出國報告（出國類別：參加研討會）

出席 2013 年國際能源應用材料會議
心得報告

服務機關：國防大學理工學院動力及系統工程學系
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派赴國家：德國
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摘要

國際研討會“材料於能源上的應用(International Conference on Materials for Energy)”乃國際間能源材料應用上知名會議，會議摘要歷經審查機制，獲接受論文必須收錄及供與會人士下載。

此會議參與學者遍及世界各國，學者研究範圍極廣，學術討論分爲：能源效率、儲存、燃料電池、電化學儲存、鎳基超合金材料之應用、氫的儲存、材料應用環境、熱電學(Thermoeletrics)、能源效率、磁性材料材料製造程序及其模擬(Modeling)、生化燃料、光電材料、催化性能(Catalysis)、導電材料、固態照明(Solid-State lighting)、奈米材料應用在電極上、奈米材料應用在燃料電池、奈米材料應用於太陽能電池等 20 種議題，極爲豐碩。

議程有 5 場專業大會報告，238 篇論文報告，本人發表“鈦合金經過儲氫/放氫後改進耐蝕性能”，此乃一新方法，參與學者積極提問，評價良好，此行除吸取新知外，經由與國外學者討論，獲益良多，有助於未來教學研究之精進。

目次

目的

1.赴德國研討會，發表研究成果。

2.與國際學者進行學術交流。

過程

此次研討會於 5 月 12-16 日假德國 Karslruhe 市會議中心(Convention Center)舉行，計有大會演講論壇、論文報告及論文海報展示及說明等事項。

此次會議著重於能源儲存運用，以開發材料來達到改進材料目及精進科技上之應用，並可望應用於嚴苛環境提昇。

5 月 12 日 1000-1800 時開始接受與會人員報到及論文海報展示備便，1800-2000 時為歡迎晚宴。5 月 13 日 1000-1030 時為大會開幕式，1030-1230 時由大會邀請之 M. Fleischer 教授就 Mesoscopic photosystems for the generation of electricity and fuels from sunlight 與C. A.Volkert 教授就 Energy storage-challenges and perspectives 實施演講，當日 1230 時即開始依大會規劃之場地就各議題實施分組報告與意見交流，期間大會另於 5 月 15 日 0845-1215 時，安排 L. Schultz 教授就 Energy efficient transportation by superconducting levitation-riding on magnetic fields、J. DeYoreo 教授就 Recent developments in solar photovoltaics : market, industry, and technology 及 D. Aranda 教授就 Challenges in the microalgae energy feasibility 實施專題報告，最後大會於 5 月 16 日 1250 時舉行圓滿閉幕式。

經聽取大會安排之五位知名教授演講內容，汲取了目前國際間對於能源產出、儲存、傳遞及運用之市場需求觀點、技術發展近況及未來挑戰與願景，其中包含太陽光催化反應系統的技術開發；能源儲存之途徑與方式及其面臨之經濟效益、儲存效率及環境影響等相關工程技術挑戰；超導磁力懸浮之能源傳輸方式；以及國際間目前積極研究開發之藻類發電方式，經查國內台電公司目前亦投入發展微藻減碳計畫，規劃一套適合運用於火力發電廠的微藻養殖技術，利用電廠發電後所產生的煙氣及燃油集塵灰當作藻類生長所需的碳源及氮源，讓藻類在低耗能的養殖系統中轉化為大量的有機體以及氧氣。藻類經回收後，可將其中成分如多醣類、藻藍蛋白等活性物質萃取出來，再利用於機能食品、動物飼料或保養品等高經濟價值

產品的生產，而剩餘的藻體，可做爲生物燃料（Biofuel），當作發電系統的燃料使用。

本人獲得邀請之論文口頭報告，大會安排於 5 月 14 日 1630-1650“Extreme Environment”議題中實施報告，由 Section, Prof .R. Moors 主持。演講主題爲“以工業重要材料 Ti-6Al-4V 合金經熱置氫製程後，經由控制氧化層而提昇抗蝕性能之應用”（附件一）。此實驗方法乃新的研究方式，嘗試以 Ti-6Al-4V 合金經熱置氫製程長出之奈米晶粒後再實以熱處理，在奈米晶粒上生長出細薄氧化層，由於此方法乃創新研究，結合 Ti 合金易儲氫特性，並可改變材質之相變化。研究結果顯示此方法具體可行，其微觀結構及成型機制也被詳細了解，報告結束獲五人積極提問並獲滿意答覆。

其中所提問題概分爲：

(1)如何確認本人在儲放氫過程中，完全將氫吸收及排放。

(2)Ti 合金理論上較不喜歡氫，易產生氫脆，儲氫效益難道不會受影響。

(3)如果產生奈米晶粒，那麼機械性質表現如何？

(4)如何量出吸氫量。

(5)如何確定氫氣已全部排出，等 5 項。

針對上述 5 項提問，本人回答如下：

(1)以 Sievert´s Volumetric Appratus（投影片 8/31）之儀器進行熱置氫(THP)處理，此法已獲肯定，可以 THP Keywords 當關鍵字去搜尋 Scrpita Mat.及 Acta Mat.等知名期刊當參考，可更了解細節。

(2)此種技術以理想氣體方程式結合壓力閥的管制，壓力量測（8/31 投影片）可精確量出其儲放氫量，已屬成熟，不必質疑。

(3)經過量測及觀察，本研究之硬度值均在 Hv＝300，是在 α 相及 β 相內，繼續切割 α 相及 β 相，而對外圍組織的大晶粒範圍，除了氧化層產生預期效果外，並無不良影響。否則以純粹奈米晶粒硬度，硬度就至少會達到 Hv＝700-800 以上。此種 THP 製程，效果極佳。

(4)Ti 合金雖然與氫結合時易有氫脆，尤其是在固溶後+水淬。然而如果在儲氫時，Ti 極喜歡與氫原子接合。此特性才使得 Ti 合金有除氫功能，且可因此產生相變化，晶粒細化等有趣及值得應用的現象。避開水淬也是一種符合避免氫脆的產生。

(5)以精確壓力的量測即可確定氫氣已排出。

事後更有美國南卡羅大學化工系教授 Prof. Jason Hattrick-Simpers 及蘇俄高階工程師（旅居德國），找本人繼續討論高解析影像的 α、β 相之奈米結構，進一步了解實驗細節。

個人於簡報後除聽取 5 月 15 日邀請報告外，並參與相關議題之參展海報交流(如附件二)，包含：

●Different types of cathode structures for lithium sulfur batteries.

●Study on the mechanism of lithium-ion battery by hyper branched polymer coated on cathode.

●Kinetics of acetic acid steam reforming over Ni/ and Co/$Ce_{0.75}Zr_{0.25}O_2$ catalysts.

●Casting process of CNTs-Al composites using composite powder precursors and intensive melt shear technology.

●Material development enabler formulation to turn active materials into finish products.

●Dual nitrogen and sulfur doped carbons as metal free catalysts for the oxygen reduction reaction in fuel cells.

●Structure, mechanical properties and conductivity of Cr and Hf Bronzes after ECAP.

●Nano-foams by continuity inversion of dispersion.

●High voltage core-shell nanocomposites as positive electrode materials for advanced lithium-ion batteries.

●Surface modification of carbons by elevated temperatures gas treatments for improved solid electrolytes interphase formation.

●In-situ stress evolution studies of (De) lithiated Si films.

●In situ and ex situ studies of lithium nucleation and dendritic growth during electroplating.

●XRD total scattering and pair distribution (PDF) measurements on $LiNi_{0.5}Mn_{1.5}O_4$ spinel.

●The EERA joint programme on energy storage.

●Nanoscale silicon as high capacity anode of next-generation lithium ion batteries.

●The influence of different carbon surfaces on electro-reduction of oxygen in different electrolytes.

●In-situ X-ray diffraction : time-resolved structure investigation of L-transition metal-fluorides as cathode materials in Li-ion batteries.

●The initial stage of lithium metal deposition studied by in situ STM.

由於大會配置識別證上有註記教授頭銜，因此在海報論文展示處，幾位學生自告奮勇邀

請本人至其海報論文前，希能給予其一些建議。本人聽其簡報後，針對電池極板材質改進後，亦給予 3 點改進意見，敘述如下：

(1)效率提升須與較重要的現有文獻報告比較，查出其差異。

(2)所提供的穿透式電子顯微鏡，雖然具有微細奈米顆粒影像，但無法證明是作者聲稱的粒子，必須輔之以 SADP 繞射圖形，證明其晶粒常數相符。必須要再多作上述實驗步驟或以高解析 TEM，以 FFT（快速傅立葉轉換）量出其聲稱的粒子繞射平面以證明。此二實驗可二選一，趕快補足，否則這篇論文若由我審查，我不會同意作者聲稱的結果，因爲“嚴謹性不足”。

(3)所提供之場發射照片雖然尚可，但本人認爲仍需重拍攝，指出其未完美聚焦之處，使得影像更完美，以符合知名期刊之要求。

本人與上述學生互動良好，雙方留下深刻印象，並對國外投入大量人力及經費於能源材料研發精進印象深刻。

大會於會後並來函（附件三），希本人提供電子檔報告內容，並經由大會平台，提供與會人士下載繼續深入研究。

心得及建議

因能源危機的影響，爲提升能源效率及因應材質性能提昇、減重、效能改進，以材料改質改善儲存方法及精進，乃今後科技發展之重心。今後將材料應用於嚴苛環境，其儲存方式、電池的性能提升、改進電池材料、燃料電池改進及太陽能電池應用等，爲世界目前研究重點。

經過此次研討會深感科技之重要性，以及清楚看到過際間研發能量投入此領域，對其日後經濟強化，有重要影響。我國學人及業界應投入更多人力及經費，以免落後喪失國際間競爭舞台，可延伸國內的相關產業及研究方向，如提昇效率、對材料材質的改善、對機械性質的要求，以因應更爲嚴格環境，如潛變的控制，材料機械性質維持也與能源同樣受到重視。

經歷此次研討會議，亦深覺教學研究責任重大，必本虛心以學習；看到國外學者最近研究成果，對材料材質改善量測技術、性能提升，不遺餘力，實值得我國相關科技人員深思及大力推展，以立足於世界競爭舞台，且深感英文能力表達及科技報告的閱讀能力之重要性，此後亦更加督促學生，使學生能與國際接軌更有競爭力。

附件一：本人受邀發表論文簡報

Controlled Oxide Layer Formation on Corrosion Behavior of Ti–6Al–4V Alloy Following Thermohydrogen Processing

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University of National Defense, Taiwan, R.O.C.

2nd International Conference on Materials for Energy

Introduction

1. Ti-6-4 alloy is a promising material.
   Major applications are in：
   - aerospace,
   - automobile,
   - military industries

   because of its ：
   - low density,
   - excellent mechanical,
   - corrosion properties

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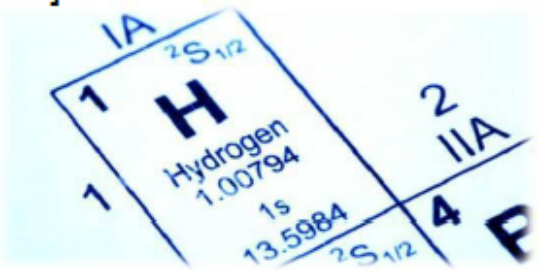
2. Recently, extensive studies have been reported on refinement of the grain size of titanium alloys using a thermohydrogen process (THP) by employing hydrogen as a temporary alloying element.

*THP, by using：
hydrogenation and dehydrogenation process [Yu,06;She,07;She,09].



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3. The refinement is achieved based on the
- modifying effect of hydrogen

  on

- phase composition and transformation of metastable phases.

4. Interestingly, even a relatively low concentration of hydrogen introduced into titanium alloys as a temporary alloying element has a great effect upon phase transformation and thus modification of microstructure and mechanical properties [Fro,04].

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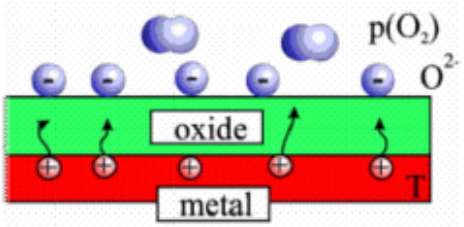
5. THP can produce nano grains. [Yu,06;She,07;She,09].

6. Oxide layer produced on nano grains may be a good way to enhance the corrosion resistance of Ti-6-4 alloy.

7. There are limited reports on the corrosion behavior of grain-refined Ti alloys resulting from the THP.



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8. Control of O_2 flowing rate into the furnace containing THP processed sample of Ti-6-4 alloy may be possible to control the desirable thickness and composition of Ti-6-4 and therefore：improve the corrosion resistance of T-6-4 alloy.

9. So this study aims to evaluate whether this goal can be achieved.

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Experimental work

Sample preparation

- as-received(AR)
- β-solution treatment at 1050℃ in vacuum for 0.5 h, followed by furnace cooling to room temperature(AR+BST)

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THP treatment

- Sievert's volumetric apparatus was used for THP treatment.
- Hydrogenation : 600 ℃/30 min
- Dehydrogenation : 600 ℃/2 h, followed by air cooling for approximately 30 min to room temperature.

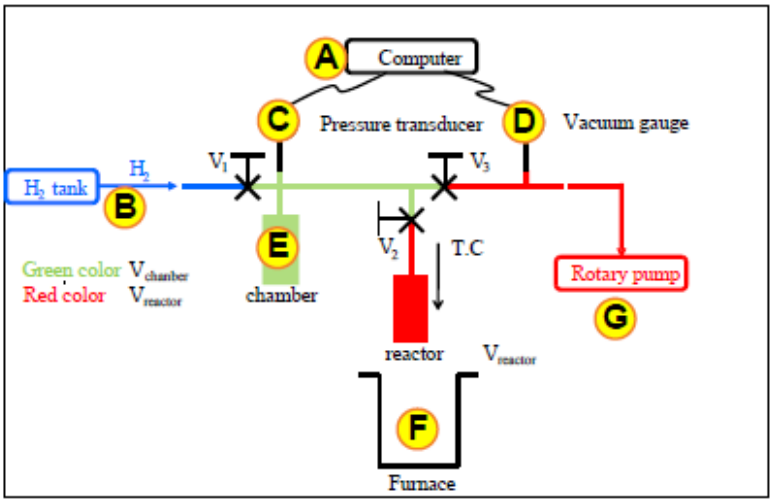

Fig.1 Sievert's volumetric apparatus diagram

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Annealing treatment

- ANN : without O_2+Ar (500cc/min) at 704℃/2h/air cooling
- ANN plus O_2 : with O_2(50cc/min)+Ar (500cc/min) at 704℃/ 2h/air cooling

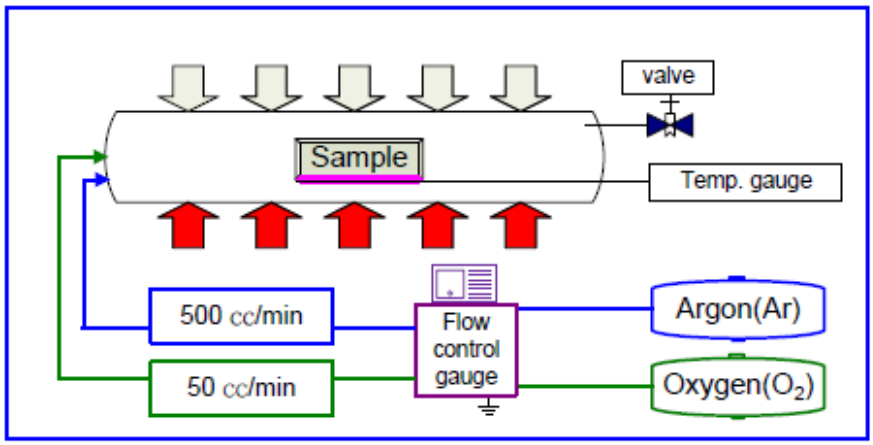

Fig.2 Annealing treatment diagram

All the samples were ground with SiC abrasive papers and further polished with fine grade diamond paste before each stage treatment.

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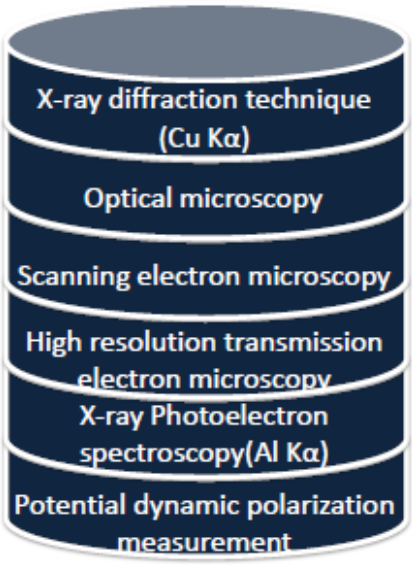
Sample Condition

- A: AR+BST (β-solution treatment)
- B: AR+BST+THP
- C: AR+BST+THP+ANN
- D: AR+BST+THP+ANN (O_2) (50cc/min)
- E: AR+BST+ANN

test



*Sample A, B treated at vacuum condition.
*Sample C, D, E prepared in argon filled atmosphere.

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TABLE I. Related processing and treatment of present samples

Sample	Treatment Procedure
AR+polished+BST*1	as-received → polished → β solution treatment → exposing in air
AR+BST+polished+THP*2	as-received → β solution treatment → polished → thermohydrogen processing → exposing in air
AR+BST+THP+polished+ ANN*3	as-received → β solution treatment →thermohydrogen processing → polished → annealing treatment→ exposing in air
AR+BST+THP+polished+ ANN(O_2)*4	as-received → β solution treatment →thermohydrogen processing → polished → annealing treatment associated with oxygen flowing into the furnace (50 cc/min) → exposing in air
AR+BST+polished+ANN	as-received → β solution treatment → polished → annealing treatment → exposing in air

*1. BST (β solution treatment) : conducted in vacuum at 1000℃/30min/air cooling
2. THP (thermohydrogen processing) : hydrogenated in vacuum at 600℃/30min → dehydrogenated in vacuum at 600℃/2h/ air cooling
3. ANN (annealing treatment) : carried out in furnace completely filled high purity argon at 704℃/2h/air cooling
4. ANN(O_2) : annealing treatment associated with controlled amount of oxygen flowing into the furnace at 50 cc/min

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Result and Discussion

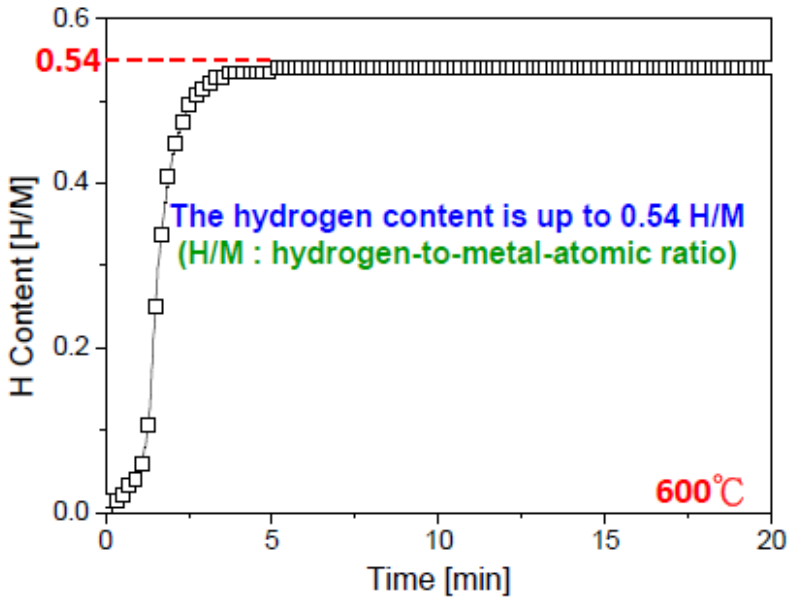

Fig.3 Typical kinetic curves for hydrogen absorption

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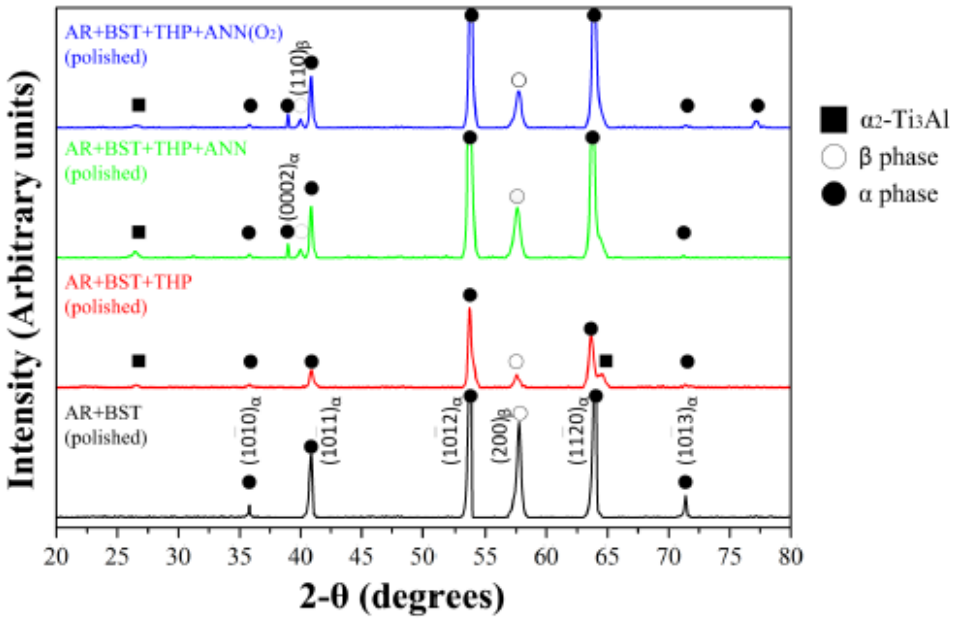

Fig.4 XRD patterns of Ti-6-4 alloy after related treatments. The identified phases of α, α_2, and β are marked.

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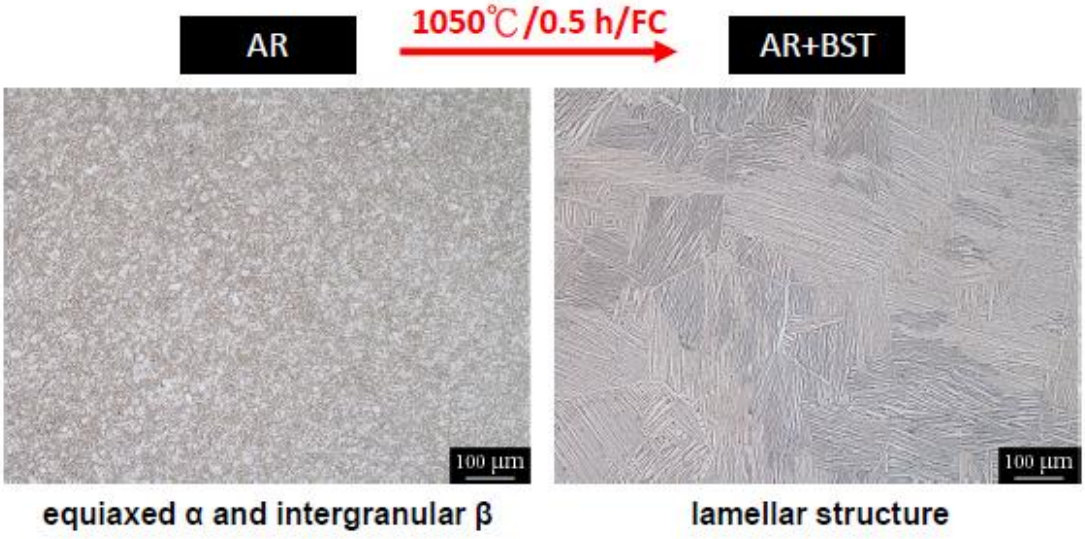

Fig.5 Optical micrographs of β-solution treated Ti-6-4 alloy

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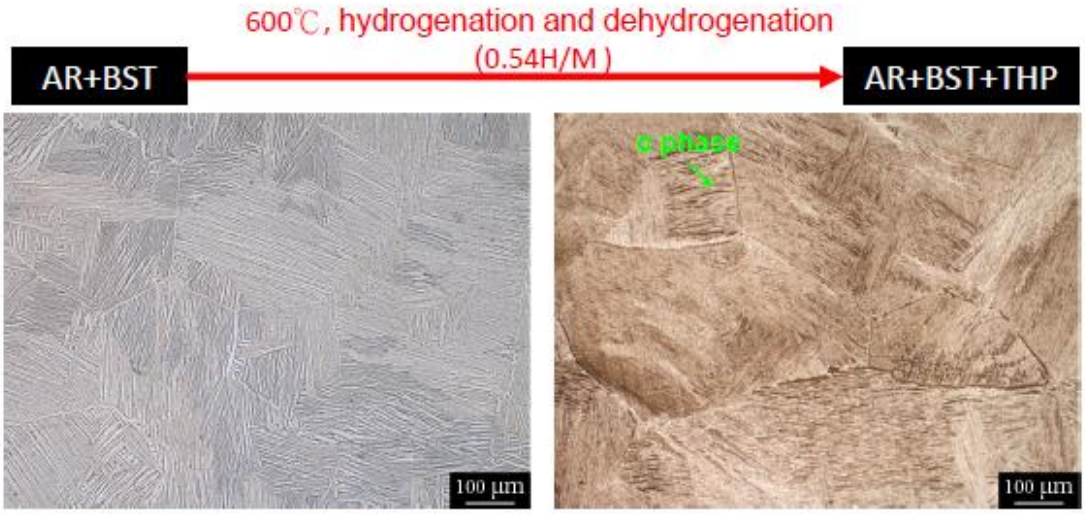

Fig.6 Optical micrographs of Ti-6-4 alloy subjected to THP treatment at 600℃ following β-solution treatment

the lamellar structure is preserved
associated with severely etched feature after THP treatment

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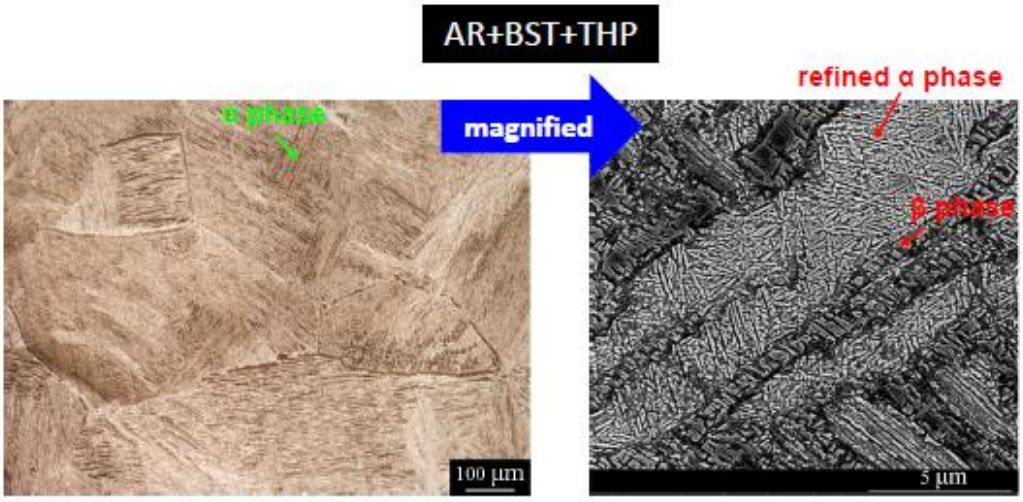

OM SEM

Fig.7 Optical and SEM micrographs of Ti-6-4 alloy subjected to THP treatment at 600℃

grain refinement within the α matrix is observed
through SEM technique

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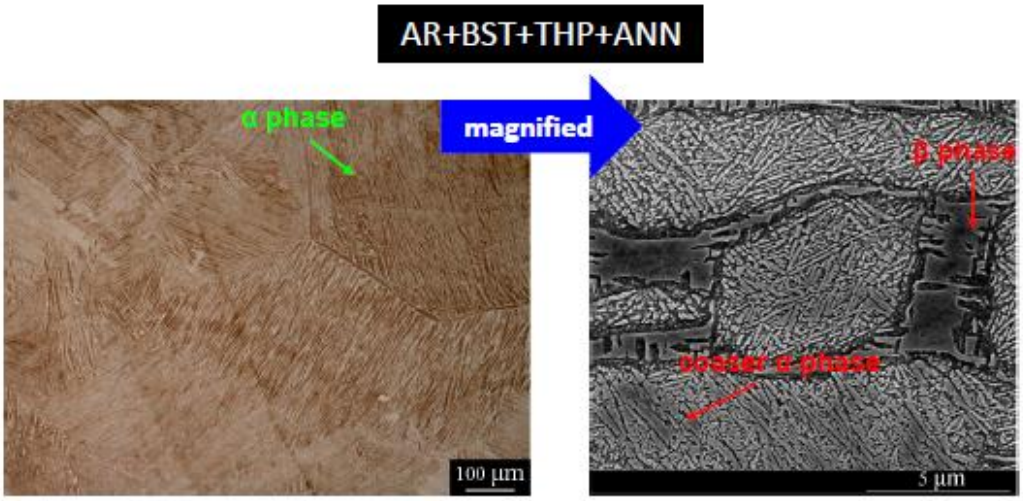

Fig.8 Optical and SEM micrographs of Ti-6-4 alloy subjected to post-THP annealing treatment (704℃/2h/air cooling)

the thicker α grains are obtained due to the effect of grain growth attributed by post-THP annealing treatment

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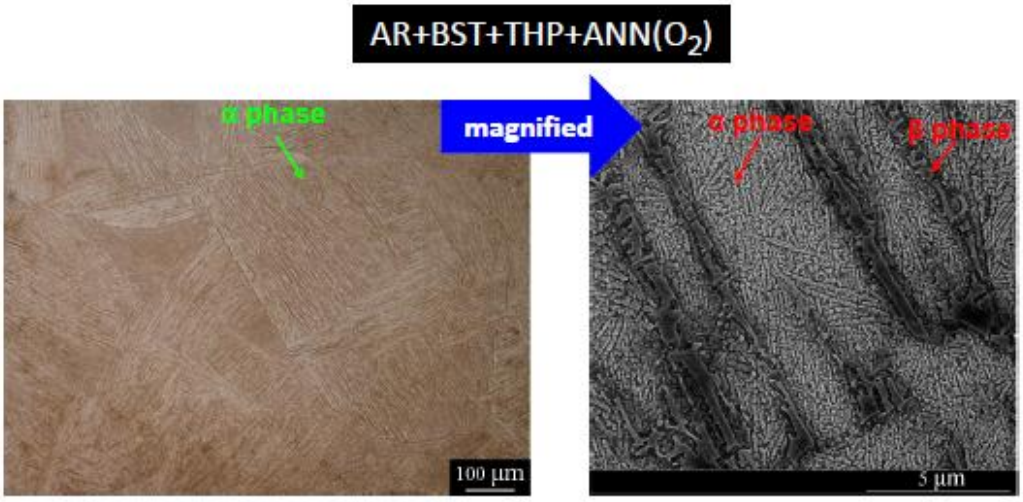

Fig.9 Optical and SEM micrographs of Ti-6-4 alloy subjected to post-THP annealing treatment with O_2

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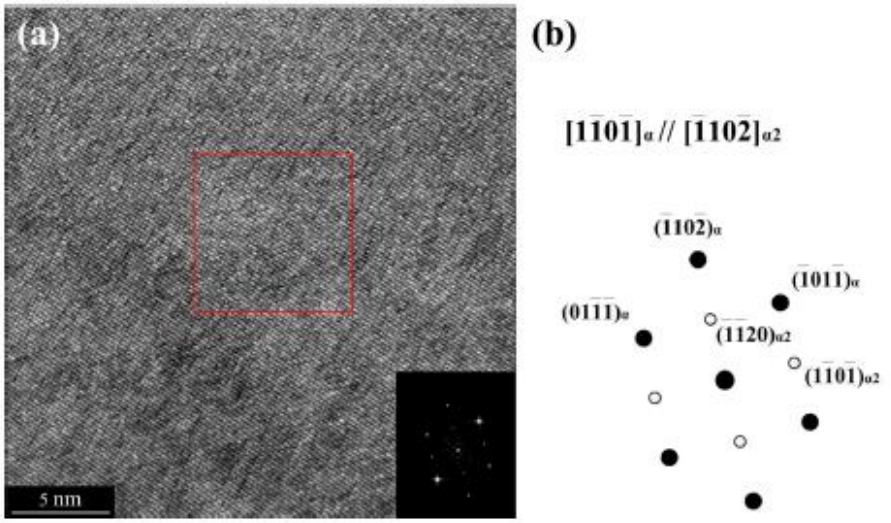

Fig.10 (a) HRTEM micrograph of AR+BST+THP+ANN condition and its Fast Fourier Transform analysis of the framed area inserted
(b) the corresponding schematic illustration of FFT pattern

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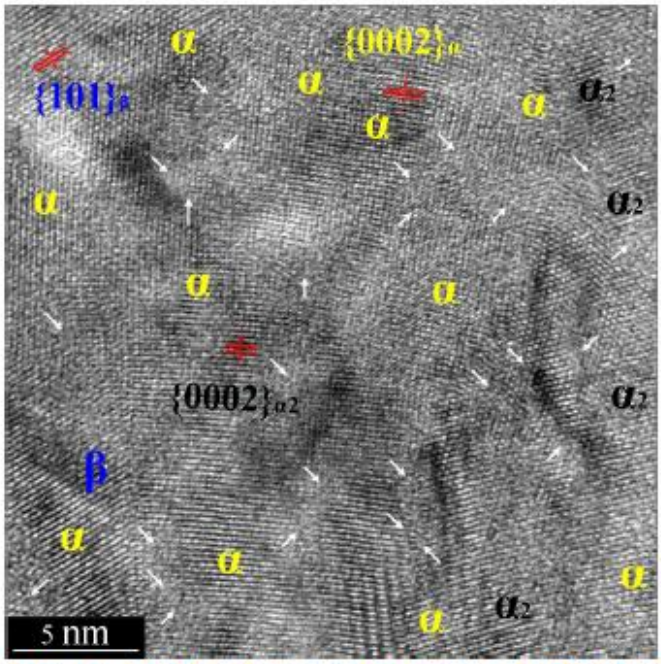

Relatively distorted region close to grain boundary are arrowed.

Fig.11 HRTEM morphology of AR+BST+THP+ANN condition. The identified phases of α, α_2, and β are marked, confirming the XRD result

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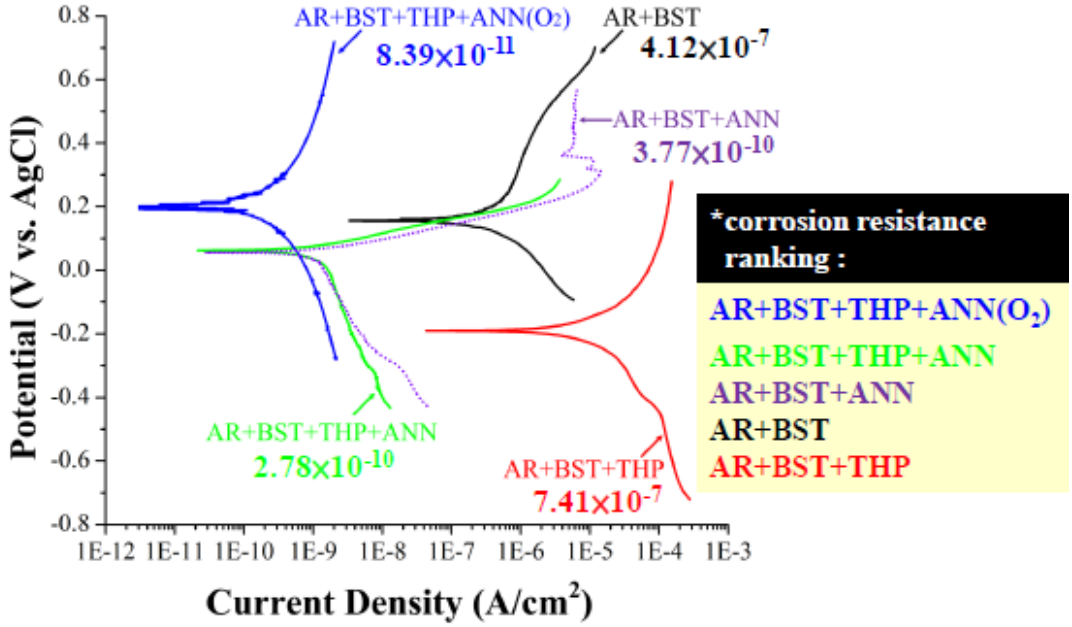

Fig.12 Potential dynamic polarization curves of Ti-6-4 alloy after related treatments in 1N H_2SO_4 solution

(all measurements are carried out with produced oxide layer)

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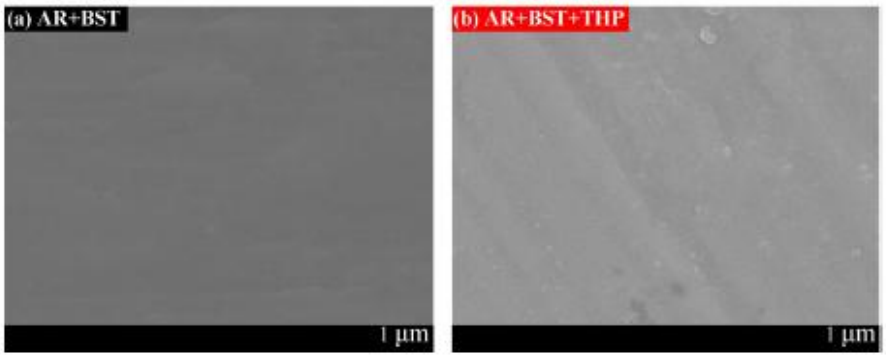

Fig.13 SEM micrographs of the top surface of oxidized Ti-6-4 alloy of AR+BST and AR+BST+THP conditions

*All the samples were ground with SiC abrasive papers and further polished with fine grade diamond paste before each stage treatment.

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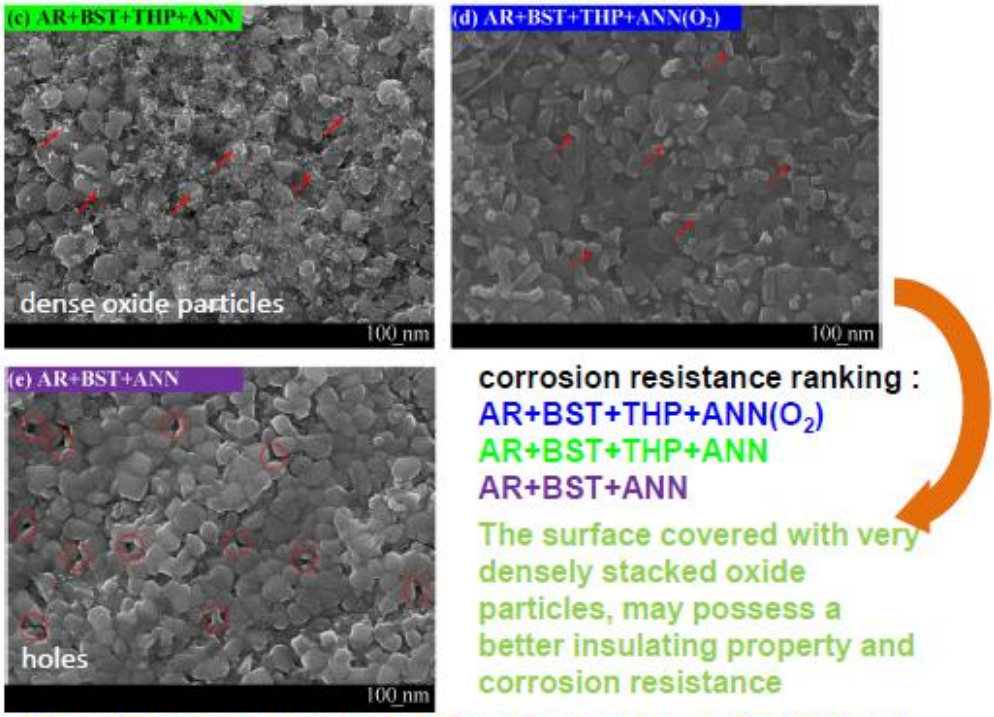

Fig.13 SEM micrographs of the top surface of oxidized Ti-6-4 alloy after related treatments

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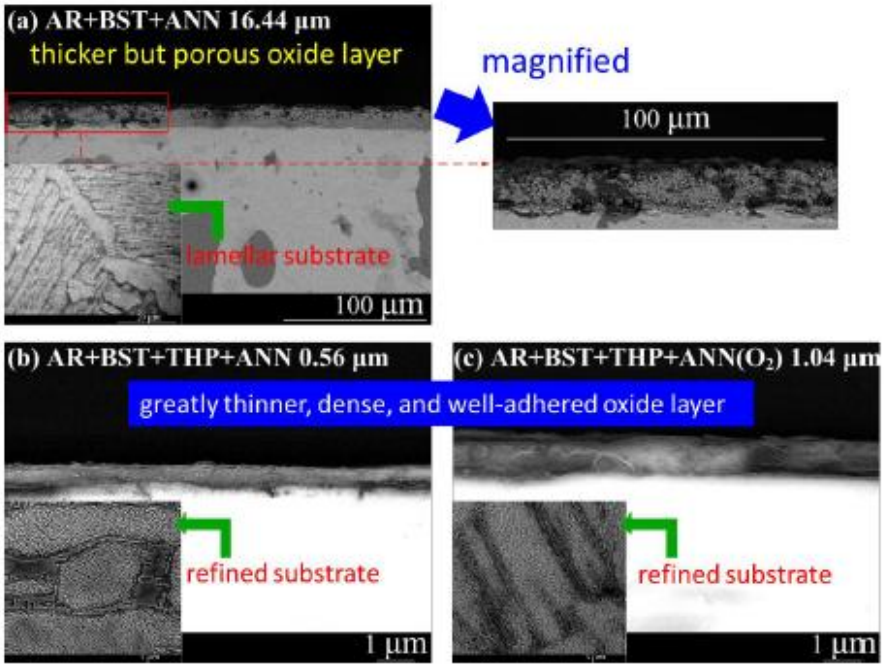

Fig.14 Cross sectional SEM micrographs of oxidized Ti-6-4 alloy after related treatments

Refined Ti-6-4 substrate producing thinner oxide layer

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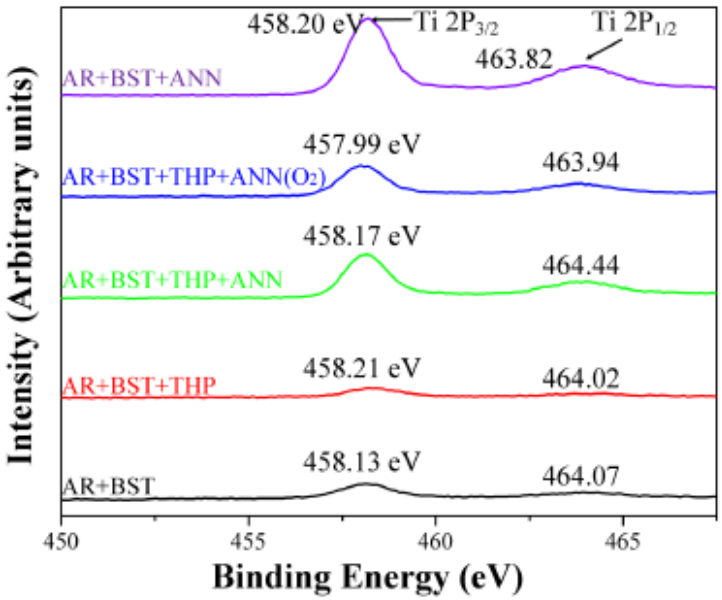

Fig.16 XPS spectra of the Ti 2p region of the top surface after related treatments

The Ti $2P_{3/2}$ peak was positioned at about 458.2 eV, indicating oxidized Ti^{4+} in the form of TiO_2 in agreement with the work of Wang et al.(JMR, Vol. 24, No.12, pp3680-3688,2009)

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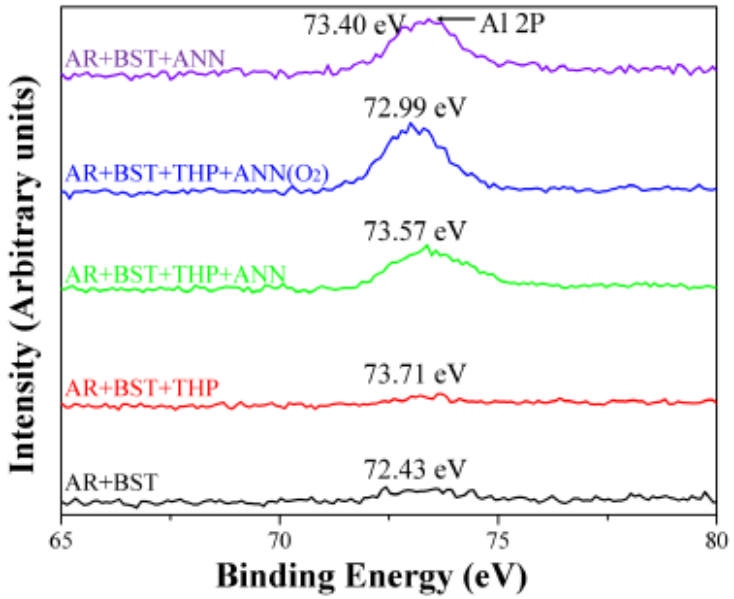

Fig.17 XPS spectra of the V 2p region of the top surface after related treatments

The Al 2P peak was positioned at about 73.2 eV, indicating oxidized Al^{3+} in the form of Al_2O_3 in agreement with the work of Wang et al.(JMR, Vol. 24, No.12, pp3680-3688,2009)

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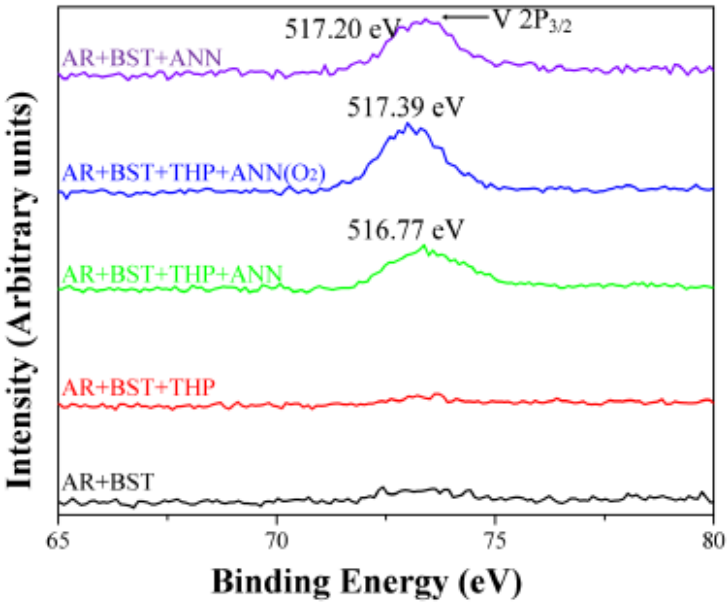

Fig.18 XPS spectra of the V 2p region of the top surface after related treatments

The V 2P peak was positioned at about 516.9 eV, indicating oxidized V^{5+} in the form of V_2O_5 in agreement with the work of Wang et al.(JMR, Vol. 24, No.12, pp3680-3688,2009)

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TABLE Ⅱ . Correlation between corrosion resistance and related of oxide layer.

Samples	Thickness (μm) _Structure of Oxide Layer	Composition of Oxide Layer and Intensity of XPS Ranking			Corrosion Resistance Ranking
		TiO_2	Al_2O_3	V_2O_5	
AR+BST+THP+ANN(O_2)	**1.04_dense**	3	**1**	3	**1**
AR+BST+THP+ANN	0.56_dense	2	2	2	2
AR+BST+ANN	**16.44_porous**	1	**1**	1	**3**
		*ranking 1 means obtained highest amount of related XPS intensity			*ranking 1 means best corrosion resistance

*the compactness of oxide layer is found a dominant factor affecting the corrosion resistance of Ti-6-4 alloy

*Under the similar compactness of oxide layer, the Al_2O_3 content becomes more crucial influencing the corrosion resistance of Ti-6-4 alloy

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Conclusions

- The thermohydrogen process results in the formation of refinement structures (refinement of α matirx by breaking it into several pieces) and the precipitation of α_2 (Ti_3Al) in Ti-6-4 alloy.

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Conclusions

- THP plus annealing treatment (704℃) together with controlled amount of oxygen (50cc/min) leads to the formation of thinner and denser oxide layers offering an effective process to improve the corrosion resistance of Ti-6-4 alloy.

- The Al_2O_3 content becomes more crucial influencing the corrosion resistance of Ti-6-4 alloy under the similar structure of oxide layer.

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Thanks for your attention

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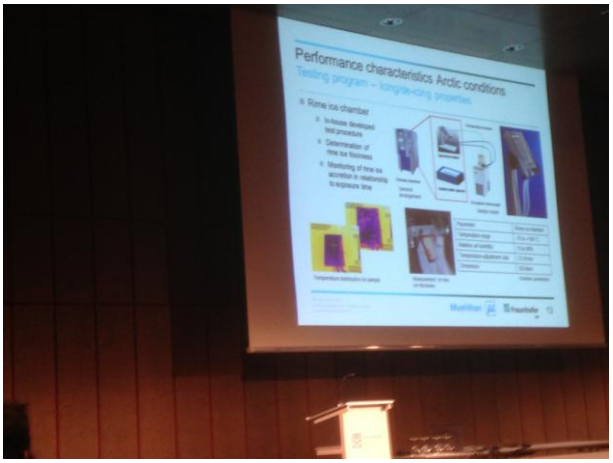
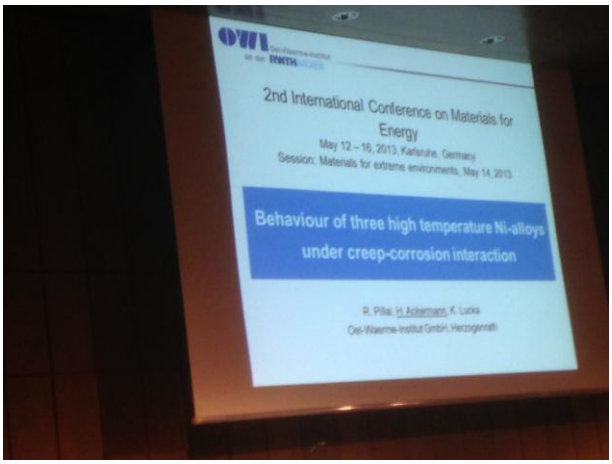
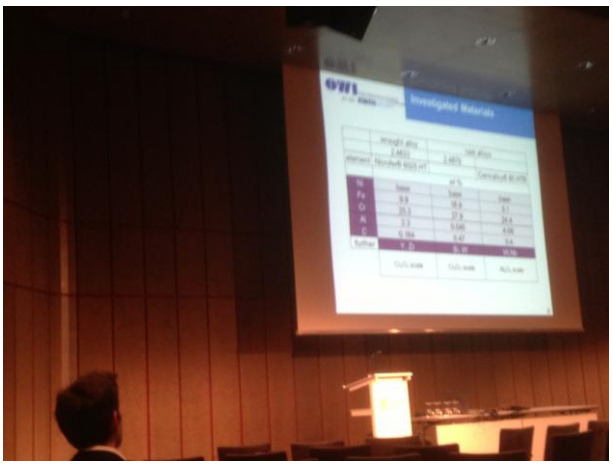
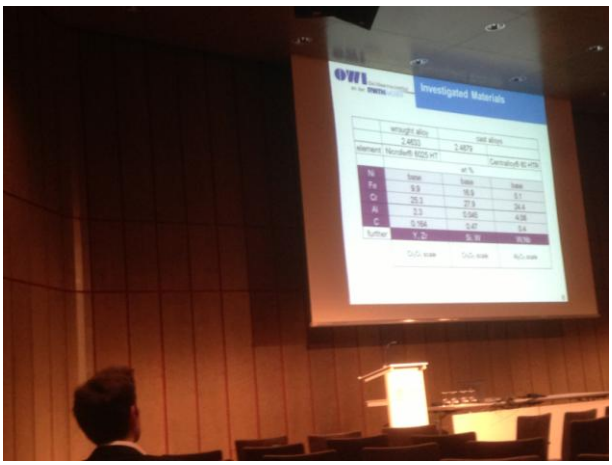
附件二：會中發表及參與研討之論文

本人參加德國 2013「第二屆能源材料國際研討會」並受邀於會中發表論文及所指導論文海報所攝之照片

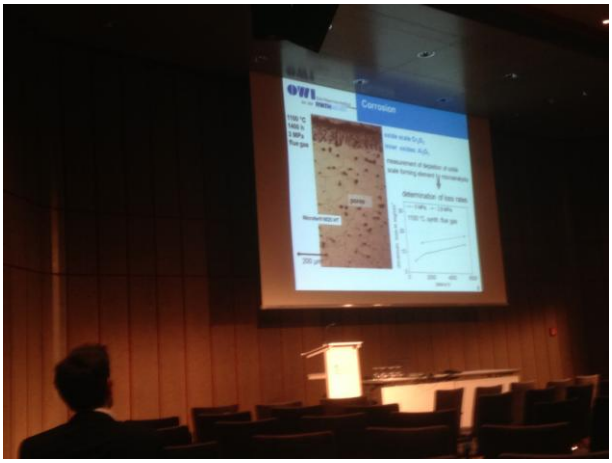


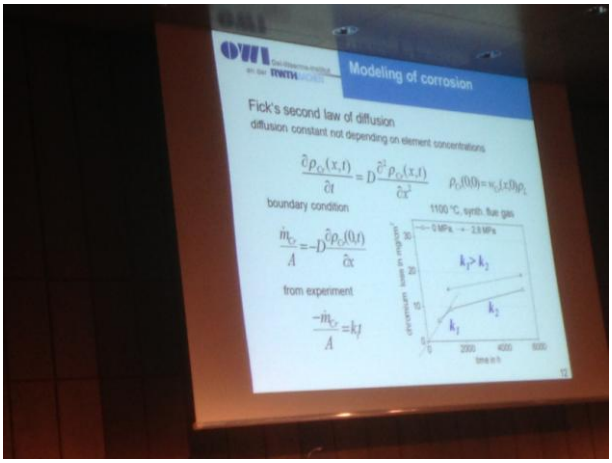


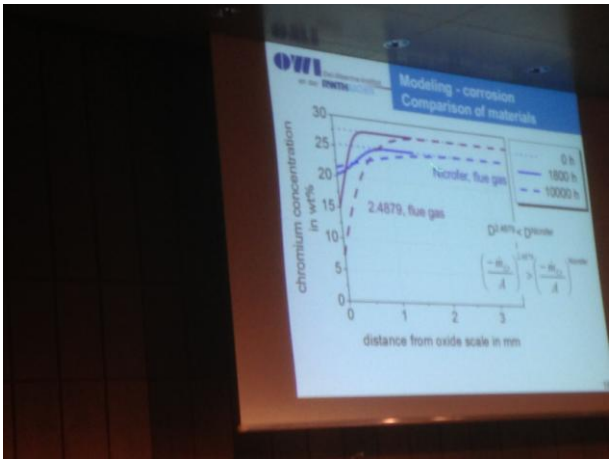





Investigated Materials

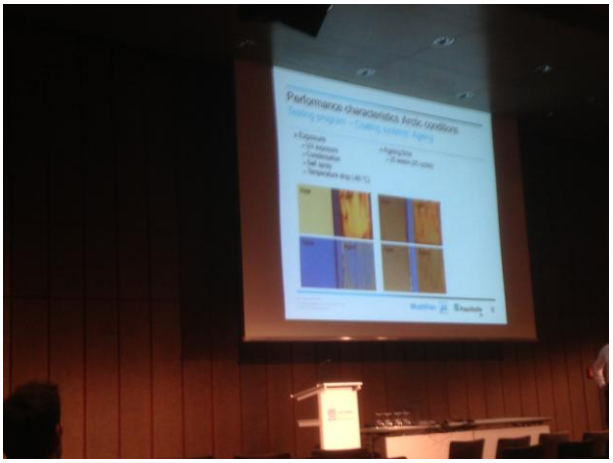

Corrosion

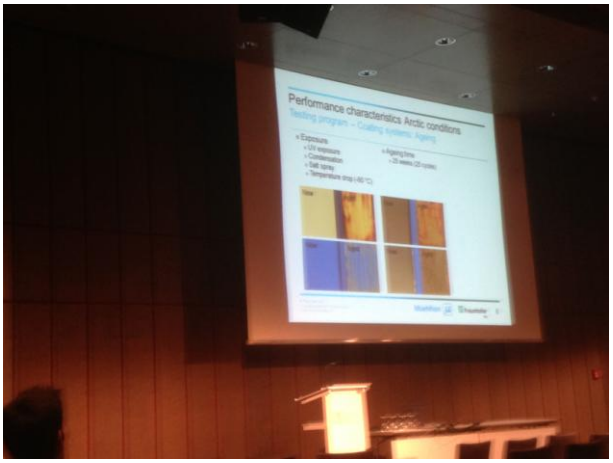

Modeling of corrosion
Fick's second law of diffusion
diffusion constant not depending on element concentrations
boundary condition
from experiment
1100 °C, synth. flue gas

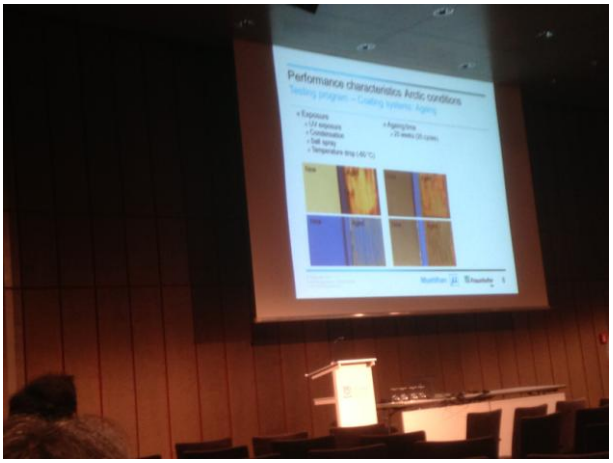

Modeling - corrosion
Comparison of materials
chromium concentration in wt%
distance from oxide scale in mm
2.4879, flue gas
Nicrofer, flue gas
0 h
1800 h
10000 h


Performance characteristics Arctic conditions
Introduction

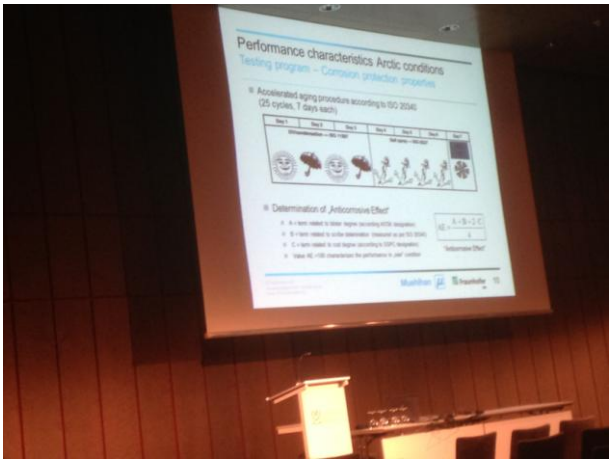

Performance characteristics Arctic conditions
Introduction


Performance characteristics Arctic conditions
Testing program – Coating systems: Ageing


Performance characteristics Arctic conditions
Testing program – Coating systems: Ageing


Performance characteristics Arctic conditions
Testing program – Coating systems: Ageing


Performance characteristics Arctic conditions
Testing program – Corrosion protection properties
Accelerated aging procedure according to ISO 20340
(25 cycles, 7 days each)
Determination of „Anticorrosive Effect"


Performance characteristics Arctic conditions
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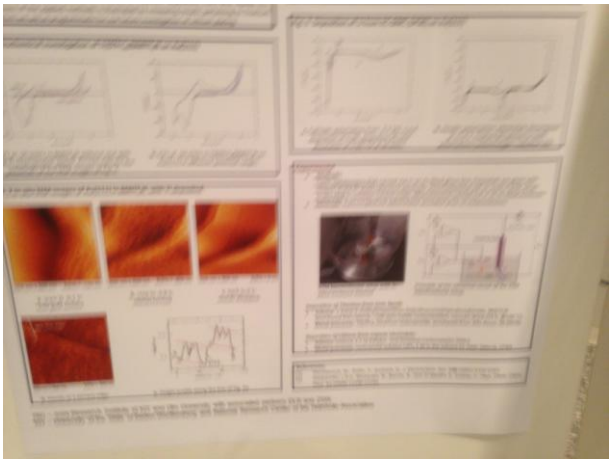

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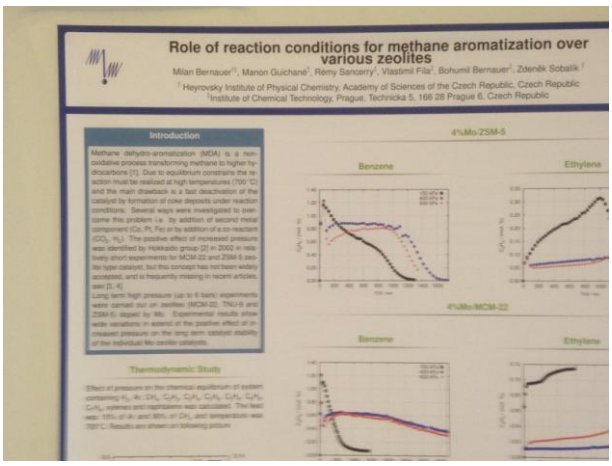

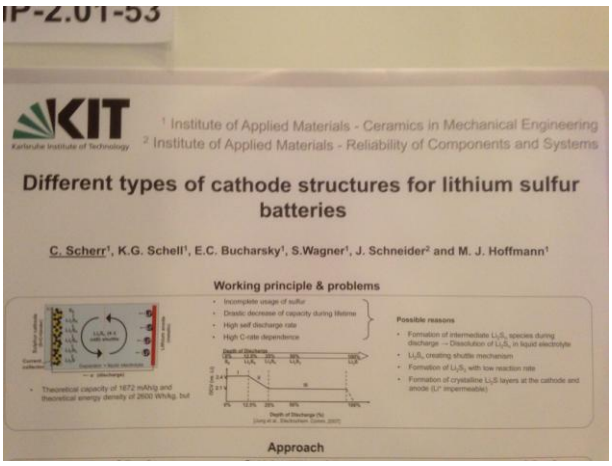

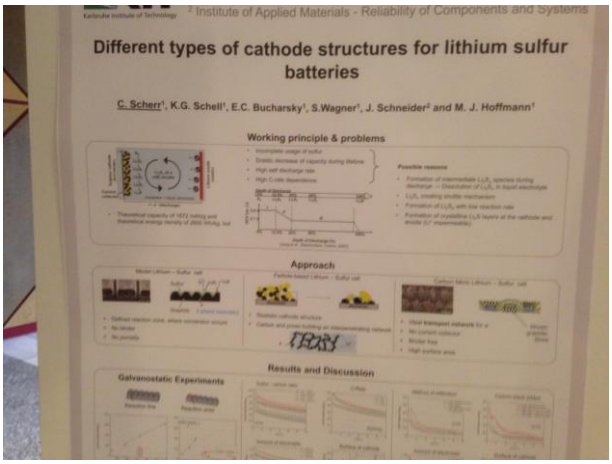

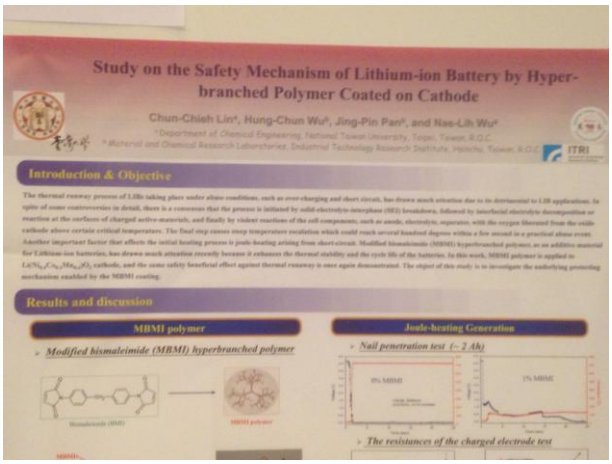

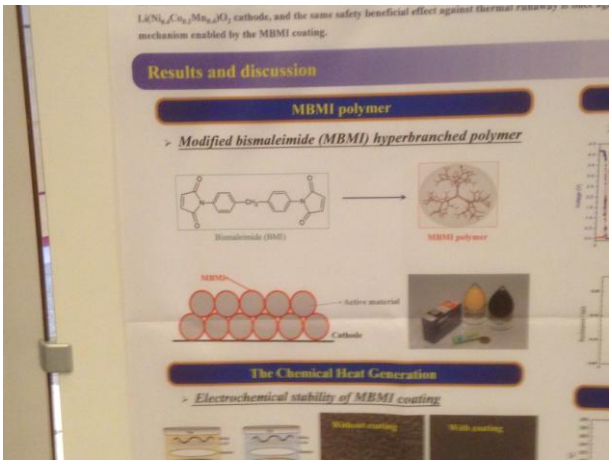

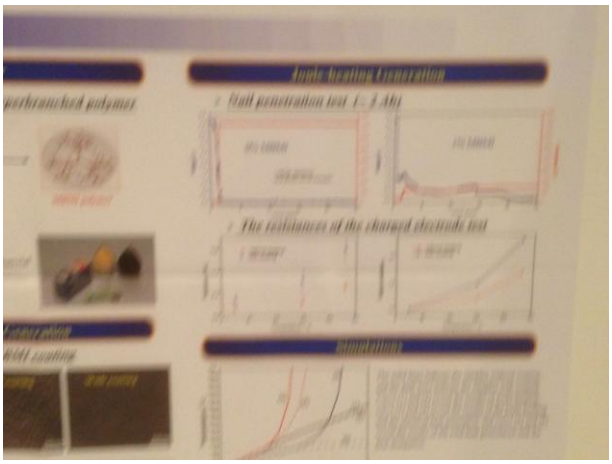

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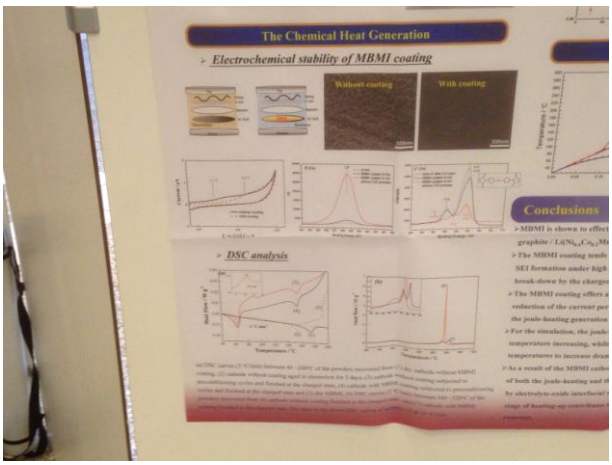

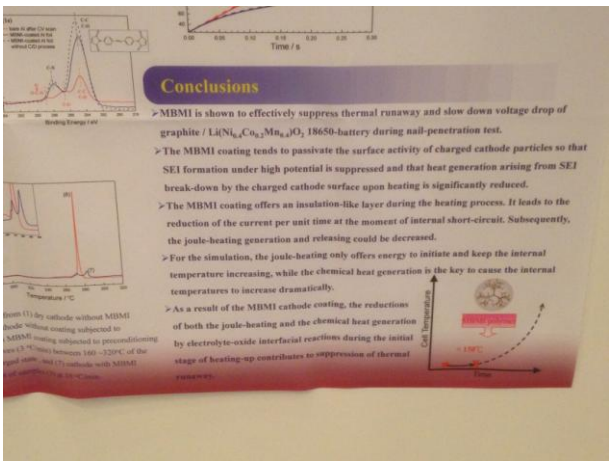

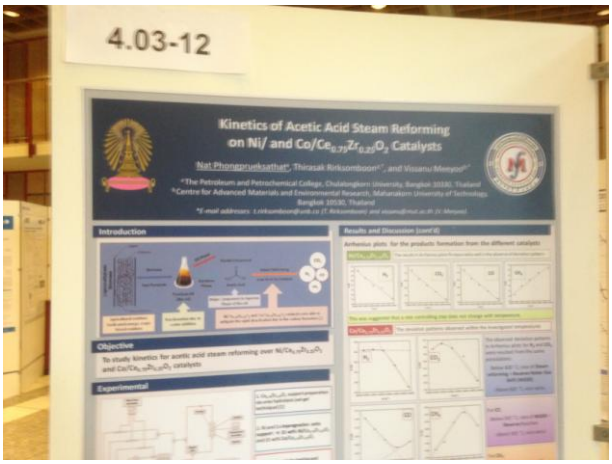

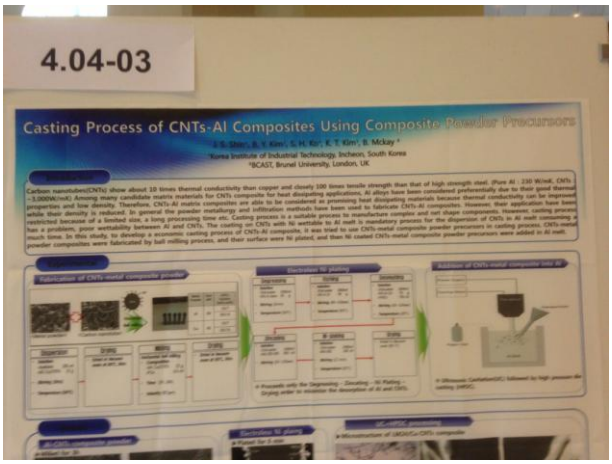

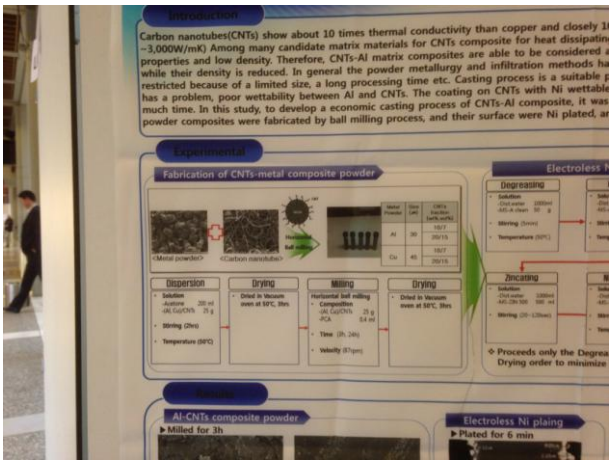

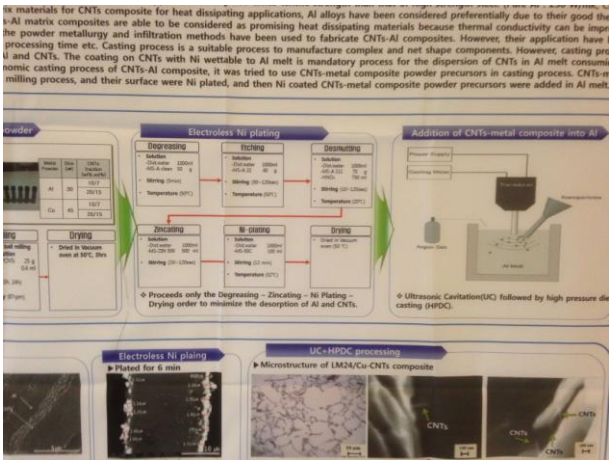

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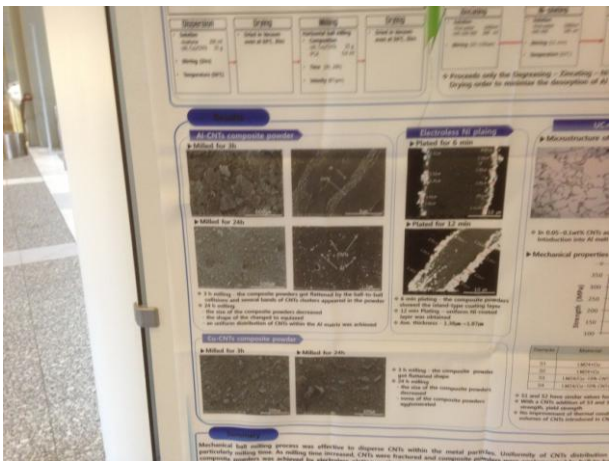

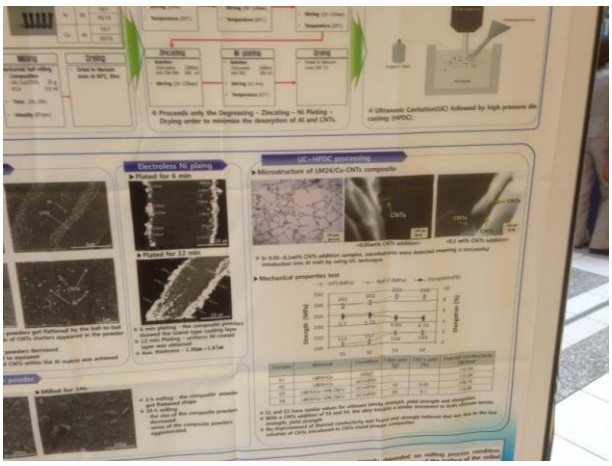

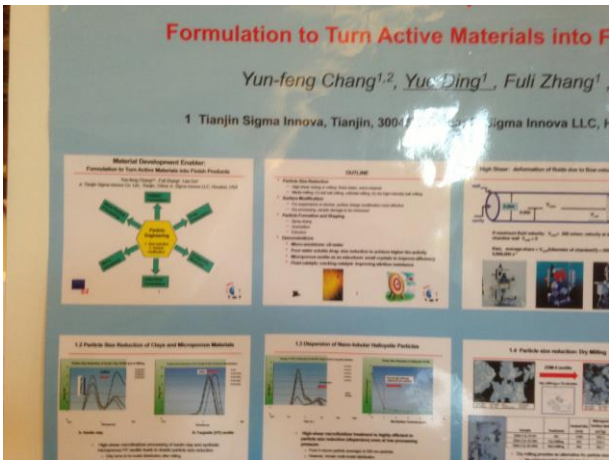

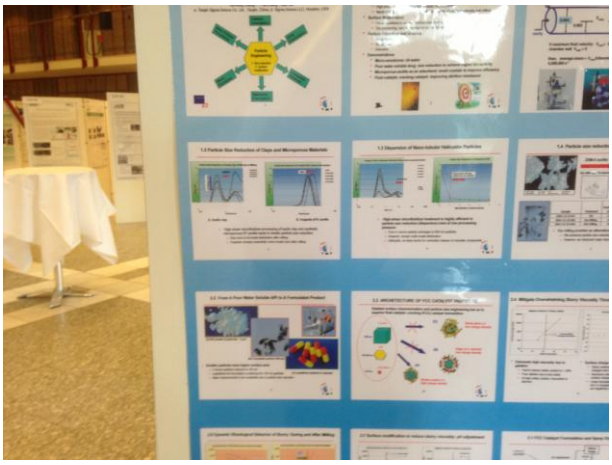

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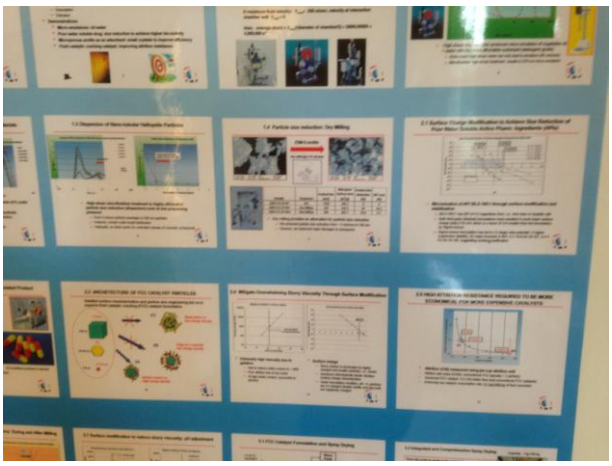

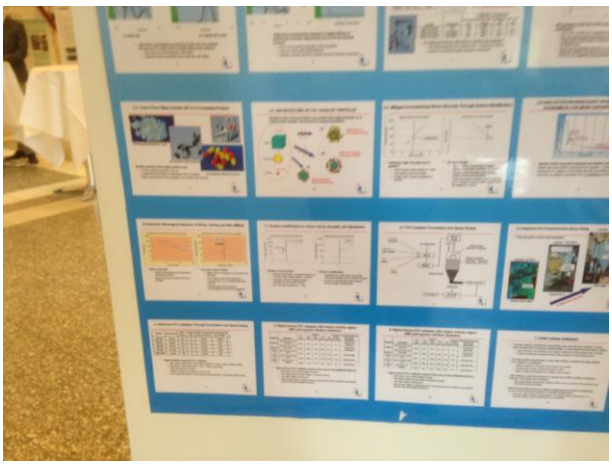

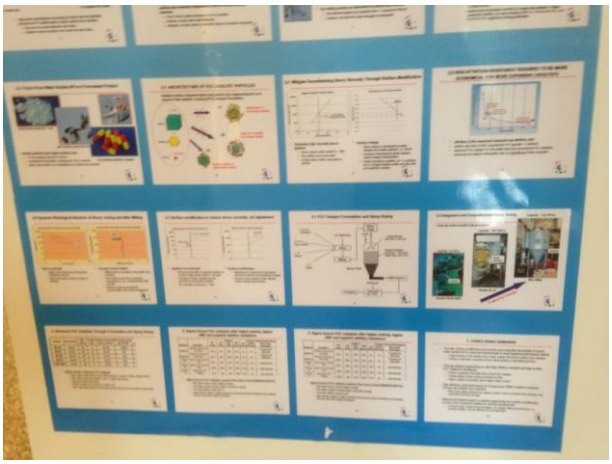

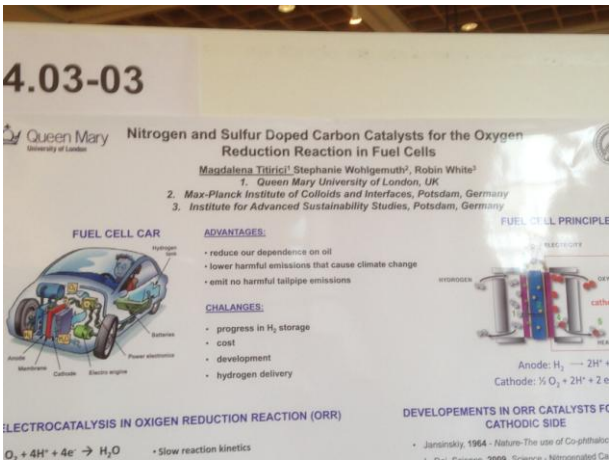

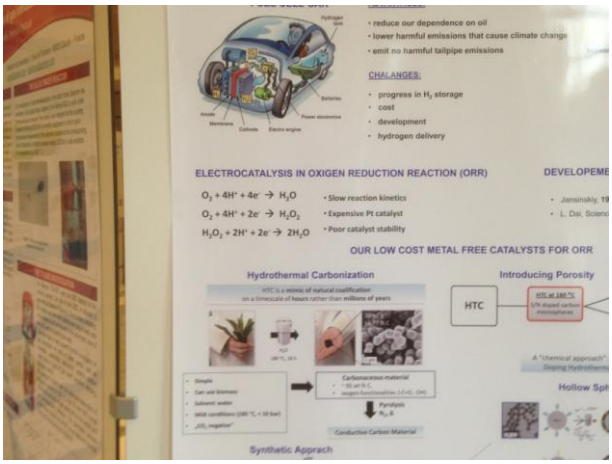

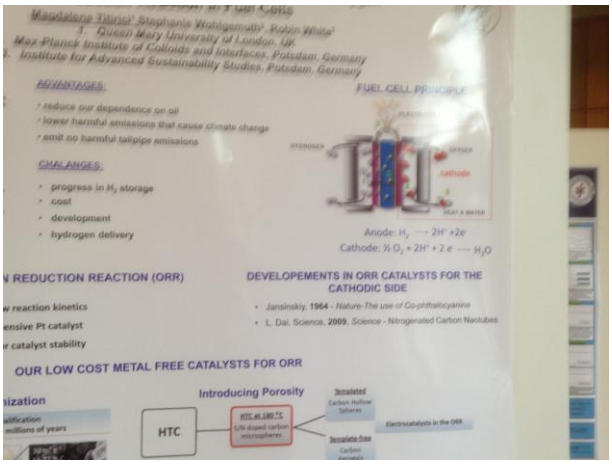

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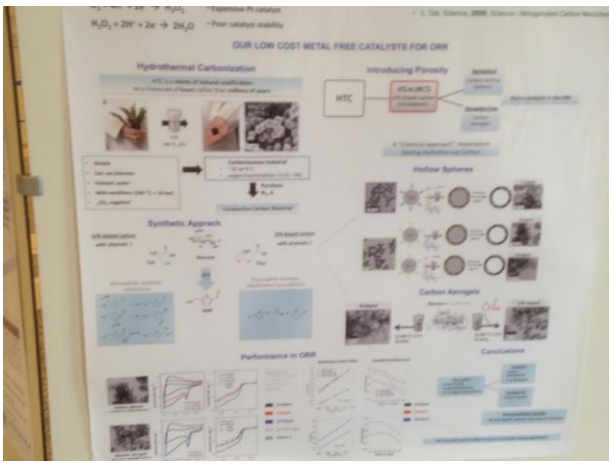
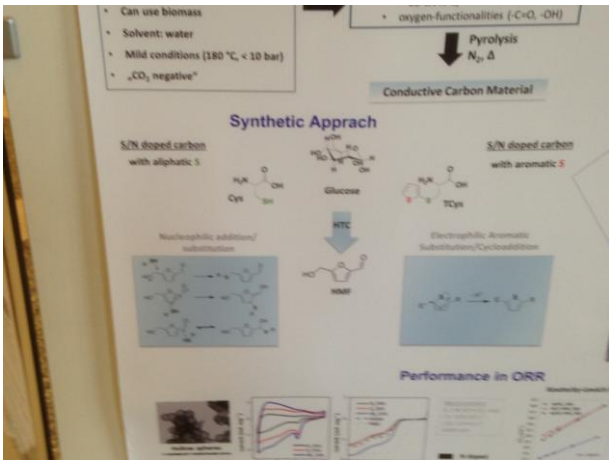
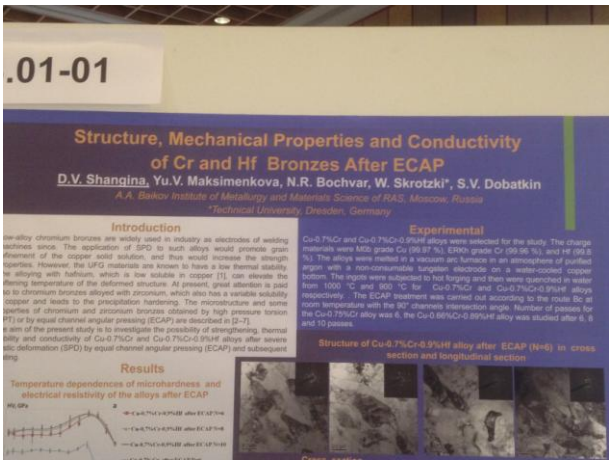
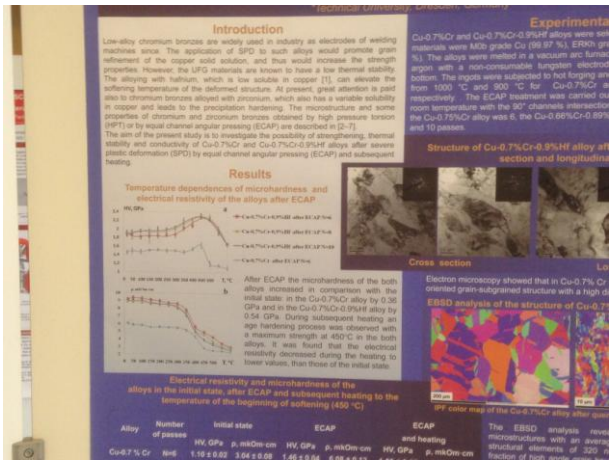
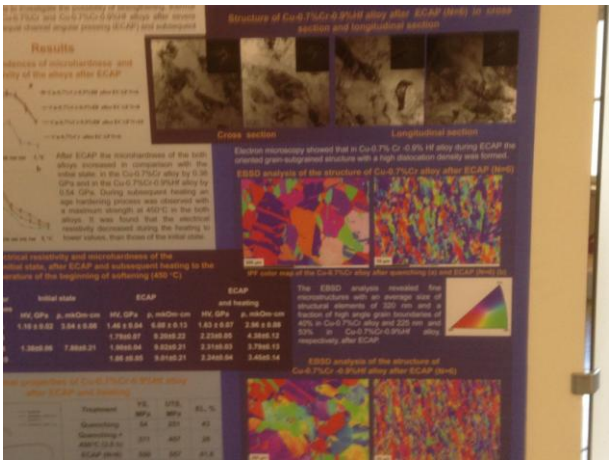


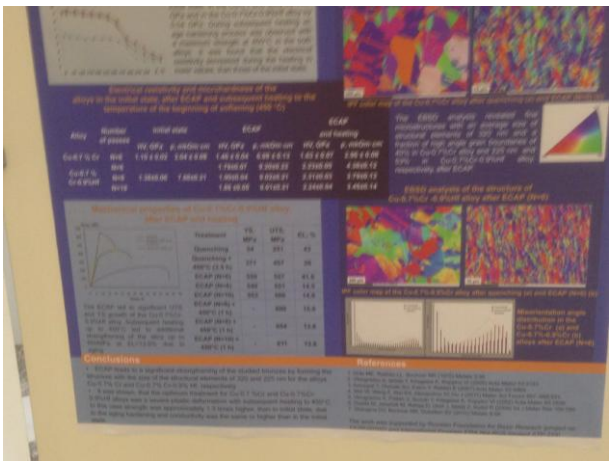


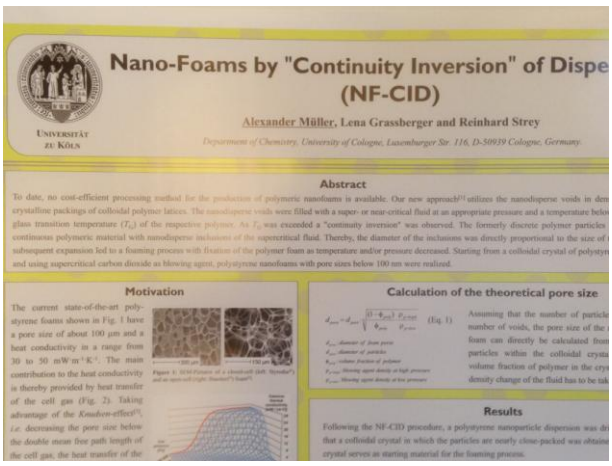


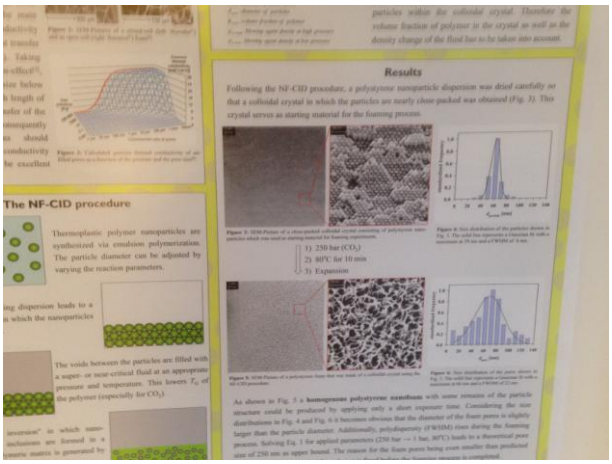


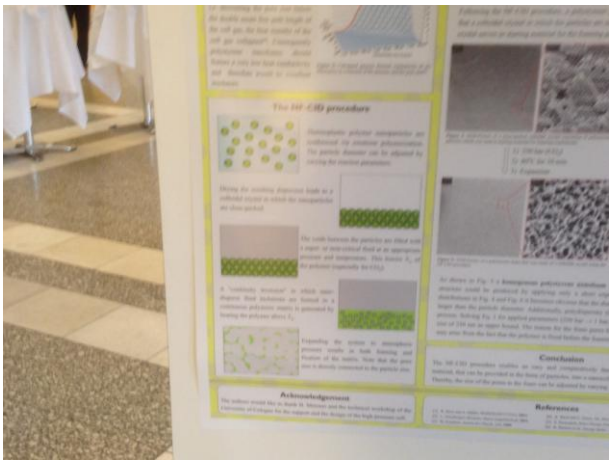


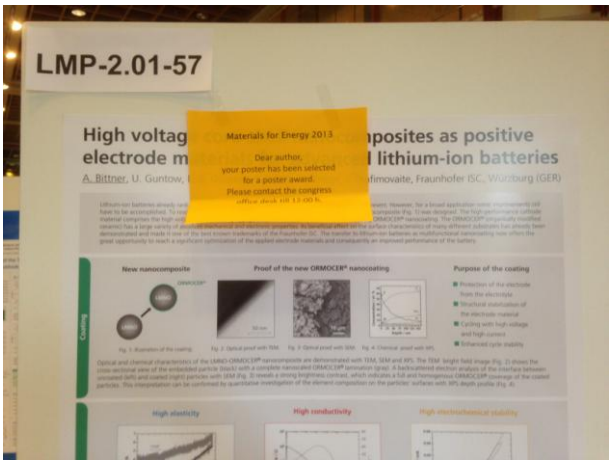
5 月 14 日閱讀研討會論文海報之照片

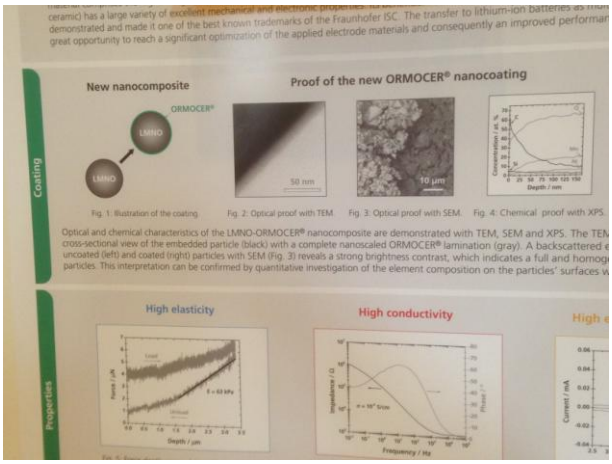




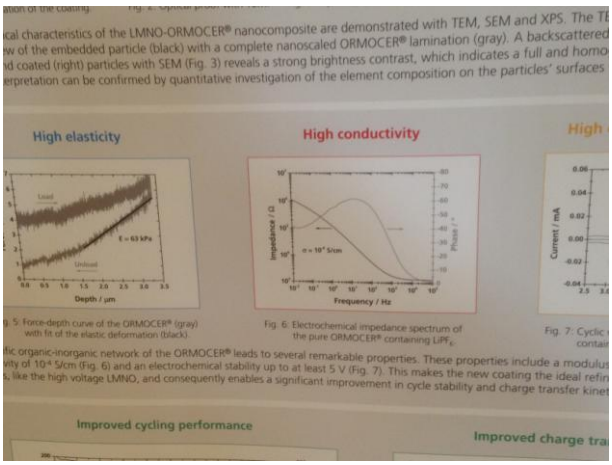


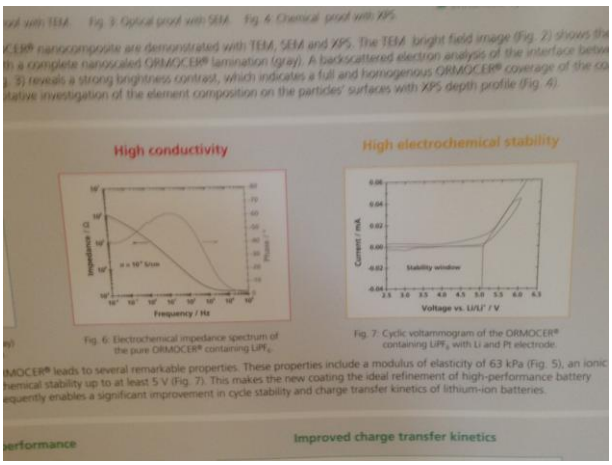


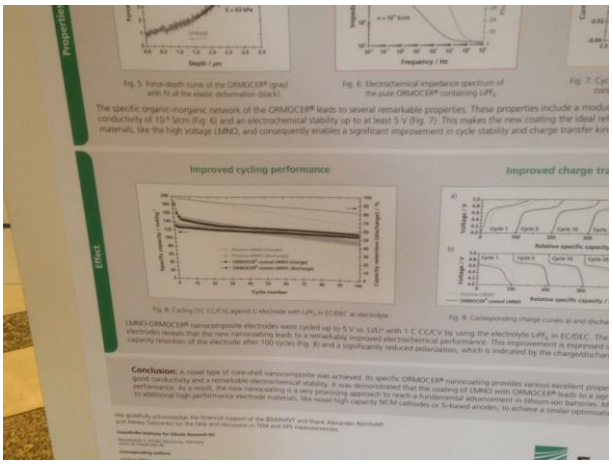


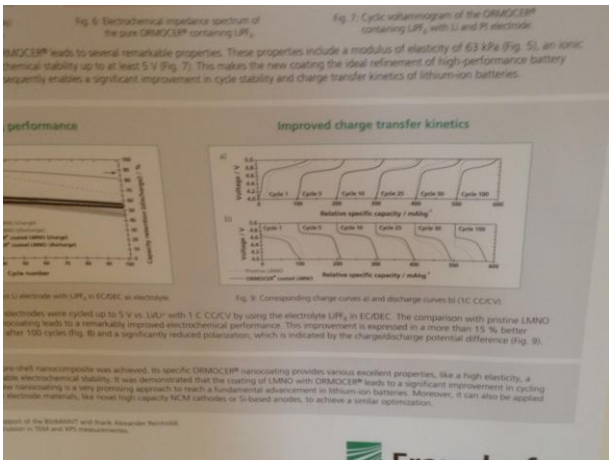


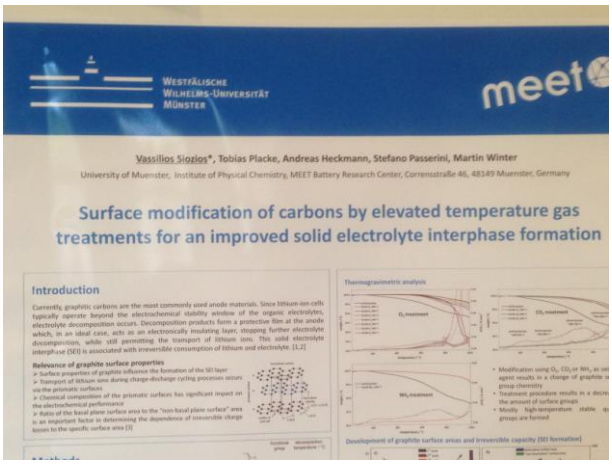
5 月 14 日閱讀研討會論文海報之照片

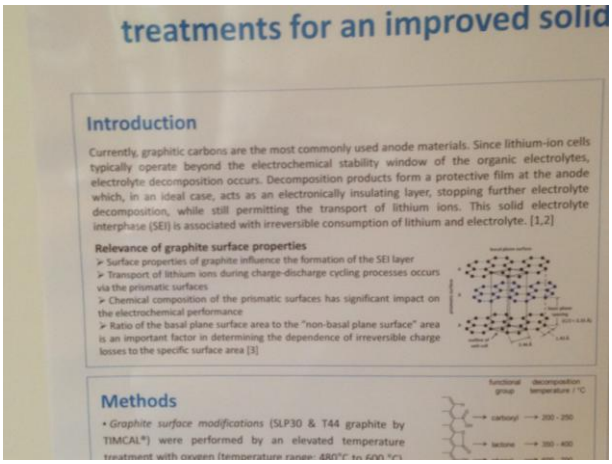












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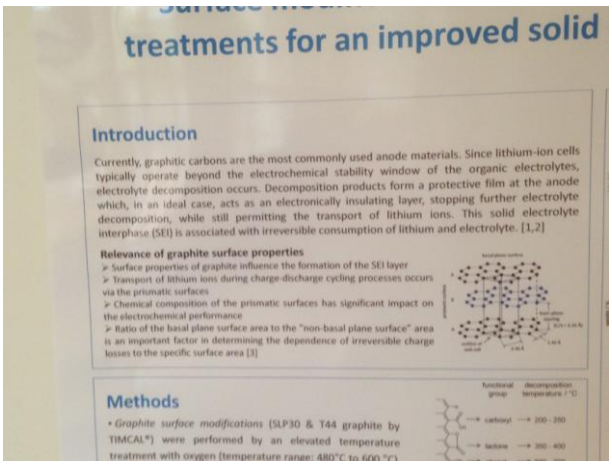
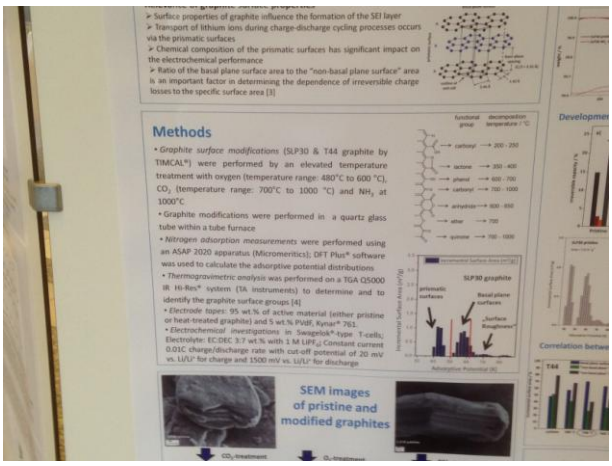
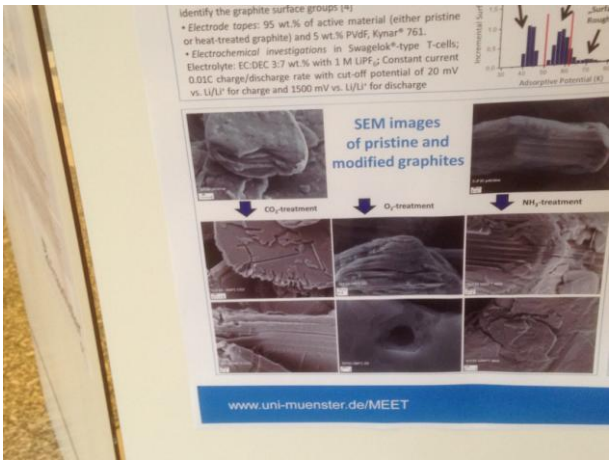
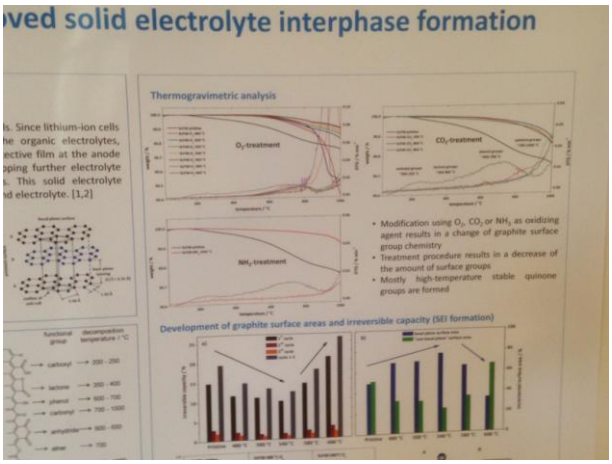
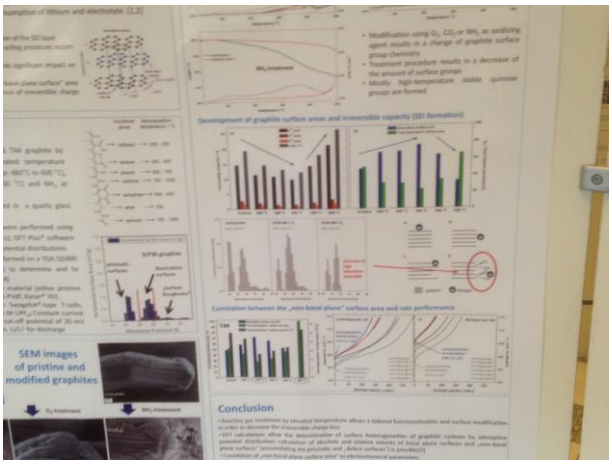
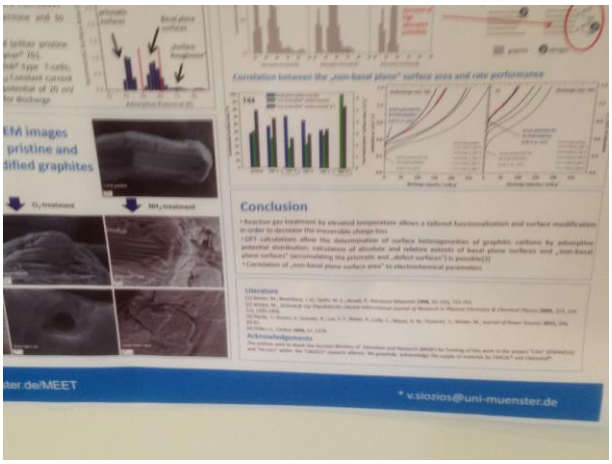




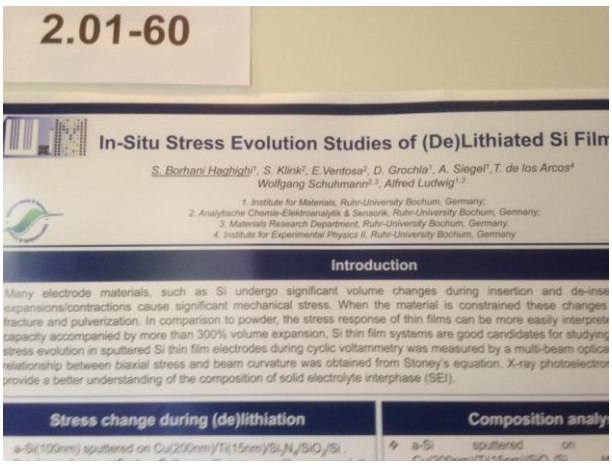


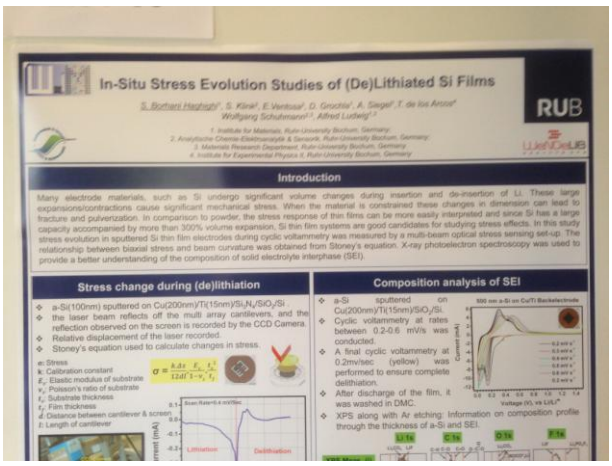


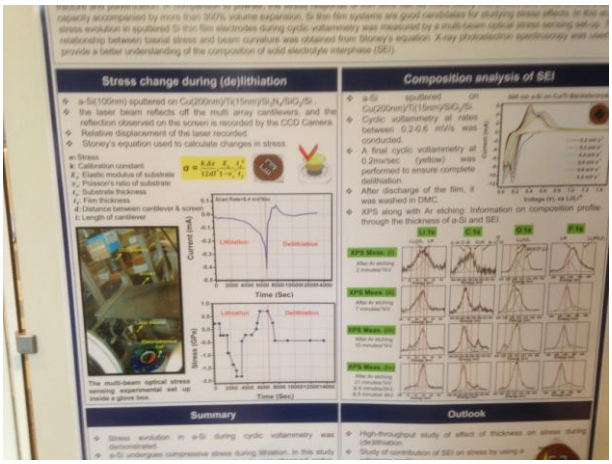


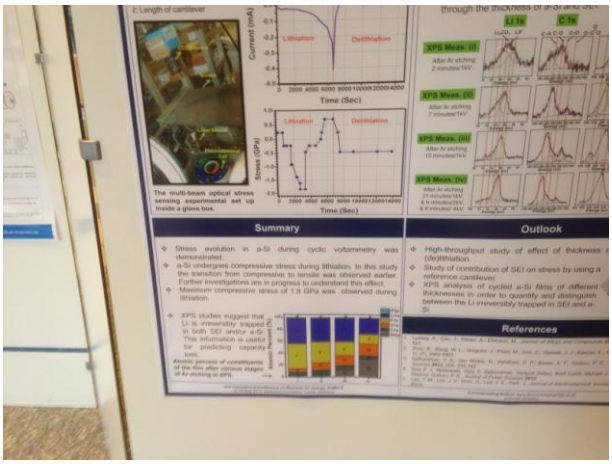


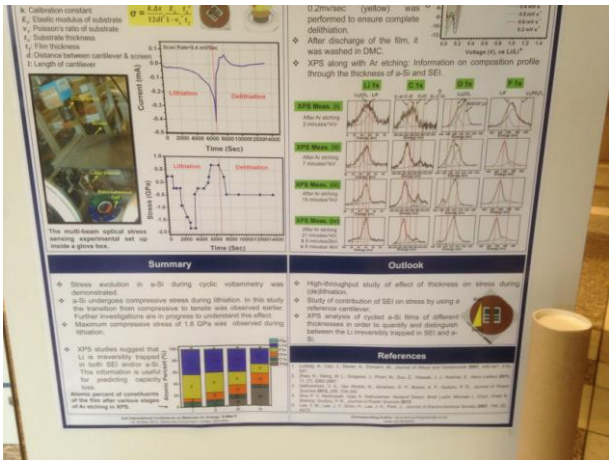
5 月 15 日閱讀研討會論文海報之照片











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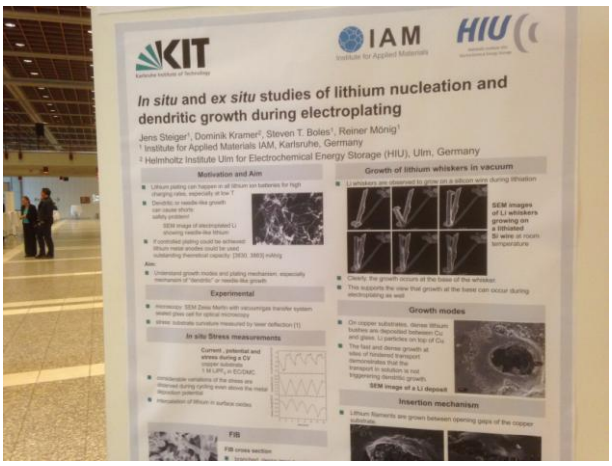

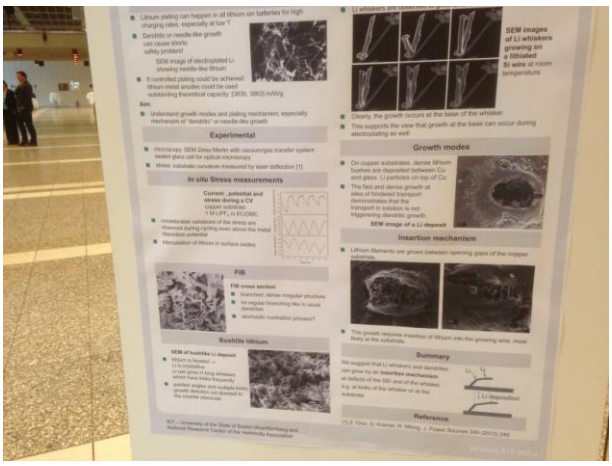

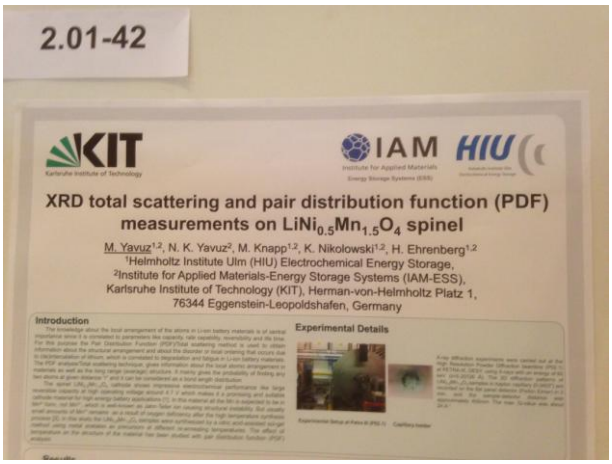

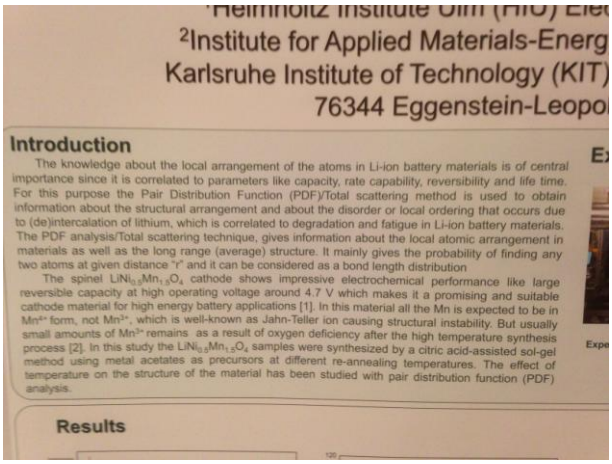

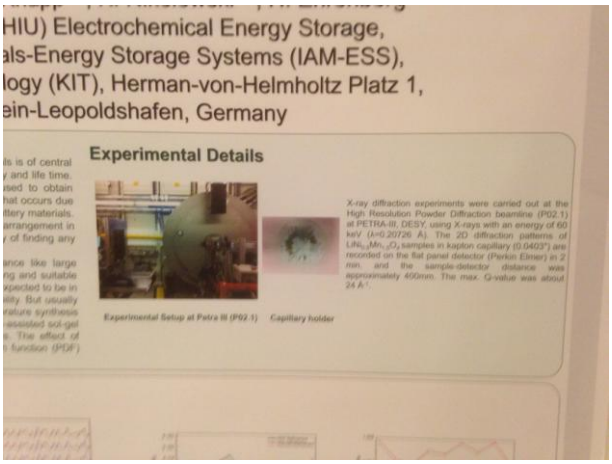

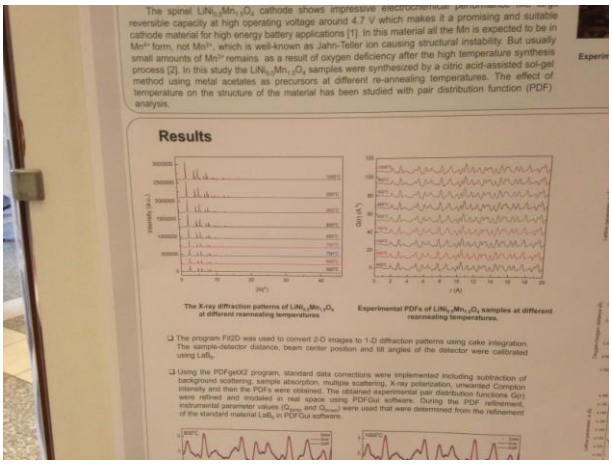

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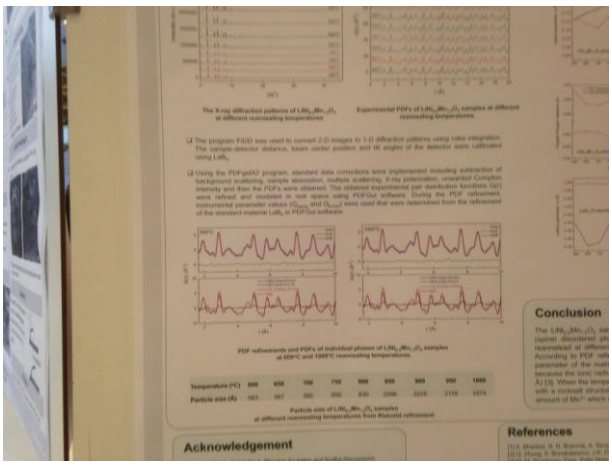

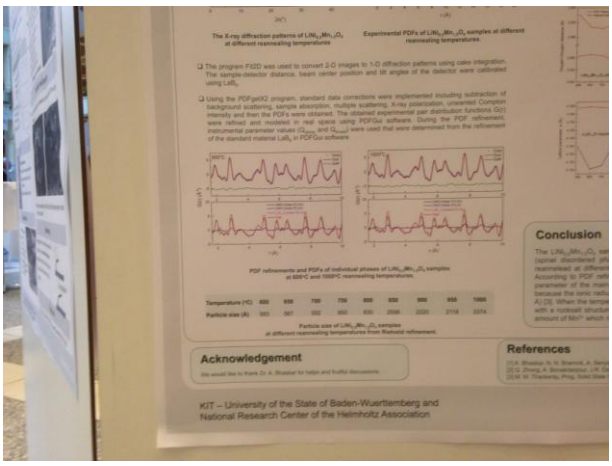

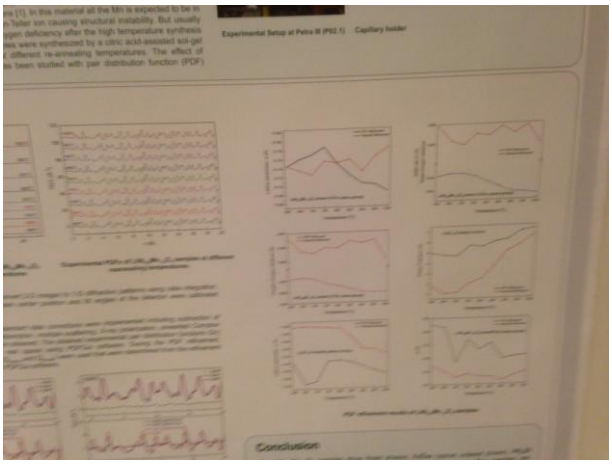

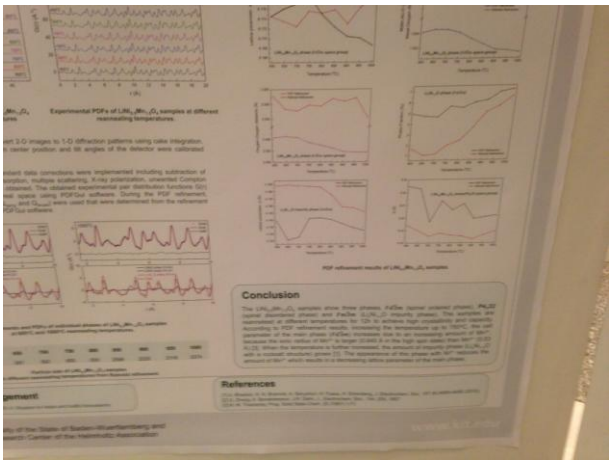

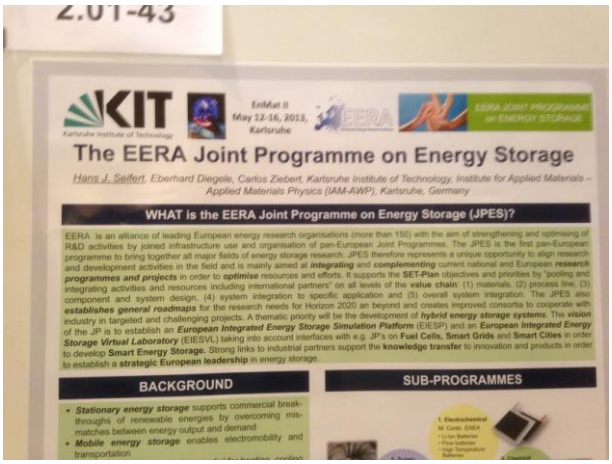

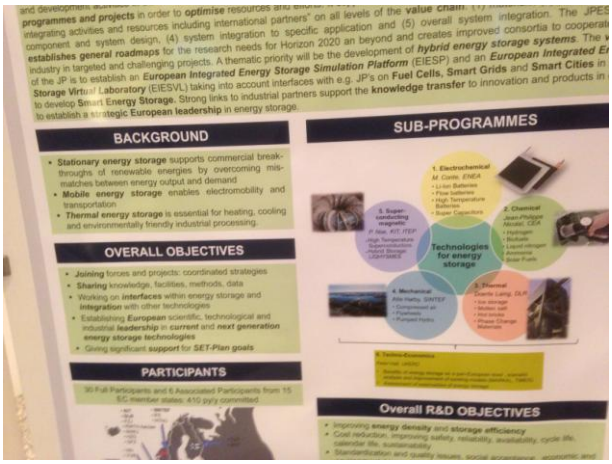

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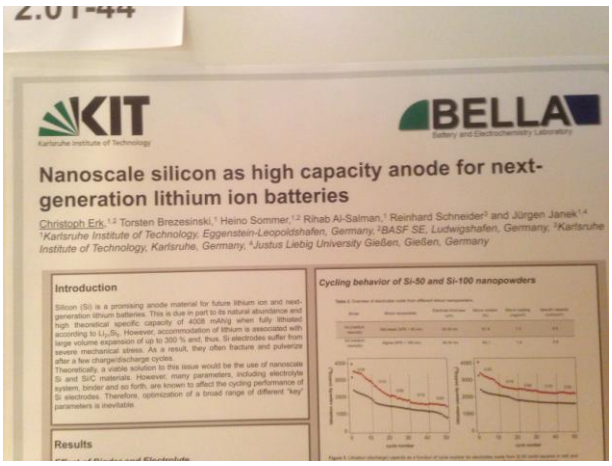
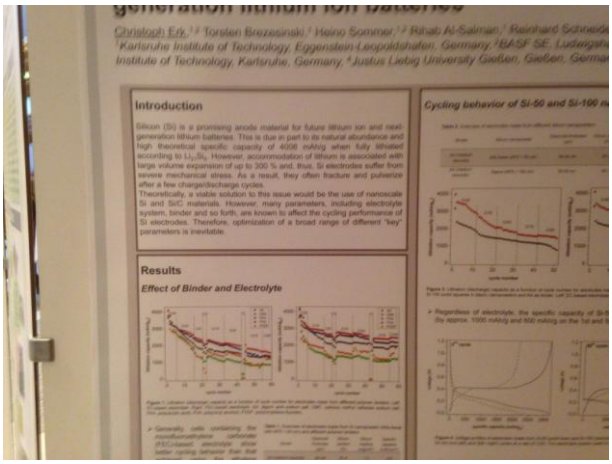
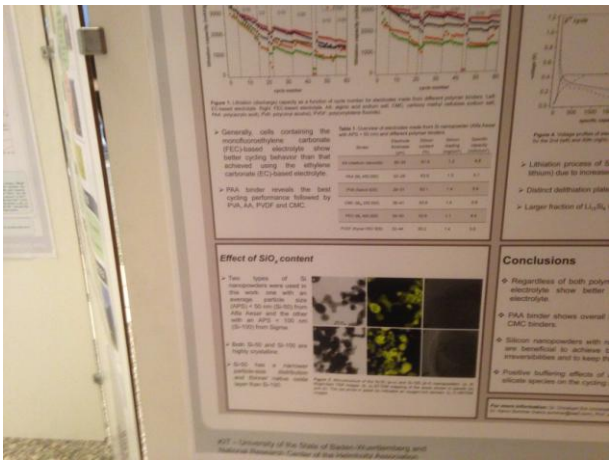
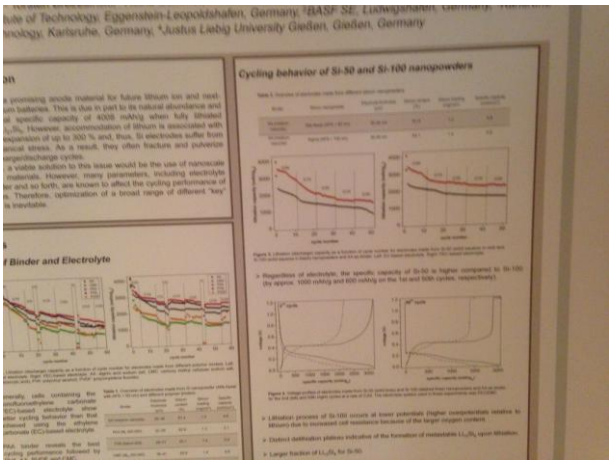
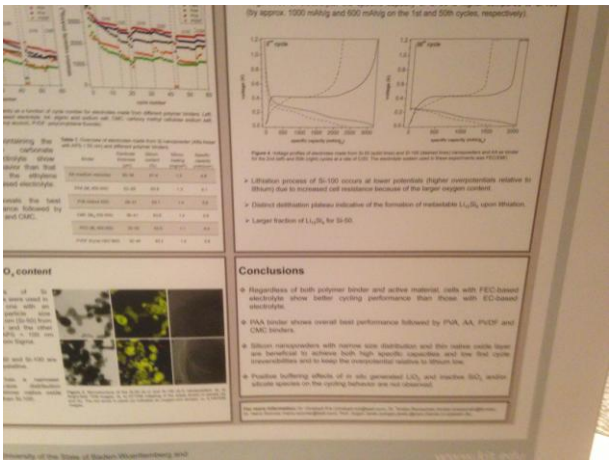


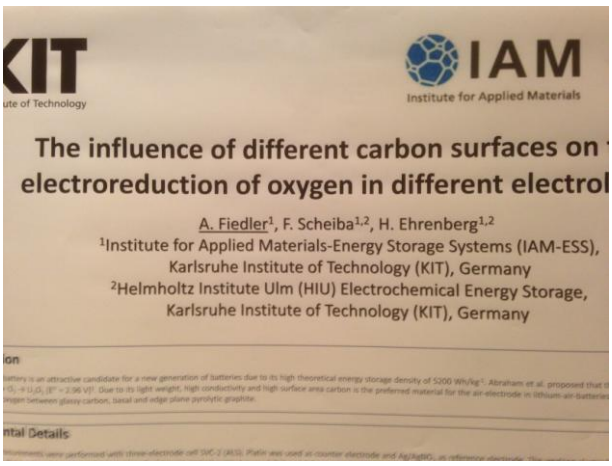


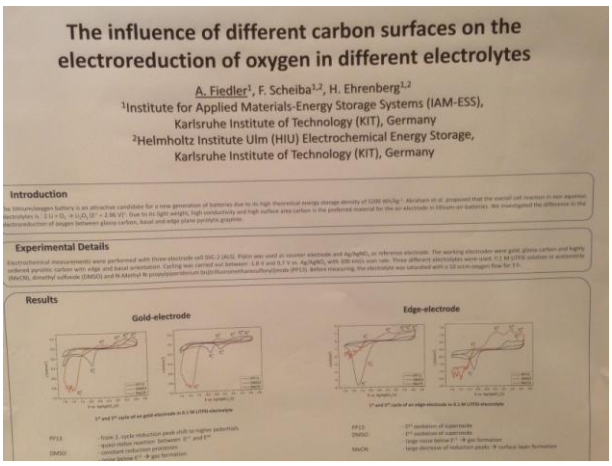


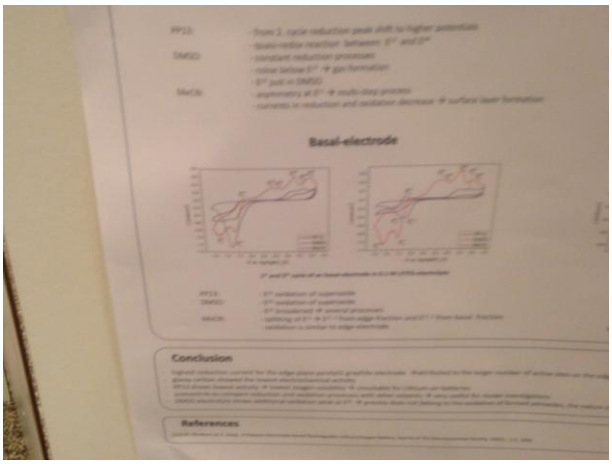


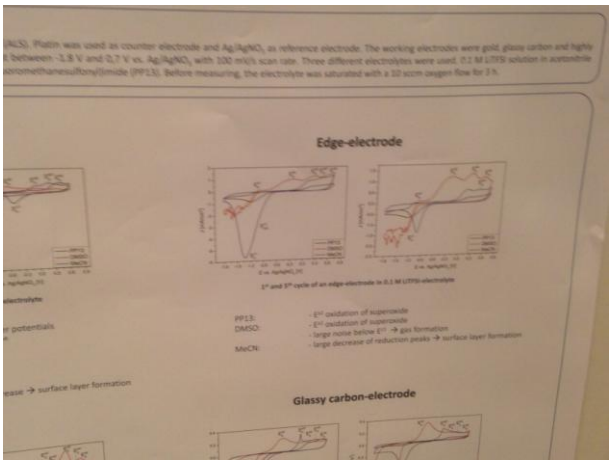


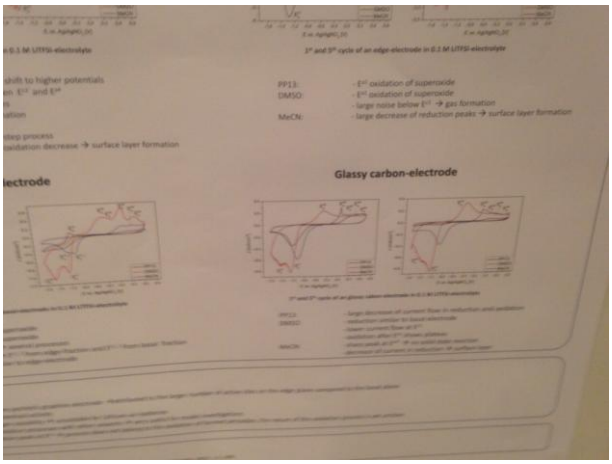
5 月 16 日閱讀研討會論文海報之照片

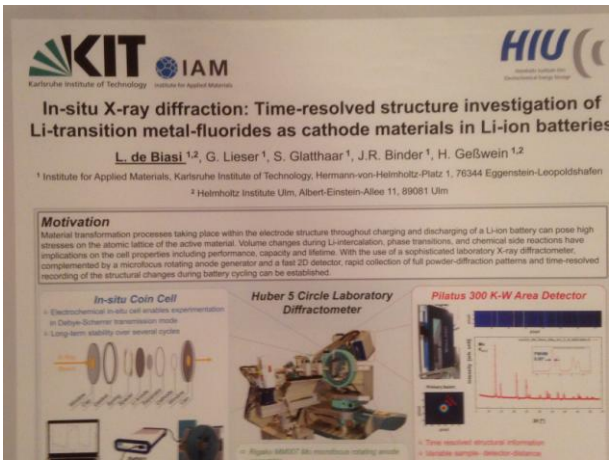












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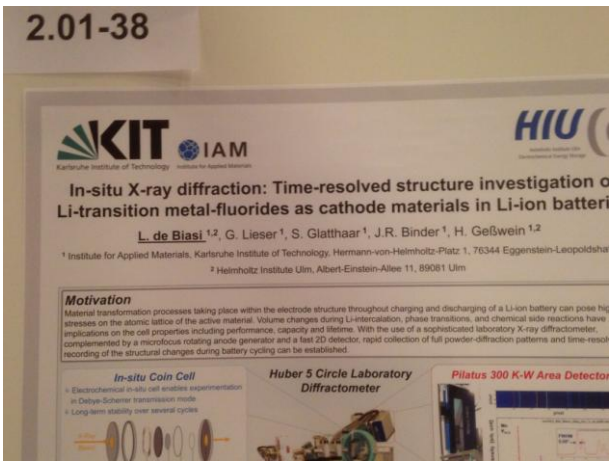

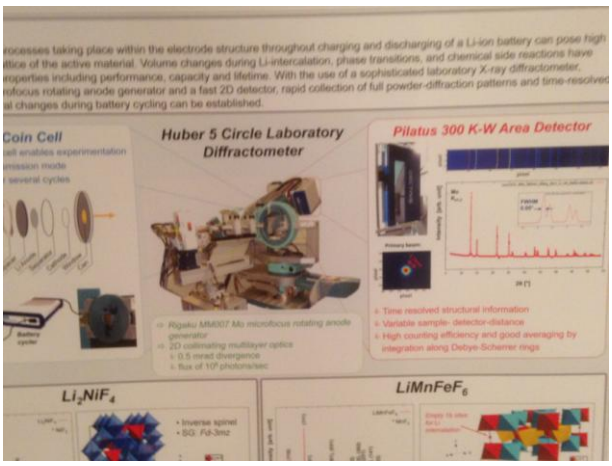

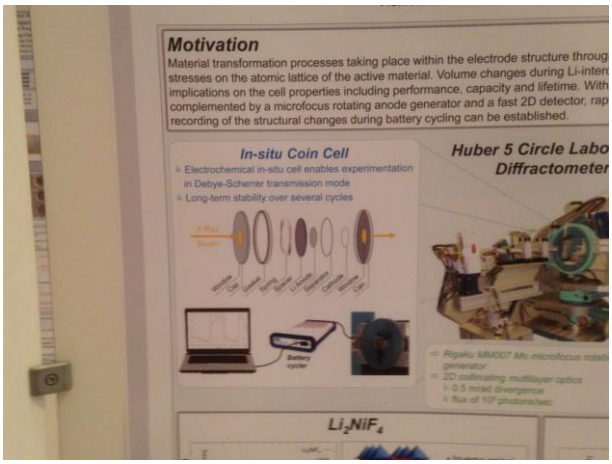

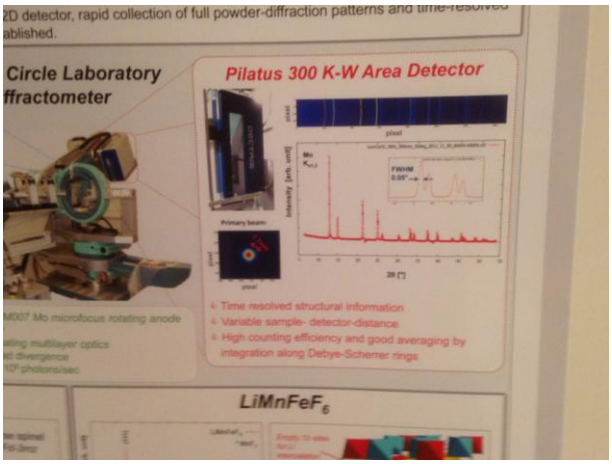

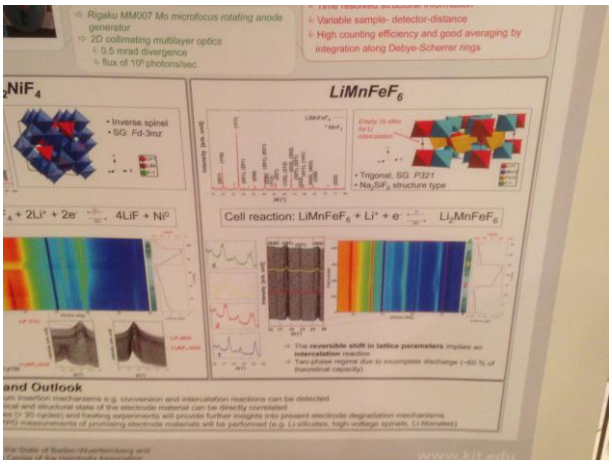

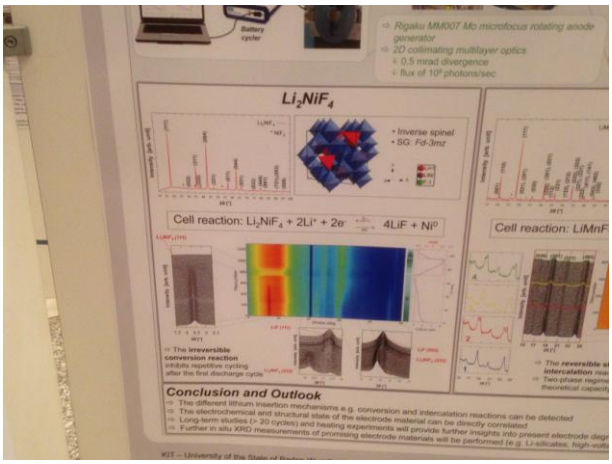

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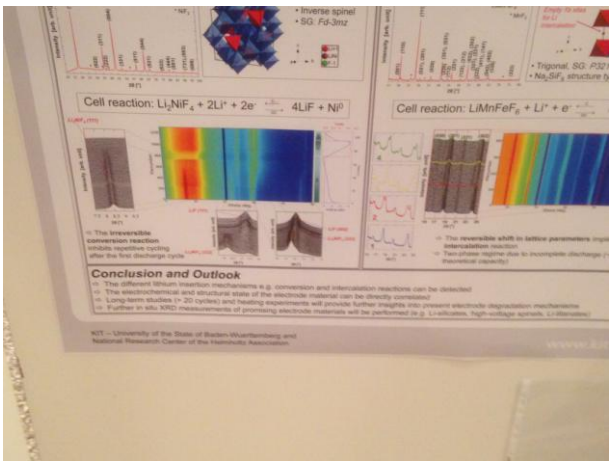

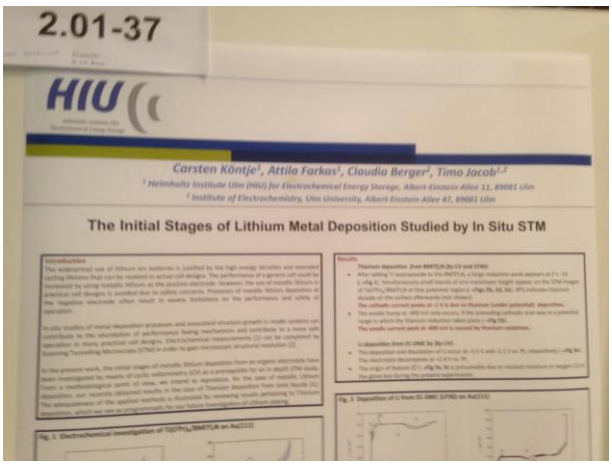

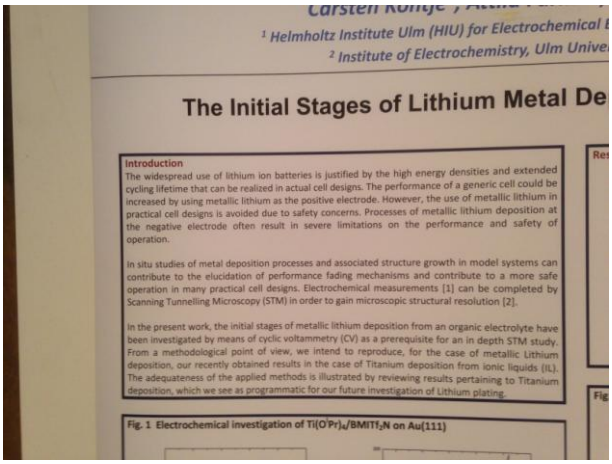

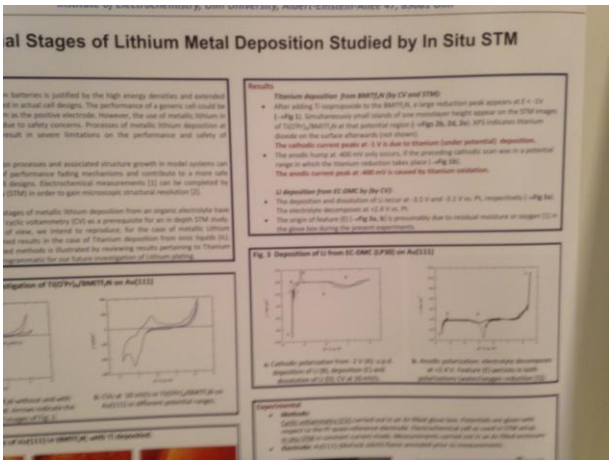

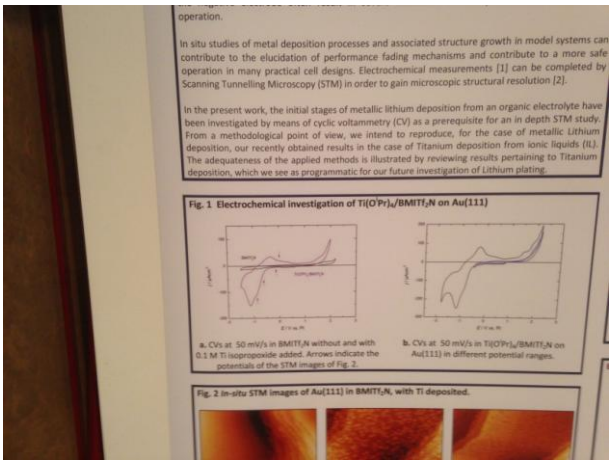

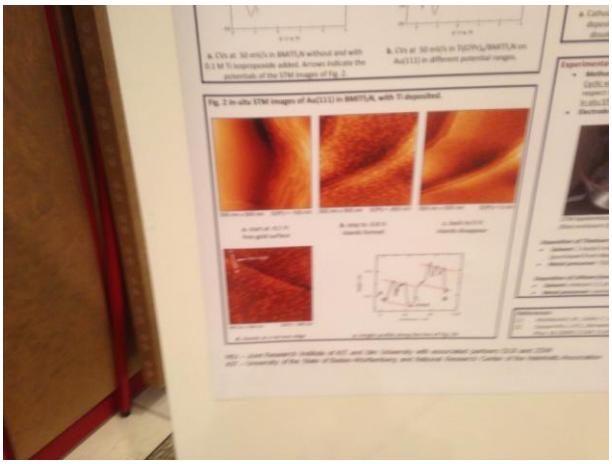

附件三：大會函文邀請本人提供簡報資料

王強尼 <**johnny.ic.wang@gmail.com**>

Materials for Energy 2013 conference - publication of your presentation

2 封郵件

martz@dechema.de <martz@dechema.de> 2013 年 5 月 23 日下午 4:56

收件者： johnny.ic.wang@gmail.com

Dear Prof. Wang

Thank you for your oral presentation at the Materials for Energy 2013 conference, titled:
Controlled oxide layer formation on corrosion behavior of Ti-6Al-4V alloy following thermohydrogen processing.

We would like to publish your presentation on a Web based platform and make it available for download for all participants of the conference. Therefore we kindly ask you to submit your presentation in pdf format electronically. Please submit your electronic file via internet till May 30 at the latest at http://events.dechema.de/en/enmatsubmissionofpresentation by using your submission number 3164.

All submitted presentations will be made available for download to all registered participants of the conference. You will be informed about the login access if available.

Best regards

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