Environmentally friendly electrode materials for solid-state supercapacitors: Green synthesis of MnO_2 nanoparticles from plant extracts

B. Mladenova, L. Soserov, M. Dimitrova, A. Stoyanova
Institute of Electrochemistry and Energy Systems, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., bl. 10, 1113 Sofia, Bulgaria

Recent advances in the field of nanotechnology and nanoscience are focused on the development of new materials with diverse structures and shapes using a green synthesis approach that is as environmentally friendly as possible. Plant extracts, rich in natural biological compounds, have emerged as valuable resources for synthesizing nanomaterials due to their reducing and capping properties. These nanomaterials find applications across various fields such as catalysis, batteries, sensors, microelectronics, and optoelectronics, including energy storage systems. In this study, MnO_2 nanoparticles were synthesized using plant extracts of *Calendula officinalis* or *Tilia cordata*. The obtained materials were subjected to comprehensive physicochemical characterization by UV-Vis spectrophotometry, transmission electron microscopy (TEM), X-ray diffraction (XRD) and Brunauer-Emmett-Teller (BET) analysis. The successful synthesis of MnO_2 nanoparticles was confirmed. In particular, MnO_2 synthesized with extracts *of Calendula officinalis* (CO-MNO_2) showed a specific surface area four times higher (80 m^2 g^{-1}) than that obtained for MnO_2 synthesized with *Tilia cordata* (TC-MnO_2, 19 m^2 g^{-1}). There was a significant difference in their average pore diameter (13 vs. 9 nm), which can be explained by the lower percentage of antioxidant activity for CO-MnO_2 compared to TC-MnO_2, suggesting a slower formation of MnO_2 with higher BET surface area.

The electrochemical properties of MnO_2-NPs as a positive electrode material in a hybrid solid-state supercapacitor were evaluated using CV curves, galvanostatic discharge/charge and long-term tests. A carbon xerogel was employed as the negative electrode material, while a commercial membrane, Aquivion®E87-05S membrane pre-activated in 1 M Na_2SO_4, served as the electrolyte. For comparison, parallel experiments were conducted in a symmetric cell.

The obtained results showed that MnO_2 synthesized from Calendula officinalis extract exhibited the highest discharge capacitance, superior cycling stability, high current efficiency and energy density of 37 $Whkg^{-1}$ at 384 Wkg^{-1} in the voltage range of 0 to 1.6 V.

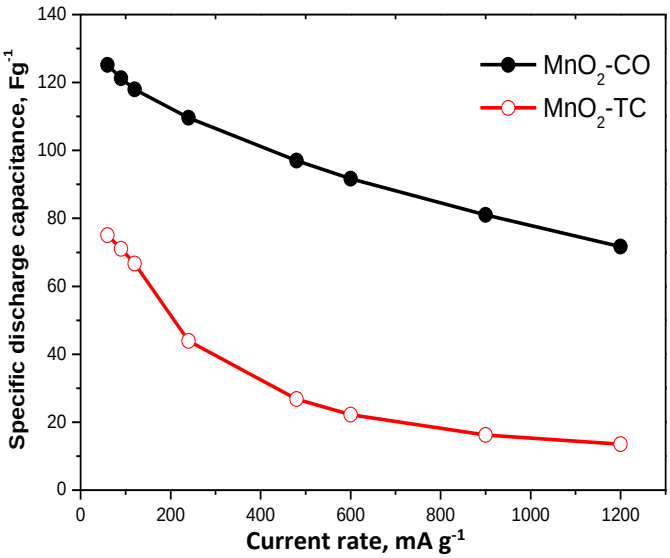

Figure 1. Specific discharge capacitance as a function of the current rate of solid-state supercapacitors with "green" MnO_2

The obtained results can be attributed to the differences in the structure and morphology of the synthesized samples. Furthermore, they underscore the potential of MnO_2 derived from Calendula officinalis extract as a promising eco-friendly electrode material for solid-state supercapacitors.

Acknowledgement: The authors are kindly acknowledged for financial support to the equipment used at the research are provided by the National Roadmap for Research Infrastructure 2017-2023 "Energy storage and hydrogen energetics (ESHER)", approved by DCM No 354/29.08.2017 under Grant Agreement DO1-160/28.08.2018.