Postdoctoral position in electrochemistry – ENIGMAKIC Carnot project

1 Context

Combine fast charging and high energy density is possible with **M-ion hybrid capacitors (MICs)** by associating the electrostatic phenomena at a positive capacitor-type electrode and the faradic process at a negative battery-type electrode. **Higher energy density than conventional EDLC** is ensured thanks to the higher voltage in hybrid configuration. Issues of dependency on critical and strategic materials as well as security are pushing research to turn to other alkali materials than lithium. This project is focused on potassium, which benefits from abundant resources, low standard electrode potential as well as low costs.

Since 2013, the CEA, a pioneer on the subject, has been developing hybrid potassium capacitors (KIC). The **first proof of concept of KIC** was carried out at pouch cell scale at **CEA LITEN in 2017** [1]. Cells in different formats (pouch, stack, cylindrical) were then produced and stable and reproducible results were demonstrated. The non-aqueous potassium-ion hybrid supercapacitor (KIC) presented here consists of an activated carbon positive electrode and a graphite negative one working in an acetonitrile-based non-aqueous electrolyte and a potassium salt. The combination of the two charge storage mechanisms (faradic and capacitive) allows to obtain systems with a higher operating voltage. Energy densities higher than those of conventional supercapacitors are then achieved.

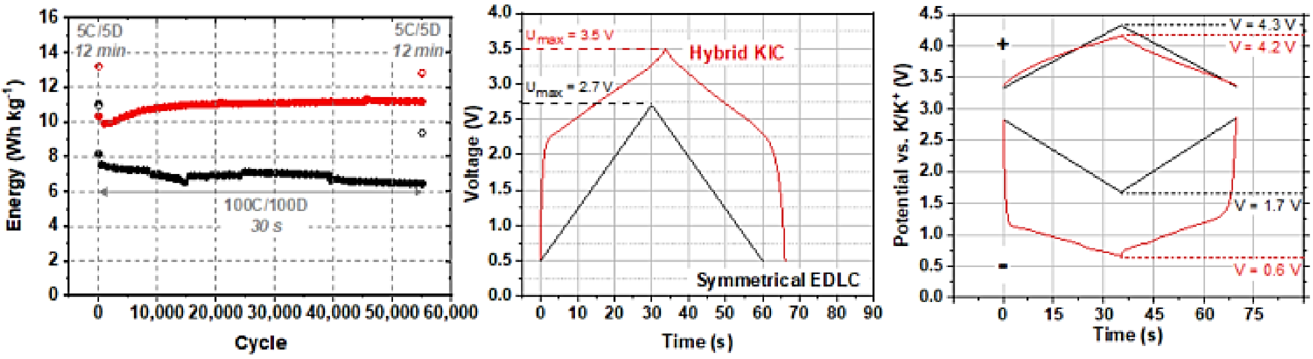

Figure 1: Cycling performance (100C/100D – Umax to 0.5 V (100% usable Depth of Discharge-DoD) at room temperature), voltage window and potential windows of each electrode of hybrid KIC (red) and symmetrical EDLC (black) systems

The KIC system therefore represents a **low-cost technology without critical and strategic materials and with competitive performance** compared to the same lithium ion-based systems. However, their energy density remains limited and is conditioned by the positive electrode which, at present, is a commercial electrode. The ENIGMAKIC project therefore aims to develop a hybrid material in order to increase the capacity of this electrode. This project aims to **prepare a hybrid positive electrode incorporating both an intercalation material** (i.e. Prussian White or PTMA) **and a capacitive material** (i.e. activated carbon) to integrate it into a KIC system. Such an electrode has never been developed before for KIC systems, in particular with a faradic material involving the anion (PTMA). The final goal would be to achieve energy densities of at least 20 $Wh.kg^{-1}$ for KIC cells.

2 State of the art

In order to improve the capacity and therefore the energy density of hybrid capacitors, a double hybridization strategy consists of constructing a hybrid electrode integrating a capacitive material and a faradic material as shown schematically below.

In the case of lithium hybrid capacitors, these electrodes then contain a Li-ion battery positive electrode material and a supercapacitor type material. Hybridization of the positive electrode in LIC by combining activated carbon with LFP (lithium iron phosphate) [2, 3] or NMC (nickel manganese cobalt) [4, 5] allows to achieve materials with higher capacity (45-65%) at low charge rate while retaining its initial capacity at high charge rate. To fully benefit from the advantages of this hybridization, several factors must be taken into account. Faradaic material content and electrode structure were identified as important parameters. It has notably been demonstrated for an AC/LFP electrode that a layered structure allows to achieve higher energy densities. On the other hand, an AC/NMC electrode with 25% NMC allows to achieve greater capacities at high charge rates compared to electrodes with a higher NMC content.

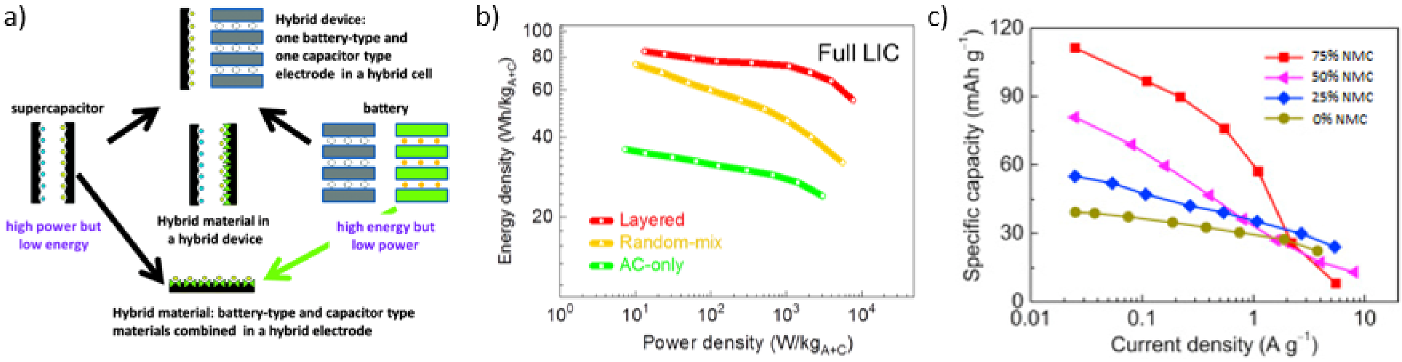

Figure 2 : (a) Schematic representations of different possible hybridization approaches between supercapacitor and battery electrode and materials, (b) Comparative Ragone plots of LIC based on the AC-only, random-mix and layered electrodes, (c) Specific capacity as a function of current density of LIC containing hybrid AC+NMC electrode with different percentages of NMC

3 Project objectives

Inspired by these studies carried out on LIC, the ENIGMAKIC project aims to produce the **first hybrid electrode for KIC systems**. For this, the use of positive electrode materials of K-ion batteries is necessary. Prussian blue and its analogues have been identified as promising materials with their high working voltages and ease of synthesis [6].

In addition, we propose a **novel approach with the use of an intercalation material involving the anion** (PF_6^-). Indeed, activated carbon is combined with a cation intercalation material (K^+ or Li^+) in the studies presented previously. One material being considered is the poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl) (PTMA), used as an organic battery component, with a flat potential profile at an average value of 3.5 V vs. K^+/K thanks to the insertion/extraction of the PF_6^- ion [7]. PTMA has already been used as a reference electrode in a KIC system [8] and is therefore compatible with all components of the KIC system, which makes it a prime candidate for the creation of the hybrid electrode in ENIGMAKIC.

4 Main missions during the postdoc

From a “process” point of view, your first missions will be to **synthesize the active materials and to prepare the slurry and realize the coating of the hybrid electrode**. At the beginning of the project, electrode at A4 format are expected. You will then scale up the synthesis and coating processes thanks to the expertise of the laboratory members. An electrode of several meters of hybrid electrode is expected in order to be able to produce larger prototypes.

From a “characterization” point of view, you will identify a counter electrode allowing the complete study of the hybrid electrode and being compatible with potassium ions and acetonitrile. Using this counter electrode, you will fabricate coin cells in order to **study and understand the charge storage mechanism** resulting from the combination of faradic and capacitive materials.

From a “performance” point of view, you will identify the parameters impacting the capacity of the hybrid electrode (i.e. structure of the electrode, quantity of faradic material). Considering the results reported in the literature for hybrid electrodes in LIC, **an increase of at least 50% in the capacity of the positive electrode** is expected, i.e. a capacity of up to 50 mAh.g^{-1} (30 mAh.g^{-1} for the commercial electrode currently used). You will produce complete KIC cells to evaluate the performance gain in terms of energy density linked to the use of the hybrid electrode. An improvement from 14 Wh.kg^{-1} (current performance) to 20 Wh.kg^{-1} is targeted. In addition, a brief analysis of the degradation mechanisms of these complete cells will be carried out in order to compare them to those identified within standard KIC cells.

Bibliographie

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