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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: 3.2

Deliverable title: Data-set of electrodes properties and performances

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2. EXECUTIVE SUMMARY

The D3.2 document, *"Data-set of Electrode Properties and Performance"* investigates the electrochemical behavior of newly developed electrodes, based on the materials provided by the WP2, as potential candidates for sustainable lithium-ion cathode materials. The study examines the influence of (i) the type of conductive material (C-dots, AB, or a C-dots/AB mixture) and (ii) the active material weight on electrode performance using a conventional three-electrode setup. Key properties, including electron storage capacity and cycling stability, were evaluated through electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) measurements in a standard organic Lithium-based electrolyte. Preliminary results highlight the promising applicability of C-dots as a conductive material in the development of alternative lithium-ion cathodes.

In addition to the electrochemical investigation of C-dot-based electrodes produced within WP2, a screening was carried out on the potential electrochemical activity of waste materials provided by the project partners.

3. INTRODUCTION

Organic cathode materials, such as quinones, offer significant advantages, including high theoretical capacity, environmental sustainability, and structural versatility. Among them, 9,10-anthraquinone (AQ) stands out due to its low cost and high theoretical specific capacity of 257 mAh/g. However, its practical application is hindered by poor electrical conductivity and solubility in electrolytes. To address these issues and explore the potential of alternative carbon-based conductive agents, AQ was combined with C-dots, either alone (Slurry A, Slurry D) or in combination with commercial acetylene black (AB) (Slurry B, Slurry E). The incorporation of C-dots aims to improve conductivity while offering a more sustainable alternative for electrode formulation. This study systematically evaluates and compares the electrochemical performance of these composites with conventional AQ-based organic cathodes (Slurry C), assessing their potential as reliable cathode materials for lithium-ion batteries.

4. METHODOLOGY

Samples identified as Slurry A_1 (C-dots alone, 1.0 mg coated material, 0.5 mg AQ), Slurry B_1 (C-dot/AB, 1.4 mg coated material, 0.75 mg AQ), Slurry B_2 (C-dot/AB, 0.8 mg coated material, 0.4 mg AQ) and Slurry C (AB, 2.9 mg coated material, 1.45 mg AQ), Slurry D_1 (C-dot alone, 2.7 mg coated

material, 1.35 mg AQ), and Slurry E_1 (C-dot/AB, 1.9 mg coated material, 0.95 mg AQ) were subjected to the electrochemical characterisation studies.

Electrochemical analyses were conducted using a three-electrode electrochemical cell setup connected to a potentiostat (Autolab PGSTAT 320N equipped with NOVA 1.11 software, Metrohm). The working electrode (WE) was represented by Slurry_A, Slurry_B, Slurry_C, Slurry D or Slurry E, while the counter electrode (CE) consisted of a platinum foil with a surface area of 1 cm^2. A saturated Ag|AgCl electrode in KCl was used as the reference electrode (RE). Cyclic voltammetry (CV) measurements were performed by applying a potential scan from +0.5 V to -2 V versus the Ag|AgCl reference electrode, with a potential increment in the anodic direction at a scan rate of 3 mV/s. The potential values were converted to the $Li^+|Li$ scale (calculated as 3.227 V) for direct comparison with recorded CV data. Potentiostatic electrochemical impedance spectroscopy (EIS) measurements were conducted at the equilibrium potential (open-circuit potential, OCP) over a frequency range of 50 kHz to 1 Hz, with a 10 mV amplitude potential and 50 points per decade sampling, yielding the Nyquist plot spectra.

The electrolyte solution consisted of 0.1 M lithium perchlorate ($LiClO_4$) dissolved in 12/15-mL N_2-sat. propylene carbonate (PC), a commonly used electrolyte for assessing the electrochemical performance of electrodes within lithium-ion battery chemistry.

5. RESULTS AND DISCUSSION

Figure 1 shows the EIS spectra at OCP acquired for Slurry A, Slurry B and Slurry C samples.

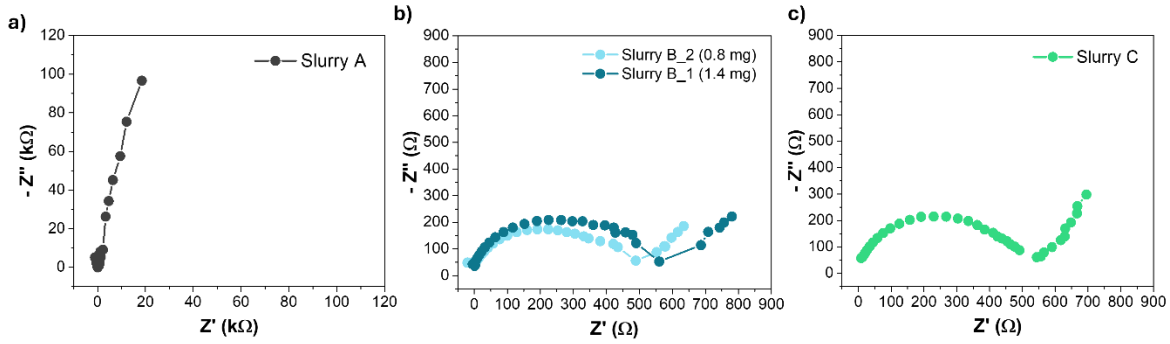

Figure 1. EIS spectra recorded at OCP for a) Slurry A_1, b) Slurry B_1 and Slurry B_2 (variable weight based electrodes), and compared to c) benchmark material (Slurry C).

The recorded OCP for all the samples were: + 0.24 V *vs* Ag|AgCl for Slurry A and Slurry B, + 0.01 V *vs* Ag|AgCl for slurry C, which can be reasonable roughly converted to 3.43 V and 3.21 V *vs* $Li^+|Li$ scale in 0.1 M $LiClO_4$ in PC electrolyte.

The real-axis intercept at the Nyquist plots observed in the high-frequency region corresponds to the electrolyte resistance (R_s), while the semicircle in the low-frequency region represents the electrode/electrolyte interface resistance (R_i). The R_s values, obtained from the intercept of on the X-

axis at 10KHz investigation, were found to be similar for all the electrodes investigated. However, distinct spectra were observed for the electrode with C-dots alone and those with C-dots mixed with acetylene black. The electrode with only C-dots (Slurry A) exhibited a straight vertical line, indicating negligible conductivity at the fresh condition. It also showed a decline in the open-circuit potential values from + 0.24 V vs Ag|AgCl to 0 V in N_2-saturated electrolyte, suggesting an unstable behavior over time. In contrast, the electrode containing C-dots and AB (1:1 wt) (Slurry B) showed a different behavior. The Nyquist spectra displayed a semi-circle in the mid-frequency region (100 Hz), similar to the one observed for the benchmark electrode (Slurry C). Specifically, Slurry B_2 and Slurry C exhibited lower and comparable interphase resistance values (~500 Ω). In contrast, Slurry B_1, with a thicker coating than Slurry B_2, showed the highest Ri value (~550 Ω). This increase is likely attributed to the greater amount of electrode material flooded by the electrolyte, which expanded the surface area in contact with the electrolyte.

To evaluate the electrochemical performance of the potential cathodes in terms of storage capacity and cyclability, cyclic voltammetry (CV) was conducted for the first three scans, within a potential sweep range of +0.5 to –2 V vs Ag|AgCl (3.9 – 1V vs Li^+|Li). Figure 2 shows the electrochemical responses of Slurry A (C-dots alone).

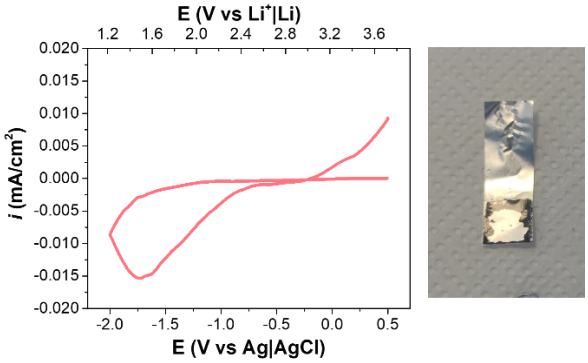

Figure 2. CV recorded for electrode Slurry A_1 (1.0 mg coating material, 0.5 mg AQ). On the right side, the picture of electrode after cycling.

Unfortunately, the electrode material undergone to gradual dissolution into the electrolyte during cycling. This behavior indicates poor adhesion to the current collector, which will be the focus of future optimization efforts to explore improved adhesion strategies.

Different CV responses were observed for electrodes Slurry B and Slurry C, as also indicated by the previous EIS measurements. Figure 3 shows the comparison between two-different Slurry B2 electrode's coating and the benchmark Slurry C.

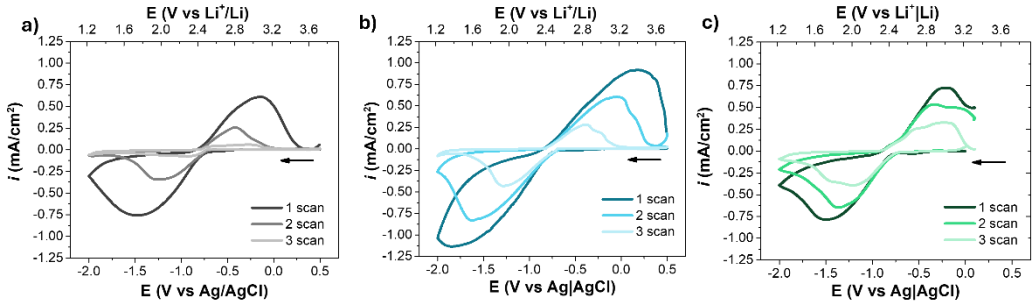

Figure 3. CVs recorded for a) Slurry B_2 (0.8 mg coating material, 0.4 mg AQ), b) Slurry B_1 (1.4 mg coating material, 0.7 mg AQ), c) Slurry C (2.9 mg coating material, 1.45 mg AQ).

The redox mechanism depicted in Figure 3 outlines the electrochemical reduction and oxidation of the quinone group in AQ from the developed electrodes when interacting with Li-ions in the electrolyte, a process that is consistent with conventional lithium-ion batteries using quinone-based active materials. Initially, a radical anion (AQ^{-}) is formed, which then transitions to a dianion (AQ^{2-}) upon coordination with Li^{+}. During re-oxidation, the carbonyl groups are reformed, and Li^{+} is released back into the electrolyte. Based on this mechanism, two pairs of redox peaks are typically expected in the CV curves. Accordingly, the CV profiles of all electrodes show a broad pair of redox peaks, with the cathodic peak centered at –1.5 V vs Ag|AgCl and the anodic peak near 0 V. The significant peak separation indicates substantial polarization during the redox process, which aligns with the presence of conductive carbonaceous materials enhancing capacitive behaviour. The variation in current density between Slurry B_1 and Slurry B_2 is due to the differing amounts of active AQ material incorporated into the C-dots/AB-based electrodes. Specifically, the electrode 'Slurry B_1' achieved a current density of 1.1 mA/cm² during the first scan, while the electrodes named 'Slurry B_2' and 'Slurry C' (which uses only AB as the conductive carbon) both reached 0.75 mA/cm². This result indicates that C-dots can significantly enhance the energy storage capacity of battery's cathodes. However, further optimization is required to prevent the dissolution of the active material during cycling. In all the tested electrodes, the anodic peaks shifted to more negative potentials, while the cathodic peaks shifted to more positive potentials, accompanied by a decrease in current density over multiple cycles. This behavior suggests that the active material dissolves into the electrolyte, a phenomenon that was particularly noticeable during the reduction process at all scans.

Figure 4 shows the comparison between Slurry D (C-dot alone) and Slurry E (Cdot/AB) obtained by ultraturrax stirring method.

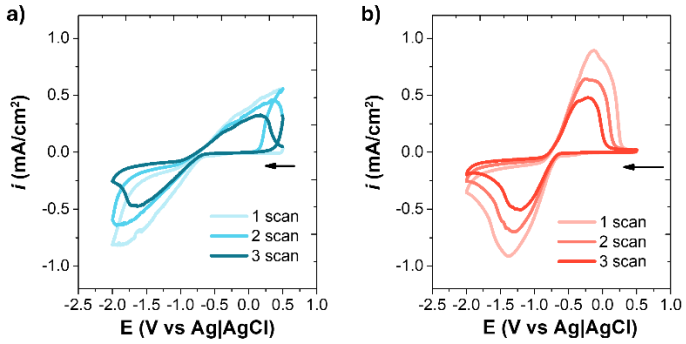

Figure 4. CVs recorded for a) Slurry D_1 (C-dot alone, 2.7 mg coated material, 1.35 mg AQ), and Slurry E_1 (C-dot/AB, 1.9 mg coated material, 0.95 mg AQ) obtained by ultraturrax stirring

Figure 4a shows that the new slurry formulation containing only C-dot (Slurry D) at an 85:15 liquid-to-solid ratio was the most effective in preserving electrode integrity over successive scans. However, some polarization effects may still occur, indicating the need to stabilize the electrode more efficiently. However, this electrode, containing 1.35 mg of AQ as the active material, achieved an overall charge current of 0.5 mA/cm² by the third scan, indicating promising charge storage capabilities.

Figure 4b shows that ultraturrax stirring significantly improved the charge storage performance of the C-dot/AB formulation, achieving 0.9 mA/cm² (at scan 1) with only 0.95 mg of AQ. Additionally, the electrode retained 61% of its capacity over three cycles, a substantial improvement compared to the 20% retention observed with a similar AQ loading (0.7 mg) in the mechanically mixed slurry (Figure 3b). These results highlight the potential of optimized electrode preparation via ultraturrax stirring to both enhance charge capacity and mitigate the dissolution issues commonly associated with organic electrodes.

In addition to the electrochemical investigation of C-dot-based electrodes, a screening was carried out on the potential electrochemical activity of various waste materials provided by the project partners. The following by-products and processing residues were considered: wine lees, tomato peels, citrus pulp, dry olive pomace extract, dry grape marc extract, and dry tomato extract.

These materials were suspended in an electrolyte solution and dispersed using an Ultraturrax homogenizer (where necessary). To evaluate the electrochemical performance of the waste materials in terms of storage capacity and cyclability, cyclic voltammetry (CV) was conducted within a potential sweep range of +0.5 to –2 V vs Ag|AgCl (corresponding to 3.9 – 1 V vs Li+|Li). The working electrode (WE) was glassy carbon, the counter electrode (CE) consisted of a platinum foil, and a saturated Ag|AgCl electrode in KCl was used as the reference electrode (RE).

The tested materials did not exhibit significant electrochemical activity.

6. CONCLUSIONS

Conductive agents are crucial for improving the electrochemical performance of organic batteries. Incorporating an optimal amount of C-dots into conventional slurries enables the development of innovative organic cathodes that can effectively address the inherently low electronic conductivity of quinones. Preliminary findings indicate that the C-dot/AB combination significantly enhances the electron storage capacity of the resulting cathode. Moreover, the use of ultraturrax stirring over the mechanical mixing and the optimization of the liquid-to-solid ratio in the slurry highlight the importance of process parameter control. This approach presents a promising strategy for advancing the next generation of sustainable lithium batteries based on organic materials.