Polytech network form for PhD Research Grants from the China Scholarship Council

This document describes the PhD subject and supervisor proposed by the French Polytech network of 14 university engineering schools. Please contact the PhD supervisor by email or Skype for further information regarding your application.

Supervisor information	
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PhD information	
Title	Coated-carbon-nanotubes polymer composites for supercapacitors
Main topics regards to CSC list (3 topics at maximum)	IV.2: Nanomaterials IV.10: Biomaterials and polymer materials

Required skills in science and engineering	- Material science : polymer manufacturing, electrical and mechanical properties of materials, knowledge of experimental techniques for the analysis of material properties.

Subject description (two pages maximum)

Context: Electrolytic supercapacitors allow to obtain high values of capacitance for storage energy, filtering, coupling. However, the manufacture of these devices is complex and doesn't authorize integration for microelectronic applications. Moreover, these devices are limited in voltage to some volts (thus limiting the storage energy) and they can't work more than typically 60 – 70°C. Finally, leakage current and conductivity are important and often temperature-dependent thus limiting also applications with these materials. Multilayer ceramic capacitors (MLCC) constitute another way to develop supercapacitors. They begin to concurrence electrolytic supercapacitor in term of the value of capacitance (many microfarad). However, the drawbacks evoked for electrolytic supercapacitors stay present with MLCC. In order to integrate supercapacitors and to increase ranges of applications, a technology in rupture must be thought. For that, two approaches must be driven, both on the principle of electrostatic capacitor. The first one is based on our recent work [1] where a high k dielectric covers a forest of carbon nanotubes (CNT), this latter playing the role of electrode. The feasibility of this approach was demonstrated but this system could be improved by modifying for example the growing of CNT for a better efficiency at the CNT- high k dielectric. Other high-k dielectrics could also constitute better candidates than amorphous BaTiO3 used in this study. The second approach constitutes to mix CNT with a polymer matrix. A multitude of publications can be found on this approach and we published reference works on this subject [2-4]. However, a problem persists: the capacitance of the system is strongly increased but in same time, the electric conductivity and dielectric losses are degraded. Therefore, the dielectric strength (i.e. breakdown voltage) is strongly reduced thus limiting applications. Even if some improvements in term of dielectric losses are observed recently, this problem is not solved sufficiently for reliable applications. In recent work (unpublished), starting from a specific coating of CNT by an insulating polymer, we reduced the influence of the percolative path for the electric conduction. As a consequence, in same time, we increase the dielectric constant of the device and we limited the degradation of the dielectric strength.

Work program: The survey was due to be extended in term of choice of polymer, choice of electrodes, and choice of nano-object to mix in the polymer. Our both approaches use composites materials with various interfaces. Trapping and driving of electric charges in these nanocomposites polymers will be investigated from the measurement of the leakage current and dielectric spectroscopy. Space-charge measurements using laser-induced pressure pulse (LIPP) will complete the analyses. Capabilities in term of supercapacitor will be measured by aixACCT ferroelectric tester.
To summary, challenges on this thesis will be on the manufacture of new electrostatic-based composites capacitors and their electric and dielectric analyses with the goal to concurrence electrolytic and

multilayer ceramic capacitors. The approach for these new devices will present the advantage of a lower cost (due to a simplified manufacturing process) and also very important an extension towards miniaturization for microelectronics applications and/or new applications at higher voltage and temperature.

Working environment: This study will be carried out at G2Elab and in collaboration with the MSSMat (Dr. J. Bai) of the Ecole Centrale de Paris. These two laboratories have been collaborating for many years in this area [2-4]. The candidate may be required to spend short periods at the MSSMat as part of his or her work.

References:

[1] S.-H. Yao, J. Yuan, H-al Mehedi, E. Gheeraert, A. Sylvestre, 'Carbon nanotube forest based electrostatic capacitor with excellent dielectric performances', *Carbon*, 2017, **116**, 648-654.

[2] J-K. Yuan, S-H. Yao Z-M. Dang, A. Sylvestre, M. Genestoux, J. Bai, 'Giant Dielectric Permittivity Nanocomposites: Realizing True Potential of Pristine Carbon Nanotubes in Polyvinylidene Fluoride Matrix through an Enhanced Interfacial Interaction', *The Journal of Physical Chemistry C*, 2011, **115**, 5515.

[3] J.-K. Yuan, S.-H. Yao, W. Li, A. Sylvestre, J. Bai, 'Anisotropic Percolation of SiC − Carbon Nanotube Hybrids: A New Route toward Thermally Conductive High -k Polymer Composites', *The Journal of Physical Chemistry C*, 2017, **121**, 12063−12070.

[4] J. Yuan, S. Yao, A. Sylvestre, W. Li, L. Zimmer, J. Bai, 'Vertically aligned carbon nanotube arrays on SiC microplatelets: a high figure-of-merit strategy for achieving large dielectric constant and low loss in polymer composites', *The Journal of Physical Chemistry C*, 2014, **118**, 22975-22983.