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European Master Course
M.E.S.C. Materials for Energy Storage and Conversion

Program of the Module “Fuel Cells” (2013) – Amiens, France
by Prof. Alejandro A. Franco (LRCS, UPJV/CNRS)
www.modeling-electrochemistry.com

Number of hours: 24 (over 12 sessions of 2h each).
Starting date: October 1st, 2013.

General overview

This course focuses on the recent research progresses and technological development on modern low, intermediate and high-temperature fuel cells. On a multidisciplinary basis, enriched with some epistemological concepts aiming to stimulate the students’ creativity, this course provides a complete and comprehensive critical review on crucial scientific topics related to fuel cell materials, electro-catalysis, transport phenomena and degradation. It provides the students with a deep learning on both theoretical and experimental tools to study, to analyze and to predict the performance and durability of fuel cells. The program includes detailed descriptions of the operation mechanisms and fundamentals as well as of available experimental techniques to characterize electrochemical, transport and aging mechanisms, in *ex situ*, *in situ* and *in operando* conditions. Furthermore, the program provides the students with novel and practical methodologies for the multiscale modeling and numerical simulation of fuel cells, jointly with demonstrations and exercises carried out with the LRCS in-house scientific software MS LIBER-T[1] all along the courses, in an environment of strong interactivity (students do not need prior knowledge on programming and software development).
All along the sessions, the courses underline strong relations with applications, and major scientific and remaining technical challenges for both the research and the industry communities are discussed.
At the end of this module (Session 12), the students will be asked to propose, in the format of short oral presentations, the schematics of improved designs or operation conditions of fuel cells vs. given technical constraints in a “challenge exercise” which will be presented in Session 1 (“Students’ Fuel Cells challenge 2013”). The best students’ presentations will be published online.

Note 1: Prof. Franco’s presentation materials will be provided to the students prior or after each session, through the ENT UPJV website and, in some cases, through Prof. Franco’s homepage.
Note 2: the scientific computational software will be provided to the students during the corresponding session.

[1] From the English spelling *Multiscale Simulator of Lithium Ion Batteries and Electrochemical Reactor Technologies* : www.modeling-electrochemistry.com

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Detailed program

Session 1/12 (2h)

General introduction

- Presentation of the courses rules, instructions.
- Presentation of the bibliography references and internet supports.

Introduction

- The “Energy” concept across the scientific disciplines: some epistemology.
- Energy in the (Multi/Uni)verse and thermodynamics principles …
- World-wide problems (e.g. global warming), need of sustainable energetic networks, challenges and opportunities for electric power generation through electrochemistry.
- Conversion electrochemistry: general concepts.
- History of electrochemical power generators (“closed” vs. “open” batteries -fuel cells-), mysteries and controversies...
- Modern types of fuel cells (e.g. PEMFC, DAFC, SOFC, MCFC, PAFC, AFC), general operation principles and application domains: reality and dreams.
- Scaling fuel cells: nano, micro, mini and macro-fuel cells, fractal fuel cells.
- “Fuel cells” in Nature.
- Fuel cells efficiency analysis based on thermodynamics principles, how to distinguish a fuel cell from a “perpetual machine”?
- Fuel cells and future energetic sustainability: role to play, technical challenges and unknowns, markets and economics.
- **Presentation of the “Students’ Fuel Cells challenge 2013”.**
- ***Interactive quiz:*** the students will be asked to respond some few detailed technical questions. This quiz is devoted to check the students’ level of knowledge on some general physicochemical concepts and mathematical tools, for an optimized presentation of the courses contents in the following sessions.

Session 2/12 (2h)

Fabrication methods: a fuel cell part by part

- Catalysts and supports fabrication methods, single crystals vs. poly-crystals, precious metal-free catalysts.
- Some physics of the polymers in solution.
- Electrodes and assemblies fabrication methods, interfaces between components, morphogenesis and self-organization (impact of the fabrication conditions -solvent, temperature, etc.- onto the electrode morphology).
- Arising multiscale structures, disorder vs. complexity, do we see the real structures?
- Arising multiphysics: competing processes at multiple spatiotemporal scales.

Electrocatalysis

- Fundamentals of electrocatalysis in liquid and gas phases.

- Fuel cell elementary reactions and overall activity problems, the case of the Oxygen Reduction Reaction, in-situ reforming reactions.
- Close environment to the catalyst: electrochemical double layers, history, theories and experimental characterization of their effects onto the overall catalyst activity.
- Influence of the chemistry and morphology of the catalysts onto their activity, selectivity and stability, symbiotic effects between the catalyst and the electrochemical double layer.
- Experimental characterization techniques: *ex situ* vs. *in situ* vs. *in operando*.
- Electrochemical characterization: cyclic voltammetry, i-V curves, electrochemical impedance spectra, galvanostatic vs. potentiostatic experiments.
- Structural characterization techniques: SEM, TEM, HR-TEM, XPS, AFM…, challenges and opportunities.

Session 3/12 (2h)

Electrocatalysis (cont.)

- Theory and modeling tools for the numerical simulation of electro-catalytic reactions: state of the art.
- The Schrodinger's cat's paradigm: *ab initio* and Density Functional Theory techniques, state of the art, calculation of the catalysts stability, adsorption properties of reaction intermediates, activation energies (Nudged Elastic Band approach), pros and cons.
- The "hazard game" paradigm: Monte Carlo modeling techniques to predict multimetallic catalysts morphologies, Metropolis algorithm, choice of inter-atomic potentials, annealing techniques. Complementarity with microscope observations.
- ***Demonstration and guided exercise with the students:*** Monte Carlo simulation for the prediction of catalysts structures *(specific scientific computational code will be provided to the students)*.

Session 4/12 (2h)

Electrocatalysis (cont.)

- Elementary kinetic reactions in fuel cells: modeling and numerical simulation.
- Mean Field vs. Kinetic Monte Carlo approaches, *ab initio*-based elementary kinetic models (parameterization of kinetic models with activation energies extracted from *ab initio* calculations).
- Comparison of simulation outcomes with experimental data.
- ***Demonstration and guided exercise with the students:*** modeling and simulation through a Mean Field approach of an elementary kinetic pathway representative of a fuel cell operation *(specific scientific computational code will be provided to the students)*.

Supports and electronic transport

- Reconstruction techniques of porous electrodes: tomography vs. Monte Carlo vs. Coarse Grain Molecular Dynamics techniques.
- The role of the supports on the catalysts activity: ad-species spillover vs. electronic effects.
- Electronic transport in highly conductive media and semi-conductors.
- Experimental characterization of electronic conductivity of catalyst supports and other electronic conductive media (e.g. Gas Diffusion Layers).
- Modeling electronic transport: mesoscopic vs. continuum approaches.

<u>Session 5/12</u> (2h)

Ionics

- Fuel cell electrolytes: liquids, polymers, solid oxides, ceramics, ionic liquids…, standards and emerging technologies.
- Bulk electrolytes: fundamentals of the ionic transport mechanisms, experimental characterization techniques.
- Electroneutrality vs. non-electroneutrality, diluted vs. high-concentrated solutions.
- Ionic transport in the electrolytes: theory, mathematical modeling and numerical simulation techniques, Molecular Dynamics and continuum modeling.
- Electrolytes inside the porous electrodes: structure, impact on the catalyst activity and on the charge and reactants transport (e.g. PFSA polymers / platinum interfaces in Proton Exchange Membrane Fuel Cells), ionic transport in confined environments, overlapping of electrochemical double layers.

<u>Session 6/12</u> (2h)

Reactants and products transport

- Multiphase transport phenomena in porous electrodes and separators: general theory and state of the art.
- Solubility and transport mechanisms of reactants and reaction products in electrolytes.
- Experimental characterization techniques of reactants and reaction products transport.
- Mathematical modeling and numerical simulation: Monte Carlo techniques, Direct Numerical Simulation approaches and Pore Network Modeling.
- Heterogeneities of fuel cell operation: fragmented cell designs.
- ***<u>Demonstration and guided exercise with the students:</u>*** modeling and simulation through a continuum approach of reactants transport across a fuel cell component *(specific scientific computational code will be provided to the students)*.

<u>Session 7/12</u> (2h)

Materials degradation mechanisms

- Reversible vs. irreversible degradation mechanisms in fuel cells, impact on performance decay, definitions of “durability” or fuel cell “lifetime”.
- Chemical vs. thermo-mechanical degradation, definitions.
- Catalyst oxidation, dissolution and ripening.
- Supports corrosion mechanisms, impact on the catalyst activity loss.
- Separators chemical, thermal and mechanical degradation.
- Components delamination.
- Synergetic and cancellation effects between degradation mechanisms.
- Experimental techniques for the characterization of degradation processes, accelerated aging protocols, un-correlating the effects of the individual mechanisms onto the overall fuel cell performance decay?
- Available mathematical tools for the simulation of degradation mechanisms: atomistic, molecular and continuum approaches, critical review.
- Techniques to predict the fuel cell “durability”: experimental vs. modeling-based tools.

- ***Demonstration and guided exercise with the students:*** modeling and simulation of a fuel cell degradation mechanism and its impact onto its performance decay *(specific scientific computational software will be provided to the students)*.

Session 8/12 (2h)

Contamination reactions
- Definition of a "contaminant".
- External gas contaminants from Air, impact on the fuel cell performance
- External solid and liquid contaminants from Air, impact on the fuel cell performance
- Contaminants of the fuel side, fuel production methods, impact on the fuel cell performance
- Internal contaminants from the fuel cell system, impact on the fuel cell performance
- Competitions, synergies and cancellation effects between multiple contaminants.
- Competitions, synergies and cancellation effects between contamination reactions and materials degradation mechanisms.
- Non-linear dynamics, self-oscillating and chaotic behaviors of the fuel cell potential.
- Mathematical modeling and numerical simulation of contamination reactions in fuel cells.
- ***Demonstration and guided exercise with the students:*** modeling and numerical simulation of a contamination reaction and its impact onto the fuel cell performance *(specific scientific computational software will be provided to the students)*.

Session 9/12 (2h)

Fuel Cells as a whole: multiscale modeling
- Multiphysics, multiscale and multiparadigm approaches, general concepts.
- Bottom-up vs. top-down modeling.
- Indirect multiscale modeling methods: presentation, practical examples.
- Network modeling: basics of bond graphs and the principles of the non-equilibrium thermodynamics.
- Parameters optimization techniques: basics.
- Modeling and simulation of competitive degradation mechanisms in fuel cells: examples.
- Modeling and simulation of competitive degradation and contamination reactions in fuel cells: prediction of durability (examples).

Session 10/12 (2h)

Fuel Cells as a whole: multiscale modeling (cont.)
- Capturing the impact of the chemistry and structural properties of the electrode materials onto the overall fuel cell response: examples of industrial relevance (e.g. fuel cell manufacturers).
- ***Demonstration and guided exercise with the students:*** demonstration and use by the students of the LRCS simulation package MS LIBER-T on a simple test case.

Fuel Cells in the system
- Fuel cells operation at the system level.
- Control-command of fuel cells, state of the art, challenges and opportunities.
- Derivation of control devoted models from mathematical reduction of multiphysics models.
- Hybridation of fuel cells with batteries (e.g. electric vehicle applications).

- Management at the system level and impact onto the fuel cell degradation and durability: issues, solutions and controversies.

Session 11/12 (2h)

Fuel Cells in the "reverse way": electrolysers

- Low temperature vs. high temperature electrolysers for fuel fabrication (e.g. PEM Water Electrolysers for hydrogen production).
- Operation principles, catalyst and supports, electrolytes.
- Degradation mechanisms, challenges and unknowns.
- Electrolysers vs. fuel cells: similarities and differences.
- Modeling and numerical simulation of electrolysers: a critical review.
- Storage of the fuel: technical developments, challenges and opportunities.
- Towards a sustainable energetic network: coupling with renewable energies and fuel cells, challenges and opportunities.

Session 12/12 (2h)

"Students' Fuel Cells challenge 2013"

- Presentation by the students of their proposed fuel cell designs and/or operation conditions to fit the technical constraints announced in Session 1. The students will be asked to apply their learning to reach the exercise objectives.
- Technical debate and discussions.
- Surprise and general conclusions.

Contact details

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