

## **AGRITECH**

***National Research Centre for Agricultural Technologies***

**BOtanical REsources for ALternative battEries -  
“BO.RE.AL.E.”**

**AMBITO: NUOVE MOLECULE, PRODOTTI E PROCESSI AD  
ALTRO VALORE AGGIUNTO PER LA VALORIZZAZIONE DI  
RIFIUTI, SCARTI, SOTTOPRODOTTI E COPRODOTTI AGRICOLI  
O PER L'AGRICOLTURA**

**ASCLA SOCIETA' COOPERATIVA IMPRESA SOCIALE (Leader)**

**RADICE CUBICA S.R.L. (Partner)**

**UNIVERSITÀ DEL SALENTO (Partner)**

**Deliverable: 3.1**

**Deliverable title: Data-set of preparation protocols**

.....

## 2. EXECUTIVE SUMMARY

This deliverable (D3.1), titled "Data-set of Preparation Protocols", presents the methodologies and results of research conducted within Work Package (WP) 3 of the BO.RE.AL.E. project. The study focuses on utilizing carbon dots (C-dots) developed within the WP2 as alternative conductive materials in the preparation of cathodes for sustainable lithium-ion batteries (LIBs).

The report details the preparation and optimization of electrode slurries and their deposition to obtain electrodes that were characterized in terms of morphology, thickness, and materials contents. SEM analysis provided insights into the structure and uniformity of the electrodes, demonstrating the effectiveness of C-dots as a conductive material. The study highlights the need for further optimization to enhance the viscosity and homogeneity of C-dot-based slurries for improved battery performance.

## 3. INTRODUCTION

The D3.1 document, titled "Data-set of Preparation Protocols" details the research activities conducted within Work Package 3 (WP3). The objective is to utilize the carbon dots (C-dots) produced in WP2 of the project as an alternative conductive material for the preparation of cathodes in sustainable lithium-ion batteries (LIBs). As an initial step, C-dots were incorporated as the conductive material in the formulation of an electrode slurry, optimizing the solid-to-liquid ratio to achieve the desired viscosity. This slurry was then deposited onto current collectors and subjected to further characterization, including morphological analysis measurements (SEM images).

## 4. METHODOLOGY

To prepare the viscous formulations (slurries) (Scheme 1), the solid components consisted of the active material, 9,10-anthraquinone (AQ, MW: 257 g/mol) – 50% by mass, the conductive agent— carbon quantum dots (C-dots) and/or acetylene black (AB) – 40% by mass, and the binder, polyvinylidene fluoride (PVDF) – 10% by mass. N-methyl-2-pyrrolidone (NMP) was used as the solvent. To differentiate the mixing methods, the slurries have been categorized into two groups: A, B, and C for mechanical magnetic stirring, and D and E for mechanical ultra-stirring.

For the electrode fabrication, an aluminum (Al) foil was used and pre-treated with an ethanol solution to remove any surface residues and impurities. The current collectors had a thickness ranging from 17 to 18  $\mu\text{m}$  and an average weight of 12 mg per electrode. The designated coverage area for each electrode was set at 1  $\text{cm}^2$ .

The slurry was thus manually deposited onto three separate Al collectors using a spatula, to obtain different electrodes. After deposition, the electrodes were dried on a heating plate, with a temperature ramp applied from 50 °C to 80 °C for 10 minutes, followed by a further increase to 100 °C for 15 minutes. After cooling, initial characterization was performed, including the measurement of the deposited material's weight and the resulting thickness.

The morphologies of obtained electrodes were analyzed with a FESEM microscope Zeiss Sigma 300 VP, using a GEMINI® technology. Such FESEM microscope comprises a fully integrated inlens detector (Inlens) for secondary electrons (SE) and an angle selective backscattered electron (HDASeB) detector, in the high vacuum mode, and a dedicated C2D detector for secondary electrons, in a variable pressure (VP) mode, performed using nitrogen as imaging gas. SEM analyses of the samples were acquired at 3.00 kV with acquisition times of a few seconds.

## 5. RESULTS AND DISCUSSION

The initial investigation focused on the visual and morphological characterization of the resulting slurries by varying the type of conductive agent, aiming to explore the potential application of C-dots as the conductive material for LIBs.

The visual representations of Slurry A, B, D and E are shown in Figure 1.

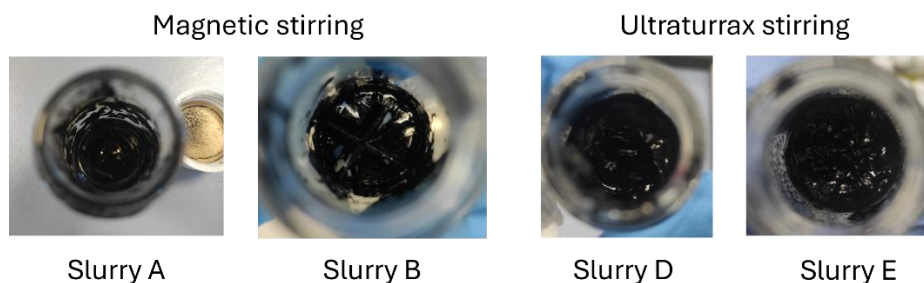


Figure 1. Slurry A and B (magnetic stirred) and Slurry D and E (ultraturrax stirred) after preparation

The slurries differ in the types of conductive agents used and the mixing procedure adopted. Slurry A and Slurry D contain only C-dots, while Slurry B and Slurry E have a 1:1 w/w ratio of acetylene black (AB) to C-dots. Process analysis for Slurry A and Slurry B revealed that sonication, compared to magnetic stirring alone, enhanced the formulation quality by providing better viscosity control. This improvement is attributed to the disruption of potential C-dots-AQ aggregates, followed by a reorganization of the particles, resulting in better homogeneity of the system. However, the formulation containing only C-dots (Slurry A) resulted in a more liquid mixture compared to those made with the conventional conductive carbon (Slurries B, C). To accomplish this, Slurry D was prepared using Ultraturrax stirring while adjusting the liquid-to-solid ratio to an optimal value. A ratio

of 85:15 (liquid-to-solid) was established for all formulations, as it provided better mechanical features between all the components.

The obtained viscous formulations were then used to prepare different electrodes with varying weights, as shown in Figure 2.

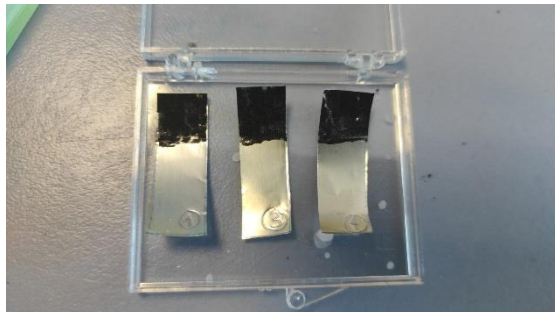


Figure 2. Coated electrode with variable weight and thickness.

The prepared electrodes were characterized by their weight and thickness, as reported in the following Table 1 and 2.

Name	Al, mg	Al + slurry, mg	Coated material, mg	Thick Al, um	Thick Al + slurry, um (n=4)	Thick of coated material
Slurry A_1	13.3	14.80	<b>1.50</b>	17	39.8	<b>22.8 ± 3.7</b>
Slurry A_2	12.4	14.59	<b>2.19</b>	18	46.3	<b>28.3 ± 8.5</b>
Slurry A_3	12.6	13.80	<b>1.12</b>	19	35.7	<b>16.7 ± 2.7</b>
Slurry A_4*	12.3	13.30	<b>1.0</b>	16	33.0	<b>17 ± 4.2</b>

Name	Al, mg	Al + slurry, mg	Total electrode mass, mg	Active material mass, mg
Slurry D_1	17.0	19.7	<b>2.7</b>	<b>1.35</b>
Slurry D_2*	16.6	19.3	<b>2.7</b>	<b>1.35</b>

Name	Al, mg	Al + slurry, mg	Coated material, mg	Thick Al, um	Thick Al + slurry, um (n=4)	Thick of coated material
Slurry B_1	13.2	14.6	<b>1.4</b>	17	42.4	<b>25.4 ± 3.5</b>
Slurry B_2	12.8	13.6	<b>0.8</b>	18	35	<b>17 ± 2.3</b>
Slurry B_3*	12.2	13.4	<b>1.3</b>	18	35.2	<b>17.3 ± 3.0</b>
Slurry B_4	13.1	14.0	<b>0.9</b>	18	34.3	<b>16.3 ± 1.5</b>

Name	Al, mg	Al + slurry, mg	Total electrode mass, mg	Active material mass, mg
Slurry E_1	17.2	19.1	<b>1.9</b>	<b>0.95</b>
Slurry E_2*	16.5	18.0	<b>1.5</b>	<b>0.75</b>

Tables 1 and 2. The weight and thickness of prepared electrodes. \*electrodes used for SEM characterisation.

The benchmark material (Slurry C) was represented by the electrode named Slurry C\_1, which has a deposited film weight of 2.9 mg (1.4 mg of active material), and 22 µm thickness.

SEM images of the prepared electrodes are shown in Fig. 3.

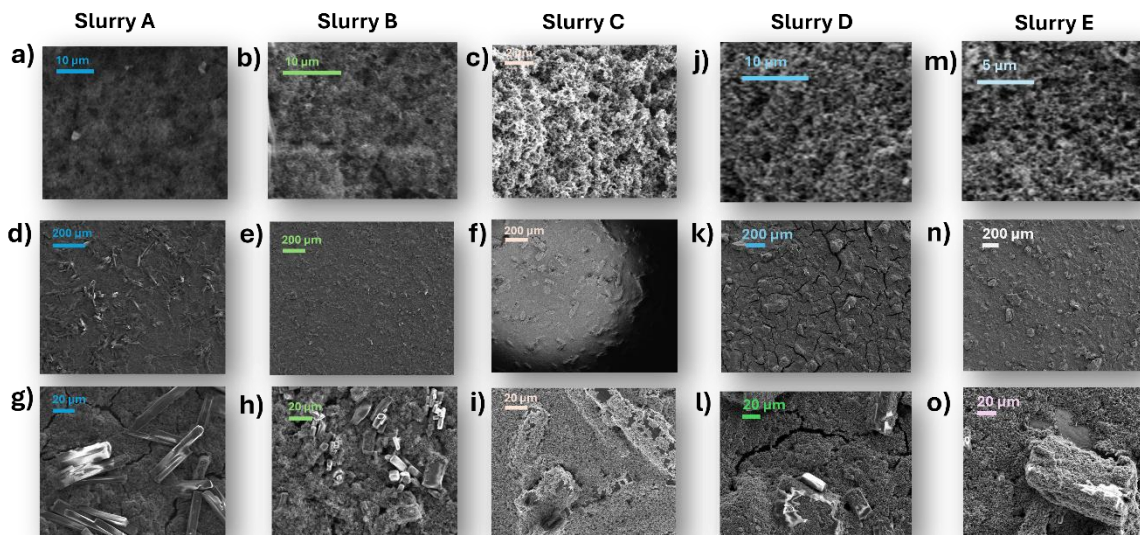


Figure 3. SEM images of C-dots-based cathode (a,j), C-dot:AB-based cathode (b,m), AB-based cathode (c) at magnification 100X, and focus at magnification 1KX (d,e,f,k,n) and 10KX (g,h,l,o).

From the SEM images, the characteristic rod-like aggregates of AQ molecules can be observed, present in all electrode types and embedded within the carbonaceous matrix of C-dots and/or AB. Each electrode exhibits a high-quality morphology, free from defects and pinholes.

At higher magnifications (Figs. 3g,l, 3h,o, and 3i), the influence of different carbon types on the nanostructure becomes evident. The electrode composed solely of C-dots (Fig 3g and 3l) shows a much finer carbon structure compared to the one based solely on AB (Fig 3i), which is consistent with the nature of the carbon nanoparticles used as building blocks in their fabrication.

## 6. CONCLUSIONS

The study presented in this deliverable successfully demonstrates the feasibility of using C-dots as an alternative conductive material in LIB cathodes. The preparation of slurries with varying compositions of C-dots and AB enabled the evaluation of their impact on electrode properties.

In particular, C-dot-based electrodes exhibit a fine carbon structure, which could contribute to improved electronic conductivity, although slurries require further optimization to achieve the desired viscosity and processability.