

Sorbonne Université/ China Scholarship Council program 2020

Thesis proposal

Title of the research project: Rational design of novel nanostructured arrays for electrochemical energy storage

Keywords: energy storage, electrochemistry, gravimetric tool, performance, electrode/electrolyte interface, interface analysis

Joint supervision: yes (Dr. Hubert PERROT at the LISE UMR8235)

Joint PhD (cotutelle): ~~yes (name/surname)~~ /no

Thesis supervisor: Dr. Ozlem SEL

Email address of the thesis supervisor: ozlem.sel@sorbonne-universite.fr

Institution: Sorbonne University, Paris, France

Doctoral school (N°+name): ED 388, Chimie Physique et Chimie Analytique de Paris Centre

Research laboratory: Laboratory of Interfaces and Electrochemical Systems "LISE UMR 8235"

Address of the laboratory: Laboratoire Interfaces et Systèmes Electrochimiques (LISE), UMR 8235, CNRS - Sorbonne Université, Campus Pierre et Marie Curie, 4, place Jussieu, 75005 Paris - France

Name of the laboratory director: Dr. Hubert PERROT

Email address of the laboratory director: hubert.perrot@sorbonne-universite.fr

Subject description (2 pages max):

1) Study context

The efficiency of the advanced **energy storage systems** such as batteries or supercapacitors is certainly related to the development of the components constituting these electrochemical devices (1). Therefore, tremendous efforts have been devoted into the design of novel materials for energy, particularly with the association of various functional nanomaterials; such as carbon, conducting polymers (CPs) and metal oxides (MOs), offering synergic properties.

Concerning carbons, graphene has spurred significant interest for supercapacitor (SC) applications due to its high specific surface area, superior electronic conductivity and chemical resilience (2). To date, RuO₂ and MnO₂ are amongst the most commonly studied metal oxides in SCs (3, 4). Regarding the typical CPs (polypyrrole, polyaniline, polythiophenes..) employed in the energy storage, main mechanism relies on ion doping and dedoping (intercalation/deintercalation), which is accompanied with volumetric swelling-shrinking during charge/discharge (5, 6). These processes are likely to lead

to a wide variety of unpredictable mechanical defects (polymer electrode fatigue, stress concentration and delamination from current collector) and thus, fast capacitance decay of the CP electrodes. Such issues are not limited to this category of electrode material but prevalent to all types. Therefore, it is important to utterly contemplate the nanostructuring strategies to achieve architectures that are electromechanically robust, which is intimately related to the generation of electrodes with true performance metrics (high cycle stability, rate capability...). As a result of these **nanostructuring** efforts in the electrode fabrication, the templating methods combined with various (electro)chemical synthesis strategies come into play, and thus, in this Ph.D. thesis, the emphasis will be on the patterning of the composite electrodes and the investigation of the structure/storage performance interplay.

2) Details of the proposal

Specifically:

- Patterned metal oxide, carbon and conducting polymer based composite thin film electrodes will be fabricated via a combined strategy of “breath-figure templating (BFT)” (7, 8) and (electro)chemical synthesis methods, aiming at their potential applications in microsupercapacitors (9).
- These structures will be studied by classical structural, compositional and morphological characterization methods (such as XRD, XPS, FTIR, SEM-FEG, HRTEM and EDX).
- The **correlation** between the **interfacial ion exchange process** and the **morphology** of the electrodes will be scrutinized by not only classical but also advanced coupled electrochemical methods, i.e., cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) and electrochemical impedance spectroscopy (EIS) and their coupling to the quartz crystal microbalance (QCM) (4, 6). Both aqueous and organic electrolytes will be investigated to reach the optimized electrode morphology/electrolyte combinations. To do so, several electrolyte compositions with different ion sizes will be tested. The (de)solvation process and the interfacial transfer kinetics of the species will be studied.
- This PhD thesis will particularly benefit from the **LISE lab’s expertise** in “**coupled advanced electrochemical methods**”: (i) coupling electrochemistry with quartz crystal microbalance (EQCM and EIS and QCM coupling) will provide the transfer/transport properties of ions at the electrode/electrolyte interface and thorough the electrode, **correlated to the rate capability of the electrodes** and (ii) coupling electrochemistry with mechanical property measures - specific mode of EQCM with dissipation monitoring (10, 11) will provide mechanical property changes of the electrodes during electrochemical processes (6, 12), **correlated to the cycling stability of the electrodes**.
- With a feedback loop between the previous bullet points, long-term cycling **performance** will be evaluated (in Swagelok configuration, etc.) for their potential application as **micropower supply** (9).

Such a thorough correlation of the fundamentals of composite electrodes by advanced coupled electrochemical methods to their true performance metrics is unprecedented and is expected to deliver high impact in the **energy storage** domain.

3) References

1. Gogotsi, Y.; Simon, P. Materials science. True performance metrics in electrochemical energy storage. *Science* 2011, 334 (6058), 917-918.
2. Yang, Z.; Jiarui, T.; Yin, Z.; Chaojie, Cu.; Qian, W. Fei, W. Carbon nanotube- and graphene-based nanomaterials and applications in high-voltage supercapacitor: A review. *Carbon* 2019, 141, 467-480.
3. Guo, W.; Yu, C.; Li, S.; Wang, Z.; Yu, J. Huang, H. Qiu, J. Strategies and Insights towards the Intrinsic Capacitive Properties of MnO₂ for Supercapacitors: Challenges and Perspectives. *Nano Energy* 2018, <https://doi.org/10.1016/j.nanoen.2018.12.015>.
4. Arias, C. R.; Debiemme-Chouvy, C.; Gabrielli, C.; Laberty-Robert, C.; Pailleret, A.; Perrot, H.; Sel, O. New Insights into Pseudocapacitive Charge-Storage Mechanisms in Li-Birnessite Type MnO₂ Monitored by Fast Quartz Crystal Microbalance Methods. *J. Phys. Chem. C* 2014, 118 (46), 26551-26559.
5. Qiufeng Menga, Kefeng Cai, Yuanxun Chen, Lidong Chen, Research progress on conducting polymer based supercapacitor electrode materials. *Nano Energy* 2017, 36, 268–285.
6. Gao, W.; Sel, O.; Perrot, H. Electrochemical and viscoelastic evolution of dodecyl sulfate-doped polypyrrole films during electrochemical cycling. *Electrochim. Acta* 2017, 233, 262-273.
7. Zhang, A.; Bai, H.; Li, Lei Breath Figure: A Nature-Inspired Preparation Method for Ordered Porous Films. *Chem. Rev.* 2015, 115, 9801–9868.
8. Sel, O; Laberty-Robert, C; Azais, T.; Sanchez, C. Designing meso- and macropore architectures in hybrid organic–inorganic membranes by combining surfactant and breath figure templating (BFT). *Phys. Chem. Chem. Phys.* 2009, 11, 3733-3741.
9. Li, J.; Levitt, A.; Kurra, N.; Juan, K.; Noriega, N.; Xiao, X.; Wang, X.; Wang, H.; Alshareef, H.N.; Gogotsi, Y. MXene-conducting polymer electrochromic microsupercapacitors, *Energy Storage Mater.* 2019, 20, 55-461.
10. Shpigel, N.; Levi, M.; Aurbach, D. EQCM-D technique for complex mechanical characterization of energy storage electrodes: Background and practical guide. *Energy Storage Mater.* 2019, 21, 399-413.
11. Lemaire, P.; Sel, O.; Alves Dalla Corte, D.; Iadecola, A.; Perrot, H.; Tarascon, J. M. Elucidating the Origin of the Electrochemical Capacity in a Proton-Based Battery HxIrO₄ via Advanced Electrogravimetry. *ACS Appl. Mater. Inter.* 2020, 12, 4, 4510-4519.
12. Gao, W.; Debiemme-Chouvy, C.; Lahcini, M.; Perrot, H.; Sel, O., Tuning Charge Storage Properties of Supercapacitive Electrodes Evidenced by In Situ Gravimetric and Viscoelastic Explorations. *Anal. Chem.* 2019, 91, 2885–2893.

4°) Profile of the Applicant (skills/diploma...)

The candidate must have a Master's Degree in:

- Materials science or physical chemistry obtained with excellent grades.
- Knowledge in electrochemistry and in energy materials' characterization is required.
- A good command of English (written and oral) is necessary.

Contacts:

Thesis supervisor

Dr. Ozlem SEL

Email address of the thesis supervisor: ozlem.sel@sorbonne-universite.fr

ED :
Nom Prénom du directeur de l'ED :
[Adresse ligne 1]

Paris, le [date]

Objet : Acceptance letter for CSC-SU scholarship 2020

Indiquer en anglais :

- Nom/prénom de l'étudiant, date de naissance, diplômes obtenus
- Thématique de recherche/champs disciplinaires
- Présenter le directeur de thèse et le sujet en qlq lignes
- Skills dont lvi en langue (anglais et ou français)

Signature et cachet Ecole doctorale

Signature et cachet IFD