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The Research Grants Council of Hong Kong
NSFC/RGC Joint Research Scheme
<u>Joint Completion Report</u>

(Please attach a copy of the completion report submitted to the NSFC by the Mainland researcher)

Part A: The Project and Investigator(s)

1. Project Title

Mechanical-Electrical-Chemical Coupling Properties of Nanoporous Metals
纳米多孔金属的力-电-化学介质多场耦合效应研究

2. Investigator(s) and Academic Department/Units Involved

	Hong Kong Team	Mainland Team
Name of Principal Investigator *(with title)*	Prof. Tong-Yi Zhang 張統一教授	Prof. Li-Jie Qiao 喬利傑教授
Post	Chair Professor 講座教授	Changjiang Professor 長江教授
Unit / Department / Institution	Dept. of Mechanical Engineering, The Hong Kong University of Science and Technology (HKUST) 香港科技大學機械工程系	Corrosion and Protection Center, University of Science and Technology Beijing (USTB) 北京科技大學材料腐蝕與防護中心
Contact Information	mezhangt@ust.hk	lqiao@ustb.edu.cn
Co-investigator(s) *(with title and institution)*		

3. Project Duration

	Original	Revised	Date of RGC/ Institution Approval *(must be quoted)*
Project Start date	01 Jan 2012		
Project Completion date	31 Dec 2014		
Duration *(in month)*	36		
Deadline for Submission of Completion Report	31 Dec 2015		

Part B: The Completion Report

5.   Project Objectives
5.1   Objectives as per original application

1. We shall conduct experiments to measure the capillarity-driven deformation strain by dilatometry and X-ray diffraction on nanoporous Au electrodes. We shall also experimentally examine the chemistry-driven actuation behavior of nanoporous Au-Pt alloys.
2. We shall fabricate Au nanobridge samples with different dimensions by using the nanoelectronic fabrication technique. We shall conduct the strain-charge-chemical coupling tests on the fabricated nanobridge samples with a special atomic force microscope (AFM) associated with an electrochemical cell.
3. We shall continue to follow our newly developed surface eigenstress and eigendisplacement models to study comprehensively the strain-charge-chemical coupling behavior. First, we

shall study theoretically flat and curved (or faceted) surfaces in an ideal system, a metallic thin film inside electrolyte. Then, we shall study theoretically the strain-charge-chemical coupling behavior of nanoporous metals with a large number of nanopores. To simplify the theoretical analysis, we shall study periodic distributed nanopore arrays.

4. We shall conduct molecular dynamics (MD) simulations including ab initio MD simulations to explore mechanisms of the strain-charge-chemical coupling behaviors of nanoporous materials. We shall simulate the strain-charge-chemical coupling tests on Au nano thin films with different thicknesses. After the simulations of flat solid surfaces, we shall simulate the strain-charge-chemical coupling tests on Au thin films with faceted surfaces. Finally, we shall simulate the strain-charge-chemical coupling tests on Au nanoporous thin films with both flat and faceted surfaces.

5.2   Revised Objectives

Date of approval from the RGC: _____

Reasons for the change: _____

_____

6. Research Outcome

Major findings and research outcome
(maximum 1 page; please make reference to Part C where necessary)

Following our newly developed surface eigenstress and eigendisplacement models and taking advantages from both Gibbs and McLean adsorption isotherms, we develop a Gibbs-approach based adsorption isotherm for grain boundary (GB) segregation in nanograined (ng) polycrystals and surface segregation in nanoparticles (np). The newly developed adsorption isotherm is able to analyze simultaneously stresses, concentrations and their coupling behaviors in grains and GBs, and surface shell and core lattice. Numerical calculations and plots are conducted to illustrate the theoretical analysis. The results show that the apparent solute concentration could be greatly enhanced in ng and np materials, due to large fractions of grain boundary volume in ng and surface volume to core lattice and a considerable increase in the lattice concentration that is, in turn, boosted by the concentration-induced stresses. (J1, J2)

We applied the Gibbs-approach based adsorption isotherm for ng and np materials to the H-Pd solid solutions. Using the published experimental data of lattice strain and sample strain in thermodynamic equilibrium with a H_2 partial pressure, we determined H concentrations and stresses, as a function of the H_2 partial pressure, in both grains and GBs, and surface shell and core lattice. More importantly, we determined the intrinsic properties of GBs and surface shell. (J3, J4)

We conducted joint first-principles and continuum calculations on a system of a system of monolayer MoS_2 or graphene inside water electrolyte. The results show that the MoS_2 monolayer thickness and inplane dimension decreases and increases, respectively, and almost linearly with negative or positive excess charges. The calculated charge volume expansion coefficient of 0.081 $|e|^{-1}$ under negative charging is about 27 times as high as that of 0.003 $|e|^{-1}$ under positive charging. The calculations give the total capacitance of the electrochemical cell, the quantum capacitance of the graphene electrode and the capacitance of the electric double layer. These findings deepen the understanding of quantum capacitance of graphene, which will stimulate novel experimental and theoretical studies and boost the applications of graphene in electrochemical and energy areas. (J5, J6)

The mainland team has conducted experiments to measure the effect of surface adsorption on corrosion, pitting and capillarity-driven deformation strain by X-ray diffraction on nanoporous Au electrodes.

The charge induced strain in nanoporous gold: The raw material was $Au_{28}Ag_{72}$, thin film with a thickness of 20 microns. After annealing 16 h at 850 ℃ in air, the alloy was put in 50 ml of concentrated nitric acid 65% solution at 30 ℃ for 12 h for dealloying, which yielded ideal double continuous porous nanostructured gold was obtained. Then, XRD was conducted in situ to measure the charge induced deformation. The results show that both cathodic and anodic polarization decreased lattice constant of the nanoporous gold, while increasing electrostatic charge by an electrostatic generator would increase the lattice constant.

Surface water adsorption: Atmospheric corrosion is closely related to the atmospheric environment of relative humidity. When metal surface is exposed to humid air, a nanometer thick water layer can be formed on the surface. This changes the surface physical and chemical properties, such as surface potential and surface strain, etc. Using scanning probe microscopy and scanning Kelvin probe force microscopy, we in situ investigate water adsorption on metal surface, including the water layer thickness and the adsorption effect on surface energy. (J7)

Selective adsorption and corrosion: Water molecules preferentially adsorb in the area with higher surface energy, such as grain boundaries. Scanning probe microscopy was used to investigate in situ the initial stage of atmospheric corrosion of interstitial free Steel. The in situ dynamic state observation found that in the air with 95% moisture, water preferentially adsorbed at the grain boundaries of the steel. Water droplets initiated and grew up at grain boundaries, which were the preferential sites of corrosion. The surface electric potential at grain boundaries was significantly lower than in the grain. Pitting was also dependent on the surface potential. (J8, J9)

Potential for further development of the research and the proposed course of action
(maximum half a page)

We may apply the newly developed surface eigenstress and eigendisplacement-based strain-charge-chemical coupled thermodynamics models to investigate the kinetics behaviors of ions in Li-ion batteries. We may experimentally and theoretically study the role of surface/interface stress and deformation of nanostructured anodes and cathodes in Li-ion batteries and in Li-air batteries.

7. The Layman's Summary
(describe <u>in layman's language</u> the nature, significance and value of the research project, in no more than 200 words)

Nanomaterials and nanoporous materials have large surface-to-volume ratios and surfaces play significant roles in surface-related behaviors such as surface-chemistry-driven actuation, absorption, catalysis, corrosion and dealloying, stress-charge interactions, etc. Due to the large surface-to-volume ratios, nanomaterials and nanoporous materials behave different from their bulk counterparts. When the conventional continuum thermodynamic theory is applied in material characterization, the material properties of nanomaterials and nanoporous materials could be size-dependent, which is the distinct characteristic of the material behaviors at the nanometer scale. In comparison with their bulk counterparts, relaxation occurs naturally in nanomaterials and annoporous materials in order to reduce the energy associated with surfaces. The relaxation may result in nonlinear initial deformation of nanomaterials and nanoporous materials under no external loads. In this project, we have developed a nonlinear thermodynamic theory to formulate and predict the surface-mediated strain-charge-chemical behaviors. Experiments, theoretical study and modeling, and atomistic simulations have been conducted in order to develop such a nonlinear thermodynamic theory for scientific understanding of surface-mediated strain-charge-chemical behaviors and for formulation and prediction of such behaviors. The successful completion of the project will facilitate the development of nanomaterials and nanoporous materials, in particular, in these academic and scientific areas of surface-chemistry-driven actuation, absorption, catalysis, corrosion and dealloying, stress-charge interactions, etc. Obviously, the outputs from this project will have a significant impact on both academic research and engineering practice, because the expected nonlinear thermodynamic theory links the conventional continuum thermodynamic theory with atomistic perspectives, and thus will have more theoretical power than that offered by either one alone. Moreover, the

outputs might become guidelines for the wide applications of nanomaterials and nanoporous materials in high-tech industries.

Part C: Research Output

8.   Peer-reviewed journal publication(s) arising **directly** from this research project
(Please attach a copy of each publication and/or the letter of acceptance if not yet submitted in the previous progress report(s). All listed publications must acknowledge RGC's funding support by quoting the specific grant reference.)

The Latest Status of Publications				Author(s) *(**bold** the authors belonging to the project teams and denote the corresponding author with an asterisk*)*	Title and Journal/ Book *(with the volume, pages and other necessary publishing details specified)*	Submitted to RGC *(indicate the year ending of the relevant progress report)*	Attached to this report *(Yes or No)*	Acknowledged the support of this Joint Research Scheme *(Yes or No)*	Accessible from the institutional repository *(Yes or No)*
Year of publication	Year of Acceptance *(For paper accepted but not yet published)*	Under Review	Under Preparation *(optional)*						
2013				**Tong-Yi Zhang* and Hang Ren**	Solute concentrations and strains in nanograined materials, Acta Materialia, 61 (2013) 477-493.	2013	No	Yes	Yes
2013				**Tong-Yi Zhang* and Hang Ren**	Solute concentrations and strains in nanoparticles, Journal of Thermal Stresses, 36 (2013) 626–645.	2013	No	Yes	Yes
2013				**Hang Ren, Xusheng Yang, Yao Gao, Tong-Yi Zhang***	Solute concentrations and stresses in nanograined H-Pd solid solution, Acta Materialia, 61(2013) 5487-5495	2014	Yes	Yes	Yes

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2014				**Hang Ren** and **Tong-Yi Zhang***	H concentrations and stresses in Pd nanoparticles, Materials Letters, 130 (2014) 176–179	2014	Yes	Yes	Yes
2014				**Sheng Sun, Heng Zuo, Tong-Yi Zhang***	Joint first-principle/continuum calculations of electromechanical properties of MoS2 monolayer, Applied Physics Letters, **105**, 061910 (2014)	2014	Yes	Yes	Yes
2015				**Sheng Sun**, Yue Qi, and **Tong-Yi Zhang***	Dissecting graphene capacitance in electrochemical cell, Electrochimica Acta, 163 (2015) 296–302	2014	Yes	Yes	Yes

2012				L.Q. Guo, X.M. Zhao, B.C. Wang, L.J. Qiao*	Water adsorption behavior on metal surfaces and its influence on surface, Applied Surface Science, 258 (2012) 9087-9091	2013	No	Yes	No
2013				L.Q. Guo, X.M. Zhao, B.C. Wang, L.J. Qiao*	The initial stages of atmospheric corrosion on IF steel investigated by in situ SPM, Corrosion Science, 70 (2013), 188–193	2013	No	Yes	No
2013				L.Q. Guo , Y. Bai, J.X. Li, L.J. Qiao*	Effect of hydrogen on pitting susceptibility of 2507 duplex stainless steel, Corrosion Science, 70 (2013) 140–144	2013	No	Yes	No

9. **Recognized international conference(s) in which paper(s) related to this research project was/were delivered** *(Please attach a copy of each delivered paper. All listed papers must acknowledge RGC's funding support by quoting the specific grant reference.)*

Month/Year/ Place	Title	Conference Name	Submitted to RGC *(indicate the year ending of the relevant progress report)*	Attached to this report *(Yes or No)*	Acknowledged the support of this Joint Research Scheme *(Yes or No)*	Accessible from the institutional repository *(Yes or No)*
May 31 - June 4, 2013	Grain Boundary Segregation and Stress-Induced Solubility in Nanograined Materials	The 10th International Congress on Thermal Stresses, Nanjing, China.	2013	No	No	No

10. Student(s) trained *(Please attach a copy of the title page of the thesis.)*

Name	Degree registered for	Date of registration	Date of thesis submission/ graduation
Yao Gao	PhD	February 2012	Feb 2016
Hang Ren*	PhD	February 2009	January 2014
Xusheng Yang*	PhD	September 2009	August 2014

*Hang Ren and Xusheng Yang are also supported by RGC General Research Project 622911.

11. Other impact *(e.g. award of patents or prizes, collaboration with other research institutions, technology transfer, etc.)*

We collaborated with Prof. QI, Yue at Michigan State University, USA, on this project. Prof. QI is an expert in first-principle calculations, especially in first-principle calculations of materials and electrochemical reactions in lithium batteries.