SORBONNE UNIVERSITÉ

CHINA SCHOLARSHIP COUNCIL

Appel à projets
Campagne 2022
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Title of the research project :

Ion exchange behaviour of MnO2 based nanostructured composite materials : effect of n

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Research Unit

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Code *(ex. UMR xxxx)* :

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Doctorate School

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Description of the research project :

Manganese dioxides (MnO_2) thin films and conducting polymer embedded MnO_2 nanomaterials are very promising materials for energy conversion and storage applications (supercapacitors **[1-3]**, batteries **[4],** metal-air batteries, water splitting). It is now well established in literature that the morphology of MnO_2 particles and thin films, their cristallinity, their electronic conductivity or yet the $Mn^{4+}/Mn^{3+}/Mn^{2+}$ distribution in their bulk all play a significant role on the performances of resulting devices dedicated to such applications. Interestingly, incorporation of cations in MnO_2 based materials is also a very important criteria for the optimisation of such materials that has been much less investigated in literature in spite of several recent and very relevant reports.

In this Ph.D. work program, MnO_2 based nanomaterials will be either deposited as thin films using the electrodeposition method **[5]** in the presence of various alkaline-earth cations, transition metal cations, or cationic surfactants, or deposited as (nano- or micro-) particles using the drop casting method and a binder. Conducting polymers will be electrodeposited in a step following or preceeding the (electro-)deposition of MnO_2 based nanomaterials. In both synthesis methods of MnO_2 based nanostructured materials, carbon based additives could be added so as to improve the electronic conductivity of the resulting materials. For the latter one, MnO_2 (nano- or micro-) particles possessing various morphologies and crystallinities will be synthesised in a preliminary step using the hydrothermal method (see below for several examples of morphologies synthesised in our research team).

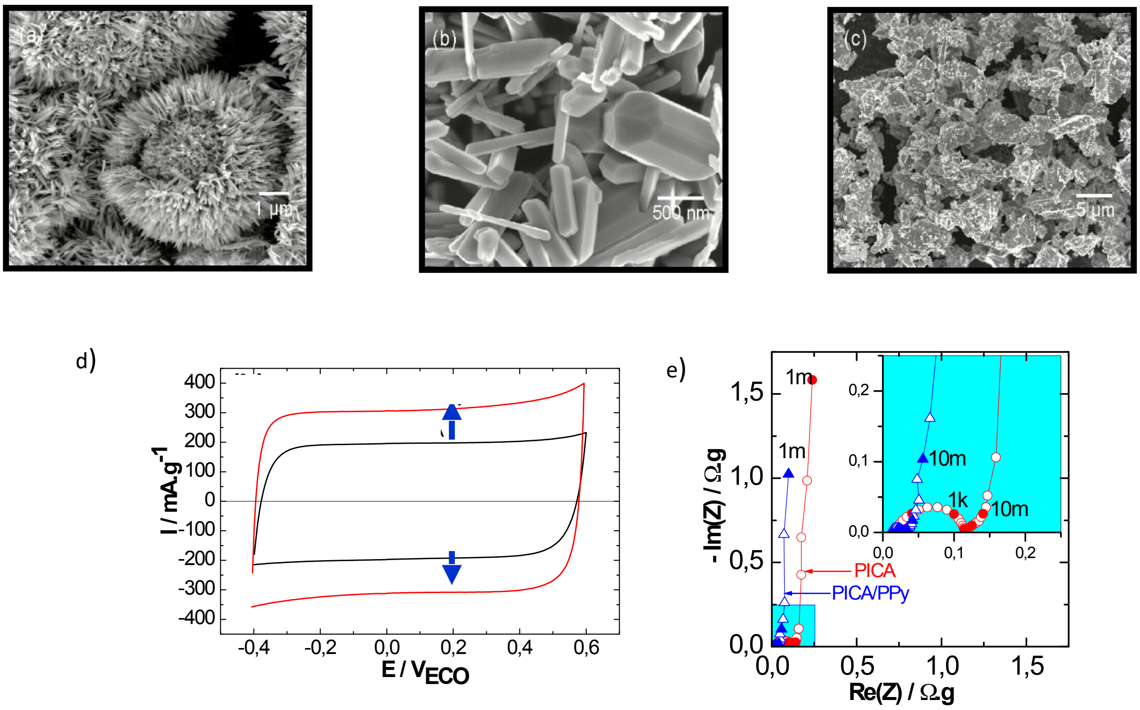

__Figure 1 :__ a,b,c) various types of MnO_2 powders synthesised recently in our research lab, d) typical CV and e) Electrochemical Impedance Spectroscopy measurements, all carried out in a Swagelok-type pseudo-capacitor.

In addition to chemical and structural analysis techniques such as EDX, nuclear techniques (NRA and RBS) and XRD that will provide respectively precious information on the elemental analysis and crystallinity of starting materials, Electrochemical Quartz Crystal Microbalance (EQCM) and/or ac-electrogravimetry (ACEG) techniques will be exploited to evaluate ion and solvent exchanges in aqueous electrolytes as a function of the synthesis conditions and starting properties of the targeted MnO_2 based nanostructured materials, with a special emphasis on the separation of diffusioncontrolled and capacitive controlled contributions. EC-AFM **[6-7]** will also be used to characterise the electrochemo-mechanical behaviour of selected MnO_2 particules and composite materials during ion exchange phenomena. Ultimately, the ACEG/EC-AFM coupling could be envisaged to produce in a single experiment a global view of the ion exchange phenomena and related/associated phenomena. In summary, the main objective of this Ph.D. work plan is to mobilize ambitious and original methodologies developped and available at LISE laboratory to deepen our understanding of ion exchange behaviours in MnO_2 based nanomaterials and composite materials.

The candidates wishing to apply for this Ph.D. are expected to be experts in electrochemistry, materials science (synthesis and characterisation) and instrumentation.

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