

- **Title : Engineering of organic binders for electrochemical energy storage**
- **Summary**

This project aims at the development of advanced electroactive carbon and polymer products as components for hybrid organic supercapacitors to combine the high capacity of redox groups and the fast charge storage kinetic of carbons. The deliverables of the project are clean, secure and low cost materials suitable for high-energy, high-power and high-stability systems. Conditions for the fulfilment of these objectives require to limit the obstruction of the carbon porosity by accumulation of molecules at their pores entrance, but also to facilitate the fast ion accessibility to their porosity, while reducing leaching of the active matter and dead masses in the charge storage process. To this end, the benefits of two complementary strategies will be cumulated, allowing a better integration of molecules in carbon supercapacitors by controlling the covalent grafting of molecules on the carbon and by introducing molecules as pendant groups in well-defined copolymers used as binder.

Keywords : Supercapacitors, storage, electrochemistry, electrolytes, polymers, stability

- **Project**

The quest to build low-cost and high-energy portable charge storage systems in an ecofriendly way feeds an ever-growing interest in pursuit of novel carbon based supercapacitors. In this context, porous carbons have demonstrated suitability as robust high-power supercapacitor electrode materials owing to their long life cycle, high capacitance and high rate capability, but are still limited in energy.¹ Strategies that have proven to be effective to boost their energy density consist in adding a faradaic component to the charge storage, yielding hybrid systems. In this context, carbon-based supercapacitors that contain attached small redox molecules have already demonstrated their potentiality because of the high modularity of organic compounds. However, limitations on cyclability and rate capability are typically obtained as a result of just physisorbed molecules and accumulation of molecules at the pore entrance of activated carbons.² For these reasons, the present project aims at developing novel molecular engineering approaches for improving the integration of molecules in the electrode material to combine their high capacity with the fast charge storage kinetic of carbons. The genesis of this project can be found in two original publications of the PhD supervisor demonstrating feasibility and relating to complementary approaches including alternately the carbon and the binder (Figure 1).³ These strategies are intended to improve the electrochemical accessibility of both the carbon and molecules either by controlling the covalent grafting of molecules on the carbon surface to avoid multilayer formation, as illustrated in the left side of Figure 1, and by introducing molecules within the polymer chain used as binder in the supercapacitor electrode, as illustrated in the right side of Figure 1. The ambition of the project is to propose a combination of these two approaches by integrating a carbon modified in a controlled way with multifunctional copolymer binders into one composite material to obtain versatile properties (redox activity, polarity, adhesion and ion conductivity) without detrimental effects on native components and avoiding dead masses in the charge storage process. The proposed integrative approach is based on both a rational molecular design of comonomers and the macromolecular engineering of binders to finely tune the chemical properties of comonomers and optimize performances of active materials (binders and modified carbons). Inspired by the remarkable degree of chemical and physico-chemical versatility of phenolic compounds,⁴ we propose to focus on quinone groups for the implementation of the redox activity (due to the $2e^-/2H^+$ (or $2 Li^+$) process per quinone unit), polar molecular properties and adhesive properties. The expected added value of such a global approach is to combine a long-term cycling stability with a high-rate capability and a high-energy density into one clean, safe and sustainable electrode material, which is one of the hot topics in this research area.

¹ Anomalous increase in carbon capacitance at pore sizes less than 1 nanometer. J. Chmiola, G. Yushin, Y. Gogotsi, C. Portet, P. Simon, P.L. Taberna, *Science* 313, 2006, 1760-1763.

² Effect of molecular grafting on the pore size distribution and the double layer capacitance of activated carbon for electrochemical double layer capacitors. G. Pognon, T. Brousse, D. Bélanger, *Carbon* 49, 2011, 1340-1348.

³ (a) Improvement of electrochemical performances of catechol-based supercapacitor electrodes by tuning the redox potential via different-sized O-protected catechol diazonium salts. E. Touzé, F. Gohier, B. Daffos, P.L. Taberna, C. Cougnon, *Electrochimica Acta* 265, 2018, 121-130; (b) A redox active binder for electrochemical capacitor electrodes. C. Benoit, D. Demeter, D. Bélanger, C. Cougnon, *Angewandte Chemie International Edition* 55, 2016, 5318–5321.

⁴ Phenolic Building Blocks for the Assembly of Functional Materials. A. Rahim, S.L. Kristufek, S. Pan, J.J. Richardson, F. Caruso, *Angewandte Chemie International Edition* 58, 2019, 1904–1927.

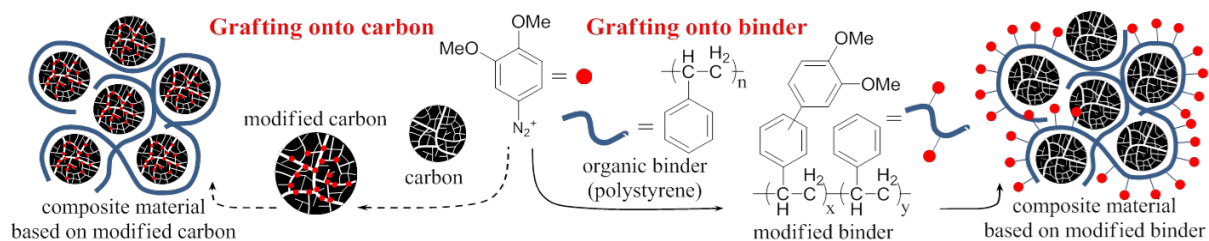


Figure 1: Strategies for improving the integration of molecules in supercapacitors

The main objective is targeted to the synthesis of well-defined (co)polymers with tuneable composition, functionality and architecture for the optimal design of dual polymers acting both as active materials and binders in supercapacitor electrodes. Preliminary results obtained with a catechol modified polystyrene binder shown that the binder polarity is an important factor, doubling the overall specific charge stored in aqueous electrolytes due to a better wettability. Importantly, recent works have demonstrated that catechol derivatives find applications in other areas than electrochemistry, especially in the sector of adhesive coatings, where they are integrated as pendant groups in mussel-inspired biopolymers.⁵ This remarkable bioadhesion propensity is anticipated to restrain leaching of the binder that improve the long-term cycling stability, which is one of the hot topics in the energy storage. The long-term stability of the supercapacitor electrode will be evaluated in organic media, but also in neutral aqueous electrolytes, which are propitious environments for such adhesive interactions and allow to extend the potential window of electrochemical capacitors by pushing the dihydrogen evolution potential away from its thermodynamic value.⁶ To ensure that the adhesive properties are optimized, it was demonstrated that both the molecular weight and the chemical composition of mussel mimetic polymers must be controlled.⁷ So, an important task for the preparation and characterization of the binders is needed to optimize the adhesion of the binder to the carbon. Here, we propose to engineer smart organic binders by the careful implementation of redox monomers (to achieve high-energy systems), polar units (to achieve high-power systems), synthetic analogues of marine biological adhesive units (to achieve high-stability systems) and ion-conducting anionic pendant groups (to improve the ion mobility).

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⁵ Mussel-Inspired Surface Chemistry for Multifunctional Coatings. H. Lee, S.M. Dellatore, W.M. Miller, P.B. Messersmith, *Science* 318, 2007, 426-430.

⁶ Novel insight into neutral medium as electrolyte for high-voltage supercapacitors. K. Fic, G. Lota, M. Meller, E. Frackowiak, *Energy & Environmental Science* 5, 2012, 5842-5850.

⁷ Molecular Weight Effects upon the Adhesive Bonding of a Mussel Mimetic Polymer. C.L. Jenkins, H.J. Meredith, J.J. Wilker, *ACS Applied Materials & Interfaces* 5, 2013, 5091-5096.