Doctoral Dissertation
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Advanced and Sustainable Materials for Batteries and Supercapacitors

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Abstract

The endless pursuit of energy has been a fundamental driving force of human progress towards modern society. Indeed, energy is the engine that drives all human activities, making it an essential component of civilization. The Industrial Revolution marked a turning point with the widespread use of coal and the development of the steam engine, drastically transforming industrial production and urban life. Concurrently, the discovery of electricity and the invention of the battery paved the way for electrification and telecommunications. The late 19th and early 20th centuries saw the rise of internal combustion engines, so that petroleum became central in global economies and geopolitics.

In the mid-20th century, renewable sources like solar, wind, and hydroelectric power gained importance. However, their intermittent nature posed challenges, highlighting the need for efficient energy storage solutions. Batteries and capacitors started to play a crucial role in storing excess energy and ensuring a stable supply to the electric grid. In this regard, the aim of this PhD thesis is to develop novel, eco-friendly active materials and components for Li-/Na-ion batteries and supercapacitors, assessing their structural, morphological, and electrochemical properties towards the enhancement of next-generation energy storage solutions. The outcome of the work contains five chapters, comprising two introductory section ones, and three chapters detailing the experimental results obtained; concluding remarks at the end of the manuscript emphasize the key takeaways, also reinforcing their importance in the broader context.

Chapter 1 deals with the basic concepts for electrochemical energy storage devices, their characteristics and working principles, also including a brief description of the common electrochemical characterization techniques and of the

historical developments of secondary batteries and electrochemical double-layer capacitors (EDLCs).

Chapter 2 discusses the main components in Li-/Na-based battery and in EDLC, with a particular focus on the prevalent materials and their preparation.

Chapter 3 presents an example of potential second-life use of face masks (FMs), namely their pyrolytic conversion into hard carbons, which can be used as anode materials in Na-ion batteries. This work was inspired from the relevant environmental issue displayed by the disposal of FMs after the outbreak of the COVID-19 pandemic in late 2019.

Being our main purpose, the recovery of a waste stream rather than the development of new materials for energy application, we adopted mild conditions for the carbonization process: i) no chemical pretreatment of FMs, ii) pyrolysis at 800 °C in N_2 atmosphere at ambient pressure for a relatively short time (30 min). The pyrolysis of both C-surgical and C-FFP2 resulted in highly disordered carbons, the former characterized by bigger particles (up to 100 μm, with respect to the submicrometric particles of C-FFP2). Additionally, both C-surgical and C-FFP2 were effectively tested in laboratory-scale Na-metal cells (with 1 M $NaClO_4$ in PC as electrolyte), displaying an acceptable specific capacity along with a wide range of current regimes, from C/20 to 1C.

Furthermore, as proof of concept of real battery operation, C-surgical was employed within a full Na-ion cell in combination with NVPF cathode, always using 1 M $NaClO_4$ in PC as electrolyte. The results evidence the possibility of obtaining amorphous carbon from FMs disposal in relatively mild conditions. The electrochemical performance obtained in such conditions, still to be optimized in terms of specific capacity output to comply with the current commercial application standards, represents a preliminary confirmation of the effective repurposing of disposed FMs into higher-value materials for large-scale energy storage from renewables by Na-ion batteries.

Chapter 4 explores the fabrication of separator membranes using commercial and recycled polyvinyl butyral (PVB). Membranes were synthesized via phase-inversion, incorporating a diisocyanate crosslinker to form a polyurethane network.

These membranes were then tested from a physicochemical perspective and later employed as separators in lab-scale lithium-based electrochemical cells. The PVB-based membranes demonstrated excellent thermal and mechanical stability

(with a degradation temperature above 300°C and a storage modulus of up to 220 MPa), good durability, and strong interfacial compatibility with lithium metal during plating and stripping for nearly 800 hours. As proof of concept, within the framework of the H2020 European SUNRISE project, the same membranes were prepared using recycled PVB (re-PVB) sourced from automotive glass waste. The re-PVB-based membrane was tested in a Li plating/stripping process, showing long-term durability and compatibility with lithium metal. The membrane was subsequently used as a separator in a Libased half-cell with an LFP cathode, achieving a stable capacity of 120 mAh g^{-1} at C/10 over 250 cycles (approximately 80% of the LFP practical capacity). This demonstrated superior cycle stability and rate capability, underscoring the practical potential and feasibility of using recycled PVB membranes as separators in lithium-ion batteries. This approach also highlights the possibility of more sustainable and environmentally-friendly battery production in a circular economy context.

Chapter 5 presents a novel gel polymer electrolyte (GPE) for Na-based electrochemical double-layer capacitors (EDLCs). Bisphenol A ethoxylate dimethacrylate (BEMA) was employed in combination with poly(ethylene glycol) methyl ether methacrylate (PEGMEMA) as a reactive diluent to produce a highly crosslinked polymer network via UV photopolymerization. The methacrylate-based membranes were swollen with a glyoxal-based electrolyte, specifically 1M NaTFSI in TEG:PC (3:7 by weight), forming a glyoxal-methacrylate-based gel polymer electrolyte (GM-GPE).

In terms of thermal stability, GM-GPE demonstrated improved stability compared to the liquid electrolyte. Its electrochemical stability window (ESW) was suitable for energy storage applications, and most importantly, GM-GPE effectively protected the aluminum current collector from oxidative corrosion. The system was then successfully used in electric double-layer capacitors (EDLCs) with a two-electrode setup and activated carbon. As expected in solid-state systems, interfacial transfer resistance led to a higher ohmic drop, resulting in lower specific energy and power. However, the ionic conductivity remained satisfactory, and capacitance values were fully comparable to those of the liquid system, avoiding the typical reductions in ionic conductivity and capacitance often seen in polymer electrolytes. These promising results suggest that the newly developed GM-GPE.

could open the door to further research and optimization in the field of polymer electrolytes for EDLCs

The sourcing and processing of materials play a crucial role in the design and fabrication of energy storage devices. Focusing on abundant, cheap, ecofriendly and recyclable materials is essential to reduce environmental impact and support a sustainable energy transition. This PhD thesis provides a solid background for further investigation into innovative, advanced materials for energy storage systems, contributing to the advancement of key technologies for the development of a more sustainable electricity-drive society.