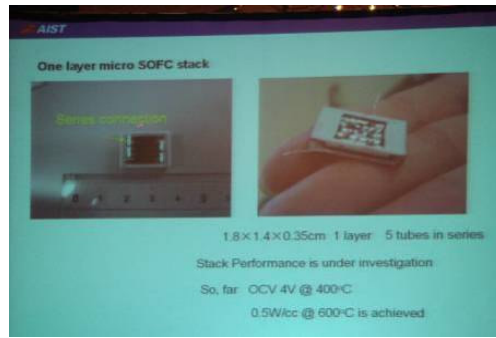


圖 12. Honeycomb-Type SOFC integrated with Multi Micro Cells

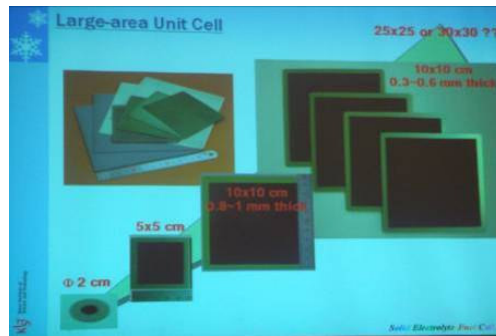


圖 13. KIST 的各種尺寸單電池

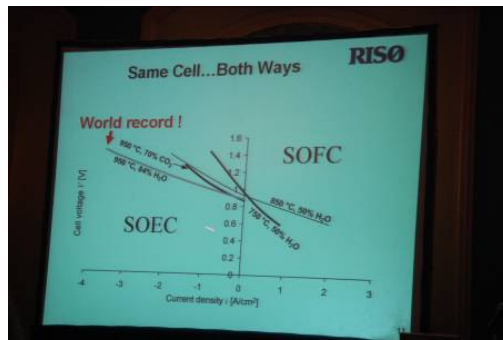


圖 14. SOEC 與 SOFC 的比較

The table lists the following parameters and values:

SOC stack	2100 US\$/m² cell area
Investment cost	6300 US\$/m² cell area*
Interest rate	5%
Depreciation time	10 years
Operation time	5 years
Deionized Water cost	2.3 US\$/m³
Electricity price	1.3 US\$/kWh (3.4 US\$/GJ)
Cell temperature	850 °C
Cell voltage, current density†	1.48 V (F _{cell} = 0.9 A/cm²)
H ₂ O utilization in the SOC stack	30%
Energy loss to heat exchanger	5%

圖 15. SOEC 經濟效益評估表

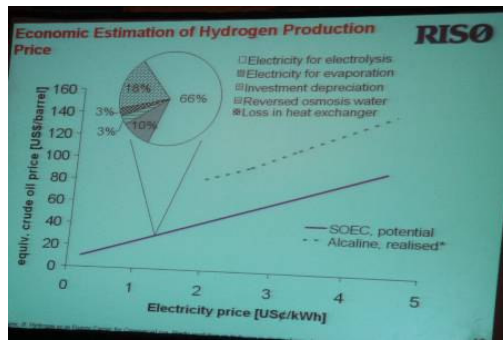


圖 16. 產氫成本評估

- Experiment Details**
- **Ni-YSZ anode supported SOFCs**
 - Electrolyte: 15 μ YSZ (TOSOH)
 - Cathode: LSM-YSZ / LSM (Praxair)
 - **Barrier/catalyst Layer**
 - 0.4mm thick, 40% porous PSZ discs
 - Rh/Alumina catalyst
 - **SOFC stability studies**
 - SOFC reduced in hydrogen
 - Introduced fuel mixture at high J
 - IF voltage stable for 8 hours, J lowered to new value
 - Below $J = J_c$, voltage degraded over time
 - **EPOx product gas measurements**
 - Agilent micro GC3000

圖 17. syngas 實驗參數

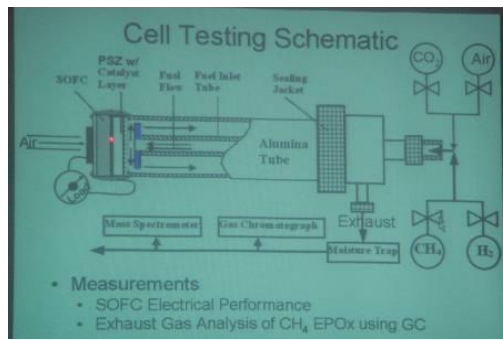
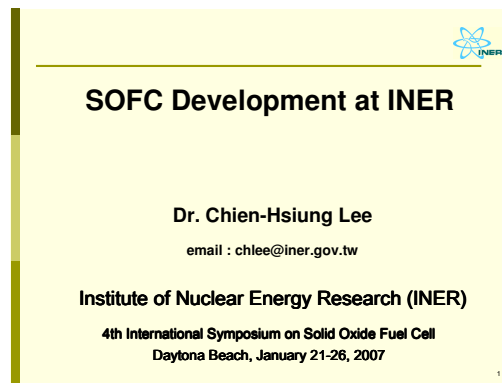


圖 18. syngas 電池組測試示意圖

附件 1. 李堅雄博士之會議報告: SOFC Development at INER



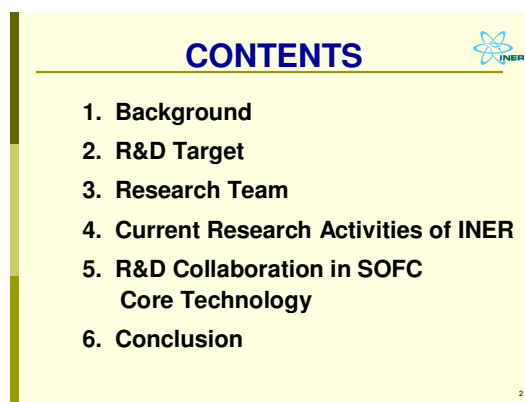
Slide 1: SOFC Development at INER. The slide features the INER logo in the top right corner. The title "SOFC Development at INER" is centered. Below the title, the presenter's name "Dr. Chien-Hsiung Lee" and email "chlee@iner.gov.tw" are listed. The affiliation "Institute of Nuclear Energy Research (INER)" and the event details "4th International Symposium on Solid Oxide Fuel Cell, Daytona Beach, January 21-26, 2007" are also included. A small number "1" is in the bottom right corner.

SOFC Development at INER

Dr. Chien-Hsiung Lee
email : chlee@iner.gov.tw

Institute of Nuclear Energy Research (INER)
4th International Symposium on Solid Oxide Fuel Cell
Daytona Beach, January 21-26, 2007

1



Slide 2: CONTENTS. The slide features the INER logo in the top right corner. The title "CONTENTS" is centered. Below the title, a numbered list of six items is provided: 1. Background, 2. R&D Target, 3. Research Team, 4. Current Research Activities of INER, 5. R&D Collaboration in SOFC Core Technology, and 6. Conclusion. A small number "2" is in the bottom right corner.

CONTENTS

1. Background
2. R&D Target
3. Research Team
4. Current Research Activities of INER
5. R&D Collaboration in SOFC
Core Technology
6. Conclusion

2

1. Background



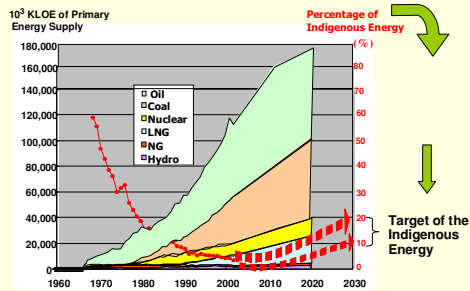
- **Taiwan's Energy**
 - Less than 2% indigenous energy
- **Kyoto Protocol Pressure**
 - More than 50% of coal based electricity
 - CO₂ emission and economic growth need to decouple
- **SOFC Contribution**
- **SOFC Market Forecast**

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1. Background – Taiwan's Energy



● Energy Security – Less Than 2% Indigenous Energy



1. Background (cont.)– SOFC Contribution

Energy security

- Diversify primary energy resource (SOFC fuels including **natural gas, biomass ethanol, diesel**, etc.)
- Improve energy efficiency (SOFC efficiency about **40 - 60%** and over **80%** with heat utilization)
- Distributed power station (SOFC power up to **100 kW**)
- Central power station (Coal based **IGCC+SOFC** power designed to **100 MW**)

Environmental Quality

- Less CO₂; Less SO_x, Less NO_x

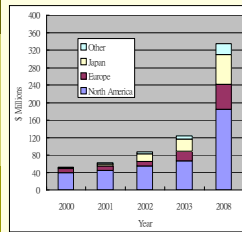
Economic growth

- New technology creates new industries
- Enhancement of national prestige in energy development

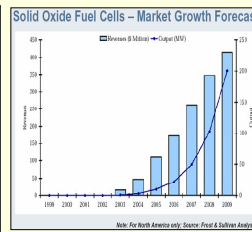
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1. Background (cont.)– SOFC Market Forecast

- SOFC market growth rate 22% per year

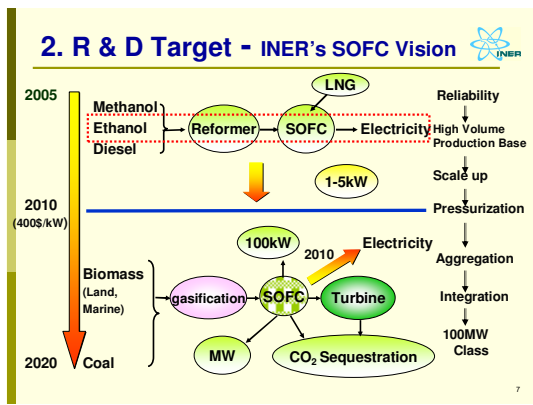


(From: BCC RGB-282, 2003)



(From: Frost & Sullivan, 2004)

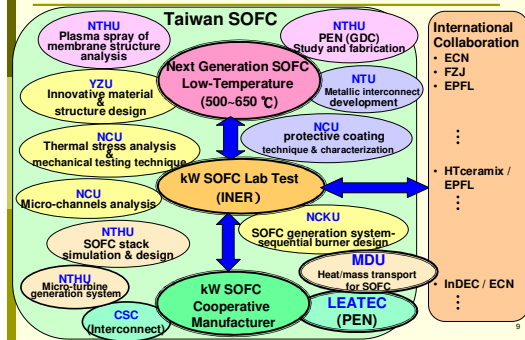
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2. R & D Target (cont'd) - Proposed Roadmap

	Phase I Small System R&D	Phase II Scale-up System Market Penetration	Phase III SOFC+Turbine Market Diffusion	Phase IV Coal Based Central Generation Market Penetration
	2005	2010	2015	2020
Power	1-5kW	250 kW	1 MW	100MW
Efficiency	40%	50%	60-70% Hybrid	Coal based efficiency 60%
Durability	4,000 hrs	40,000 hrs	5 years stack life, 25 years system life	
Degradation rate	0.5% / 1,000 hr	0.1% / 1,000hr		
Operation Temp.	750°C	650°C		

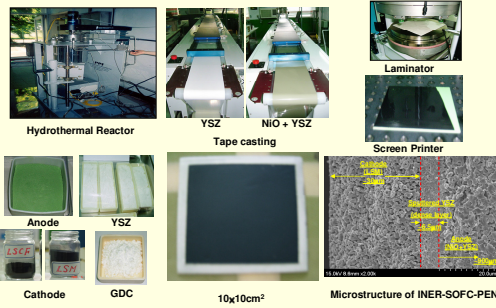
3. Research Team – INER Strategic Alliance



4. Current Research Activities of INER - SOFC Program

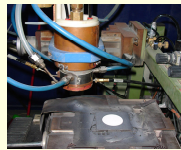
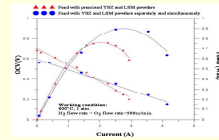
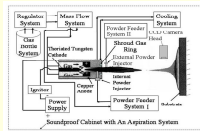
	2006	2006	2007	2008	2009	2010	2011	2012	2013	2014
Upstream	Advanced & innovative material and process development(500-650°C)		Tape casting: Atmosphere Plasma Spray (APS) Assembly testing and technology for micro-grade PEN							
			Power density	100 mW/cm ²	300 mW/cm ²	1 W/cm ²	2W/cm ²			
Midstream	SOFC PEN stack components development (650-800°C)		Tape casting: APS Power density 300mW/cm ² 500mW/cm ² Long term reliability testing and cost down							
			PEN interconnect, stack, reformer		High temperature heat exchanger, sequential burner					
Downstream	SOFC system design, testing & analysis		Optimization of SOFC system and cost analysis							
			Efficiency	50%						
Downstream	SOFC kW-grade demonstrative system and its simulation		SOFC system 1 kW 2 kW 5 kW degradation 0.5%/1,000hr System reliability testing							
			SOFC micro-turbine system		250 kW					
Downstream	Industry participation		PEN mass production technique							
			kW-grade stack mass production		degradation 0.1%/1000hr					

4. Current Research Activities of INER (cont'd) – SOFC-PEN Development



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4. Current Research Activities of INER (cont'd) – INER Plasma Spray System for Nanostructured PEN Development



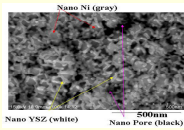
Electrical performance of plasma sprayed SOFC unit cell

Typical experimental plasma spray parameter values

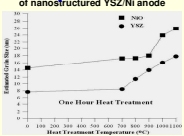
Parameter	Value
Distance	7.5 - 10 cm
Current	400 - 600 A
Argon gas flow rate	400 - 600 sccm
Hydrogen gas flow rate	6 - 12 SLPM
Powder feed rate	2 - 10 g/min
Power density	3 - 4 W (Pd/C Argon)
Spray distance	7 - 12 cm
Evaporation substrate temperature	200 - 400 °C
Shielding gas flow rate	400 - 600 SLPM (Argon)
N ₂ bubble scan speed	800 - 1000cm/min

12

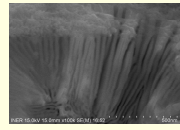
4. Current Research Activities of INER (cont'd) – Nanostructured Composite Anode by Plasma Spraying



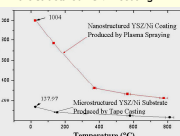
Nano Ni (grey) Nano YSZ (white) Nano Pore (black) 500nm



Estimated grain sizes of YSZ and NiO versus heat treatment temperatures



Cross section view to show nano gas channels in the structured YSZ/Ni coating



Measured conductivity results for nanostructured YSZ/Ni coating and microstructured YSZ/Ni substrates

4. Current Research Activities of INER (cont'd) – Assembling and testing of SOFC Stack



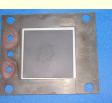
Improved process for the production of glass ceramics



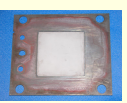
Leaking test for a SOFC cell



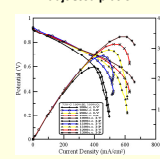
Components flatness adjusted platform



Integrity of cell/frame was maintained after stack testing at elevated temperatures



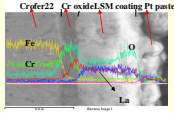
Integrity of cell/frame was maintained after stack testing at elevated temperatures



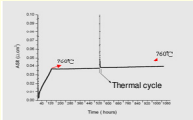
I-V curve for a one-cell stack

4. Current Research Activities of INER (cont'd) – Interconnect Protective Coating and ASR Measurement

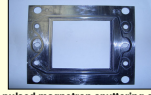
- Develop the optimized material and coating technique for SOFC interconnect (IC)
- Investigate the effectiveness and long term stability of IC coating
- Design the alternative alloys for IC application



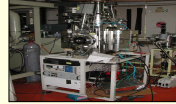
EDX analysis of LSM-coated Crofer22



ASR measurement of LSM-coated Crofer22



DC-pulsed magnetron sputtering coating

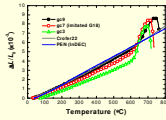


A large-scale LSM sputtering station (coating area 20*20 cm²)

15

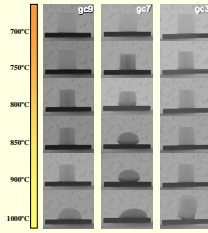
4. Current Research Activities of INER (cont'd) – SOFC glass-ceramic seals

- Explore the mechanism of "sealing"-- Hermetic layer formed between sealant and cell components
- Establish the standard packing process
- Study the long term stability of sealant and the compatibility with other components



Thermal properties measurement

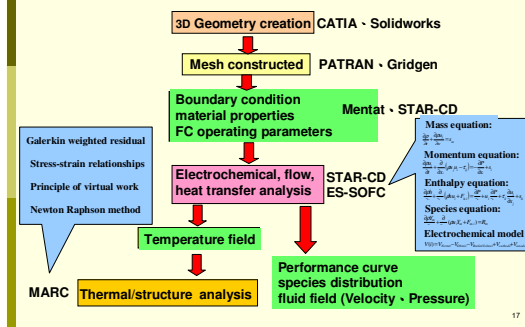
#	CTE ($\times 10^{-6} / ^\circ\text{C}$)	T_g (°C)	T_m (°C)
g-c3	7.74	616	691
g-c7	8.83	618	709
g-c9	9.48	652	745
Crofer22	-12.60 (at 750 °C)		
PEN	-10.20 (at 750 °C)		



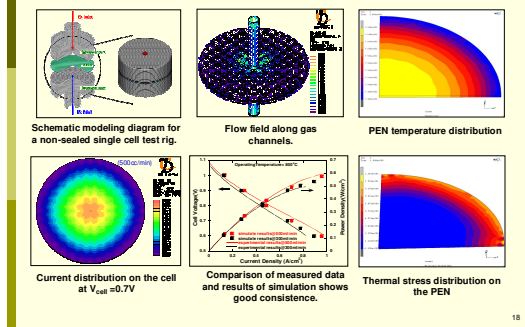
Adhesion and wetting behavior

16

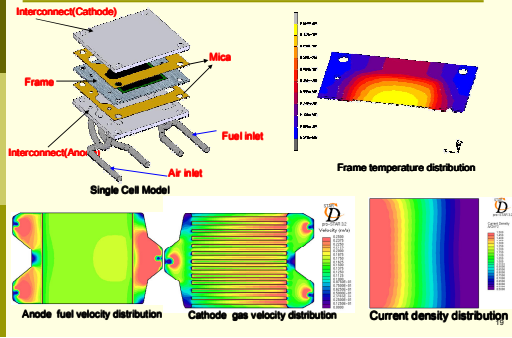
4. Current Research Activities of INER (cont'd) – SOFC Simulation Tools



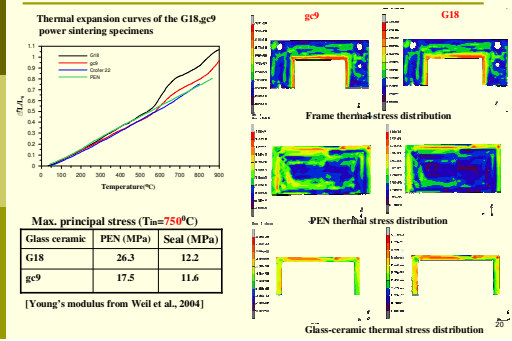
4. Current Research Activities of INER (cont'd) – SOFC Single Cell Simulation



4. Current Research Activities at INER (cont'd) – SOFC Single Stack Simulation




4. Current Research Activities at INER (cont'd) – SOFC Single Stack Simulation

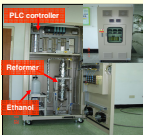


4. Current Research Activities of INER (cont'd) – SOFC Ethanol Reformer

1 kW Lab Reformer

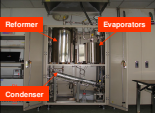


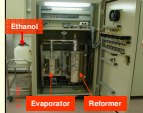
1 kW Compact Reformer



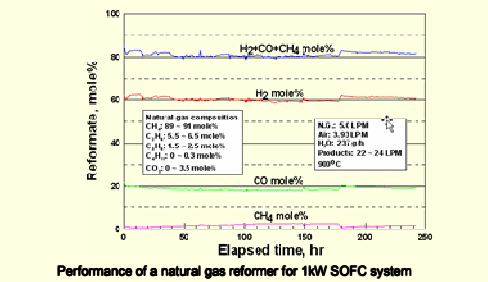
Feed: C_2H_5OH : 23.6 moles/hr
 H_2O : 42.8 moles/hr
 Air : 36.9 moles/hr
 Catalyst: monolithic
 (33 mm dia. X 90 mm long)

Sample	Temperature	
	Tin=150 °C (Before Catalyst)	Tout=430 °C (After Catalyst)
Product gas	(Vol %, dry)	
H_2	40.88	
CH_4	3.57	
CO	9.29	
O_2	0.00	
N_2	26.52	
CO_2	17.16	
C_2H_4	1.51	
C_2H_6	1.99	
> C_4	0.13	
C_2H_5OH	0.17	

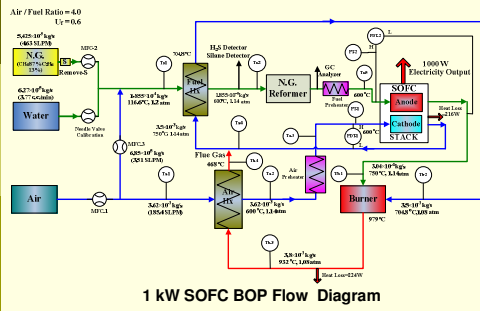




4. Current Research Activities of INER (cont'd) – Performance of a natural gas reformer for 1kW SOFC system



4. Current Research Activities of INER (cont'd) – 1kW SOFC System



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4. Current Research Activities of INER (cont'd) – 1kW SOFC Demonstration System



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4. Current Research Activities of INER (cont'd)

Feasibility study of 25-50 kW demonstration system

- Estimate the SOFC Early Market Potential for the Distributed SOFC Power System
 - SOFC Power/Year
 - Durability
 - Cost
- Evaluate the Current Status of SOFC Core Technology for the 25-50 kW SOFC Power System
 - PEN Power Density
 - Stack / System Scale – up Technology
 - Degradation and Failure Management
- Propose a SOFC Power System Demonstration Program
 - **System** Technical Specification
 - Project Period
 - Budget Plan

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5. R&D Collaboration in SOFC Core Technology (cont'd)

Some possible collaboration topics

- Development of Interconnect and Sealant materials for SOFCs
- Modeling, Simulation and Design of Functionally-Graded Structures (for Optimal Performance and Thermal/Mechanical Stability...)
- Novel Materials for a New Generation of SOFCs (Low-Temperature SOFCs)
- Design of Novel SOFC Stacks and Systems

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6. Conclusion



- SOFC technology should be emphasized as one of the most important subjects in the area of renewable energy development in Taiwan, and in INER as well.
- Reliability, durability and cost are among the major concerns for SOFC technology development.
- International collaboration is essential to facilitate demonstration and industrialization of SOFC technology in Taiwan.

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**Thank You
for Your Attention**

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附件 2. FZJ Dr. Nabielek 報告內容: Reducing degradation effects in SOFC stacks manufactured at FZJ-approaches and results

Forschungszentrum Jülich
an der RWTH Aachen University

Reducing degradation effects in SOFC stacks manufactured at FZJ-approaches and results

Heinz Nabielek,
L Blum, H-P Buchkremer, V Haanappel, L G J de Haart,
W J Quadackers, R Steinberger-Wilckens,
R W Steinbrech, U Reisgen, and F Tietz

Forschungszentrum Jülich, Germany

Fuel Cell Project Projektleitung: PBZ Institut für Werkstoffe und Verfahren der Energietechnik IEF Zentralabteilung Technologie ZAT Heinz Nabielek, Dülmen, Jan. 2007

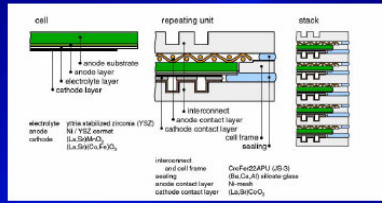
Forschungszentrum Jülich
an der RWTH Aachen University

Topics of SOFC Materials Research at FZJ

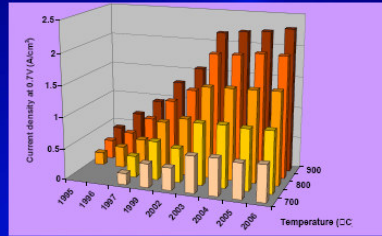
- Materials**
 - ceramics and ferritic materials
 - high reliability, low ageing rate
 - low costs
- Cells**
 - high power density, stability under all operating conditions
- Stacks**
 - optimum design
 - transient operation (thermal)
 - low weight, low volume
- Manufacturing** (pre-industrial) of cells, stacks and components
- Systems** (packaging of components)
- Modelling**
 - understanding of processes
 - prediction of cell, stack and system behaviour and lifetime

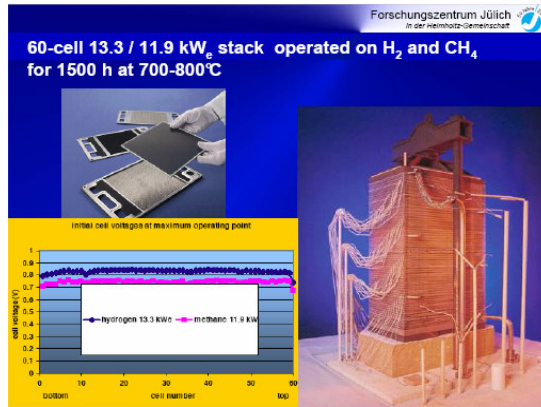
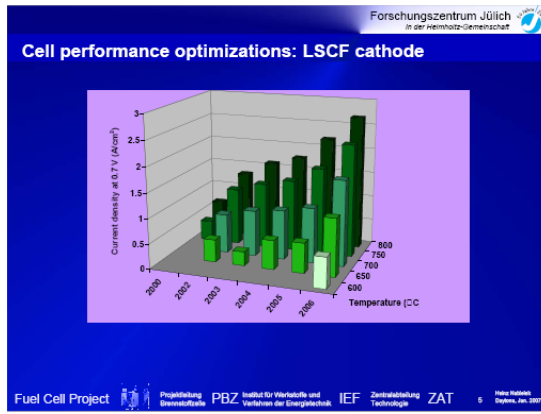
Fuel Cell Project Projektleitung: PBZ Institut für Werkstoffe und Verfahren der Energietechnik IEF Zentralabteilung Technologie ZAT Heinz Nabielek, Dülmen, Jan. 2007

SOFC stack design at Forschungszentrum Jülich



Cell performance optimizations: LSM cathode

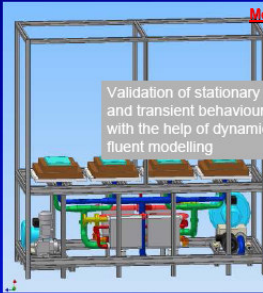




Forschungszentrum Jülich
in der Helmholtz-Gemeinschaft

20 kW SOFC System Development

Validation of stationary and transient behaviour with the help of dynamic fluent modelling



Module-Components:

- SOFC-Stack
- Heating plate
- Insulating plate
- Deflection plate
- After-burner
- Heating plate
- Air-pre-heater
- Deflection plate
- Pre-reformer
- Interface

Fuel Cell Project Projektleitung: Gressler/Carle PBZ Institut für Werkstoffe und Verfahren der Energietechnik IEF Zentralabteilung Technologie ZAT Hans Hübner, Leiter, 04.10.2007

Forschungszentrum Jülich
in der Helmholtz-Gemeinschaft

SOFC degradation

Cathode side	Electrolyte	Anode side
Three phase boundary reduction by <ul style="list-style-type: none"> - Cr poisoning - Particle sintering 	Phase instabilities	Ni-agglomeration Ni-coarsening S poisoning
Phase changes Interdiffusion	Interdiffusion	Interdiffusion Destruction by re-oxidation
Contact degradation Resistivity Cr transport		Contact loss by <ul style="list-style-type: none"> - by sintering - by seal swelling - temp. gradient
Interconnect: <ul style="list-style-type: none"> - Cr evaporation - Corrosion cracking - Inner oxidation 		Resistivity Interconnect: <ul style="list-style-type: none"> - Scale resistance - Embrittlement by carburization - Corrosion cracking
Ceramic glass sealant <ul style="list-style-type: none"> - Interaction with gaseous species/ contaminants - Interaction between components - Leakage or short circuit during thermal cycling - Degradation due to impurities in raw materials 		

Chromium poisoning

- In a purely ceramic environment (no steel, no Cr), degradation is near zero
- In stack tests with metallic interconnect, we observe
 - Cr evaporation
 - transport across air channel and
 - deposition-reduction in the cathode functional layer that may lead to degradation

Most Cr is transported efficiently across air channel

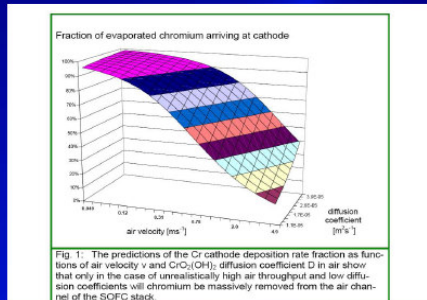
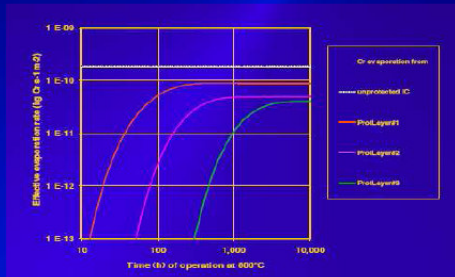
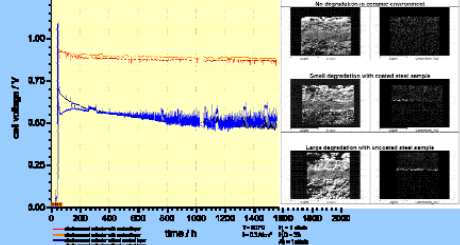


Fig. 1. The predictions of the Cr cathode deposition rate fraction as functions of air velocity v and $\text{CrO}_2(\text{OH})_2$ diffusion coefficient D in air show that only in the case of unrealistically high air throughput and low diffusion coefficients will chromium be massively removed from the air channels of the SOFC stack.

IC protective layers delay and retain Cr evaporation

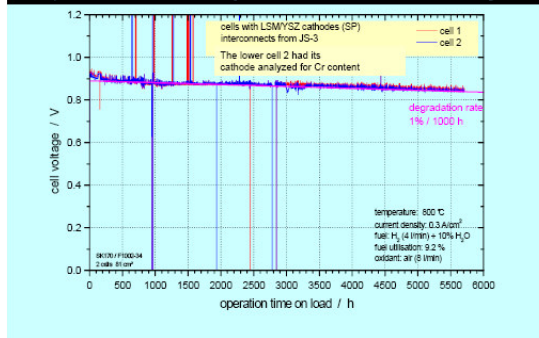


Degradation in cell measurements



Single cell performance measurements with or without steel samples in the gas stream: uncoated steel leads to high Cr concentration in cathode functional layer consistent with Cr transport predictions.

Low degradation rate of FZJ stack at 800°C operated for 8,000h with Co-based perovskite cathode contact layer



Cr poisoning:

Degradation does not correlate linearly with Cr deposits in cathode, but is also strongly influenced by current densities and temperature. Cr presence is, however, a necessary condition.

Ideally, we need a protective coating that

- is gastight
- has high electrical conductivity
- has good adhesion
- has same thermal expansion as the other cell materials
- is stable under all operating conditions
- and stops Cr evaporation efficiently for all times

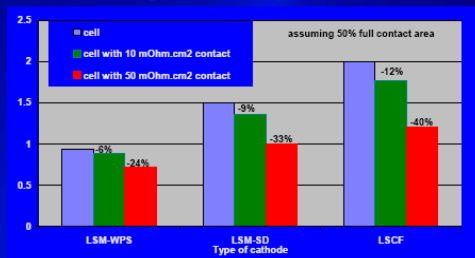


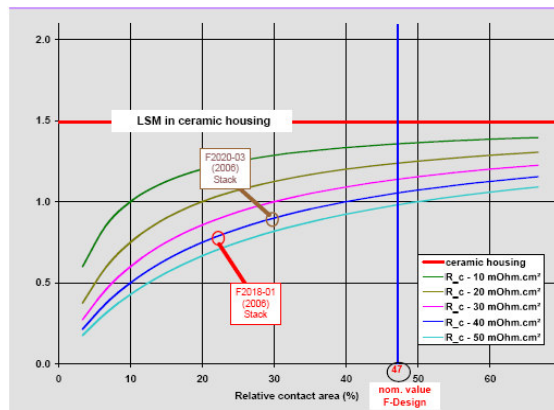
Sulfur poisoning

- 0.5 ppm H₂S may poison the anode (doe fc handbook)
- some small system can withstand sulfur at 950°C (HEXIS)
- sulfur poisoning may be irreversible
- options are
 - remove sulfur
 - develop sulfur tolerant anodes

Assessing the effects of contact area and ceramic cathode contact paste resistance:

47% contact in F-design, 10-50 mΩcm² specific resistance





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Cathode side contacts

- limit stack power
- contact area needs to be improved, particularly in the light weight design
- better contact powders are available, but long-term performance has to be investigated
- new cathode contacting methods are under consideration
 - design
 - materials

Fuel Cell Project Projektteilung PBZ Institut für Werkstoffe und Grenzflächen IEF Zentralabteilung ZAT Hans Hubert Oktober, 2007

Summary

- different requirements:
 - ⇒ SOFC stack available for stationary applications
 - ⇒ SOFC stack in development for mobile (APU) applications
- basic studies to reduce degradation
 - ⇒ chromium poisoning
 - ⇒ sulfur poisoning
 - ⇒ re-oxidation (see 2 other FZJ presentations during this conference)
- applied studies to understand performance limitations in stacks
 - ⇒ contact area
 - ⇒ contact resistance
- intensive work is going to be continued in Jülich

Acknowledgment



we are grateful for the good Jülich-internal cooperation, the support from international contacts and the financial support from the German government and the EU.

附件 3. PNNL Dr.Singh 報告內容: Corr of Metals and Alloys under SOFC Interconnect Exposure Conditions

Corrosion of Metals and Alloys under SOFC Interconnect Exposure Conditions



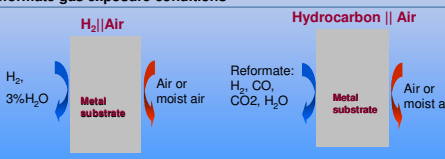
Z. Gary Yang, Gordon Xia, Jeff W. Stevenson, Prabhakar Singh

31st INTERNATIONAL COGDA BEACH CONFERENCE & EXPOSITION ON ADVANCED CERAMICS & COMPOSITES
Hilton Daytona Beach Resort & Ocean Center • January 21-26, 2007
Daytona Beach, Florida



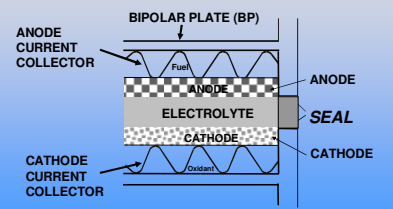
Objectives

- ✓ Examine the corrosion behavior of metallic interconnects under single and bi-polar / dual atmosphere exposures
- ✓ Investigate the corrosion of metallic interconnects in simulated reformat gas exposure conditions



Current collector design: Exposure conditions

Design dependent – Single or bi-polar exposure

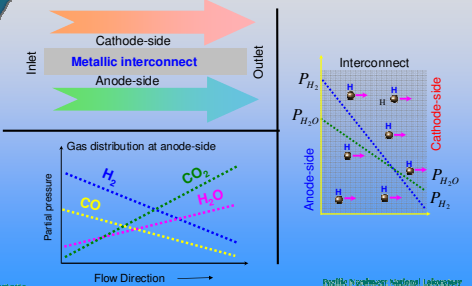


Fuel- Coal derived gases, Fully or partially reformed hydrocarbons, Hydrogen
Oxidant – Air, Oxygen

EPRI/EPRI

EPRI/EPRI National Laboratory
U.S. Department of Energy

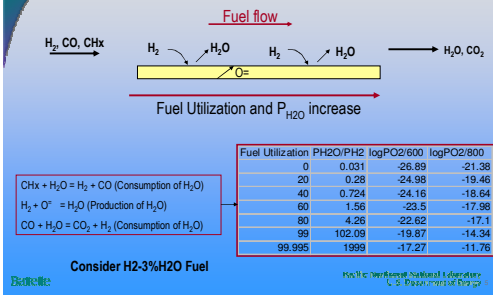
Interconnect Exposure



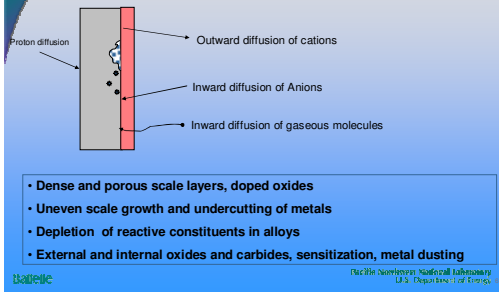
EPRI/EPRI

EPRI/EPRI National Laboratory
U.S. Department of Energy

H₂O Formation in SOFC: Fuel Utilization



Corrosion Processes



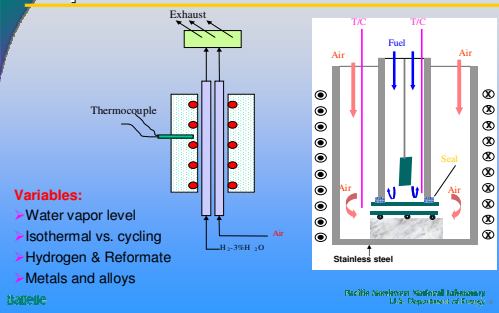
Status

- ✓ Corrosion of Fe and Ni base alloys under bi-polar / dual exposures differ from that under single atmosphere conditions.
- ✓ Ferritic steels are susceptible to iron oxide formation and Fe doped outer scale formation under H₂/air dual exposures. Such trend was not observed under reformat || air, possibly due to a lower hydrogen gradient.
- ✓ For Ni-Cr base alloys, dual exposures tended to improve scale adherence.
- ✓ No carbon induced corrosion or metal dusting was observed under the reformat (a_c<1).
- ✓ Long term effects of multi oxidant corrosion is being examined

ORNL

ORNL Neutron Scattering Laboratory
U.S. Department of Energy

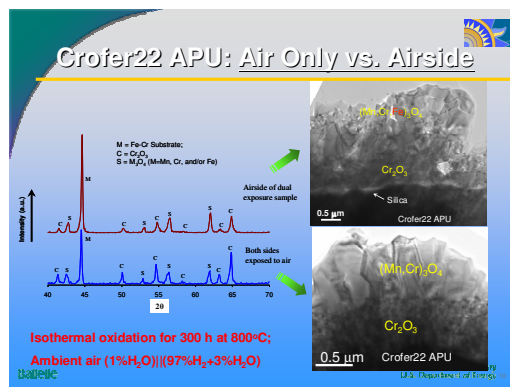
Experimental

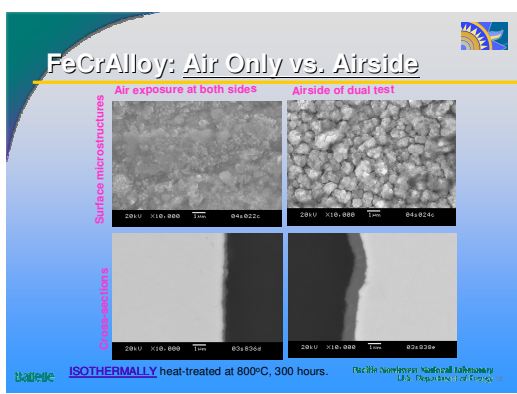
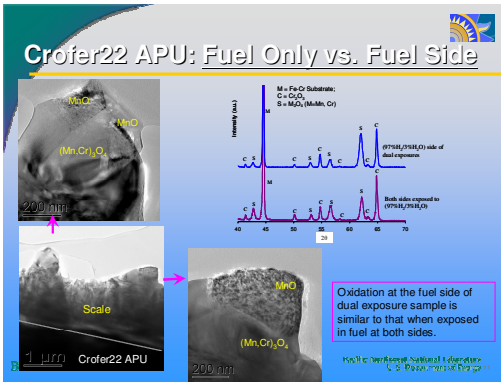


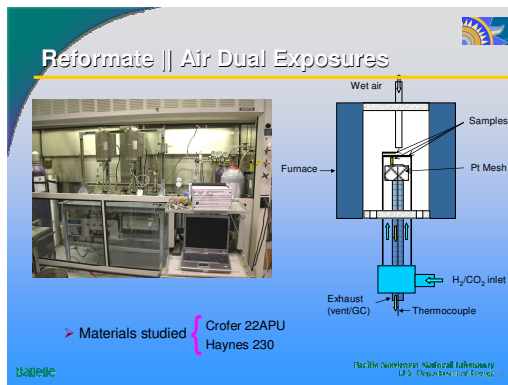
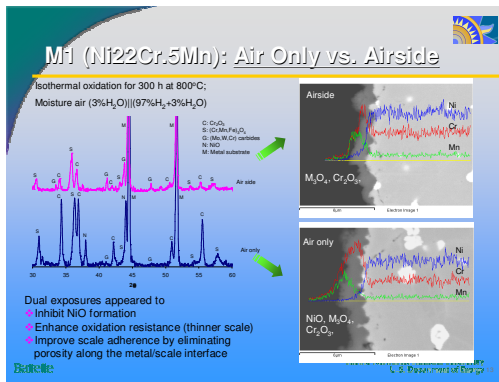
Metals and Alloys Studied

1	Ferritic Stainless steels (Fe-Cr base)	<ul style="list-style-type: none"> E-brite-27%Cr Crofer22-22%Cr AISI430-17%Cr Fecralloy-4.5%Al 	<ul style="list-style-type: none"> Chromia-forming Alumina-forming
2	Ni-Base Alloys (Ni-Cr base)	<ul style="list-style-type: none"> Haynes 242-9%Cr Hastelloy S-17%Cr Haynes 230-22%Cr M1-Haynes 230+1%Mn M2-Haynes 230+2%Mn 	<ul style="list-style-type: none"> Chromia-forming
3	Elemental metals	<ul style="list-style-type: none"> Ni Ag Fe, etc. 	
4	Surface modified:	(Mn,Co) ₃ O ₄ coated Crofer22 APU	

E.ON Energy Research Center
Purdue University National Laboratory for Energy & the Environment
U.S. Department of Energy



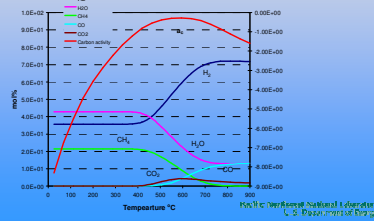




Fuel Chemistry and Carbon Activity

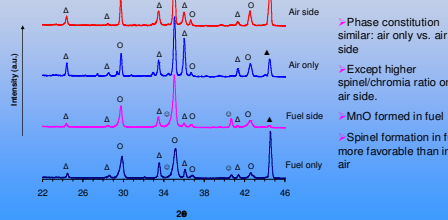
Temp. (°C)	H ₂	CO	CH ₄	CO ₂	H ₂ O
800 (calc.)	72.1	12.4	0.2	2.5	12.8
800 (exp.)*	74.2	8.8	0	6.2	9.7

*Outlet composition analyzed with GC



Scales Grown on Crofer 22APU

Δ: Cr₂O₃
 ○: (Cr,Mn,Fe)SO₄
 ▲: Fe-Cr substrate
 □: MnO



Scales Grown on Crofer 22APU

Air only

Air side

Difference in scale surface microstructure: air side vs. Air only

- Scale on air side thinner, and richer in Fe from EDS analyses
- BUT no hematite nodules formed

Battelle
Battelle National Laboratory
U.S. Department of Energy

Scales Grown on Crofer 22APU

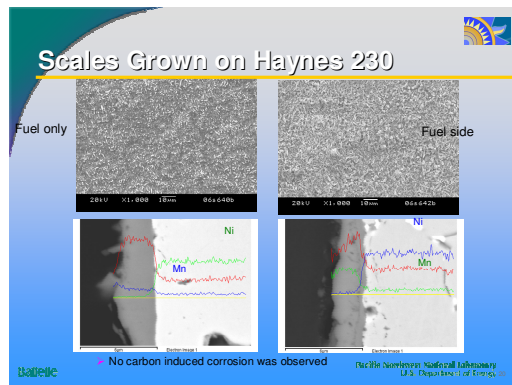
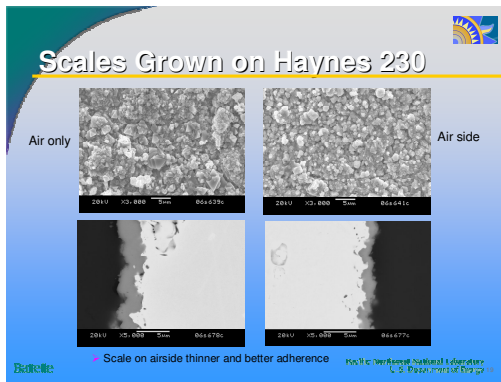
Fuel only

Fuel side

Scale structure and composition similar: fuel side vs. fuel only

- No observable carbon induced corrosion

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U.S. Department of Energy

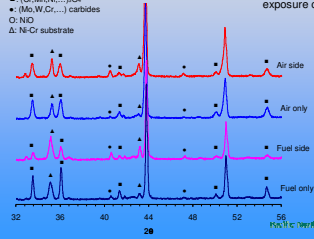


Scales Grown on Haynes 230

After 1,000 hrs, 800°C

- Cr₂O₃
- ▲ (Cr, Mn, Ni, ...) ₂O₃
- (Mo, W, Cr, ...) carbides
- NiO
- △ Ni-Cr substrate

Scale structure and composition similar under all exposure conditions



Summary and Conclusions

- Oxidation/corrosion behavior under dual exposures differs from that under single exposures.
- Fe-Cr base alloys appeared susceptible to iron oxide formation under H₂||air dual exposures. This was not observed under reformat || air, possibly due to a lower hydrogen gradient.
- For Ni-Cr base alloys, dual exposures tend to improve scale adherence.
- No carbon induced corrosion or metal dusting was observed in the reformat (a_c<1) under experimental test conditions.

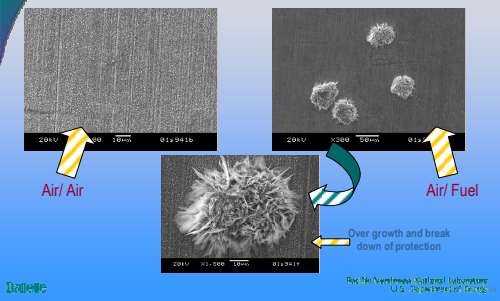
Acknowledgements

- The work described in this paper was performed under the U.S. Department of Energy's Solid-State Energy Conversion Alliance (SECA) Core Technology Program.
- Metallographic preparation and SEM: Jim Coleman, Shelley Carlson, Nat Saenz.

Deltec

Pacific Northwest National Laboratory
U.S. Department of Energy

Accelerated Corrosion in Dual Environment



Deltec

Pacific Northwest National Laboratory
U.S. Department of Energy