Synthesis and characterization of carbon cathode materials for secondary lithium-oxygen cells

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The presented research is focused on the development and optimization of carbon-based cathode materials for lithium-oxygen batteries (Li-O_2). The main goal is to establish synthesis methods and structural modifications that significantly improve the electrochemical performance of obtained materials, especially in terms of the first cycle discharge capacity, reversibility, and cyclability. This study proposes different routes to the synthesis of carbon cathode materials, like carbon nanofibers (CNF), activated carbons (ACs), CNF/AC composite, and carbon aerogels. Additionally, wide range of functionalization techniques via *in-situ* and *ex-situ* approaches is presented. The in-depth investigation of the influence of parameters of the synthesis on the properties of obtained materials is conducted with the utilization of various techniques, including SEM, specific surface area (SSA) and porosity measurements, Raman spectroscopy, XRD, XPS, and elemental analysis. Also, the impact of changes in properties of materials on the performance of Li-O_2 battery is researched via electrochemical measurements. The experimental section of the work is divided into subsections, each targeting specific group of materials and their performance as cathode in the lithium-oxygen battery.

Firstly, carbon nanofibers were synthesized via chemical vapor deposition (CVD) on the conventional nickel-based catalyst using propane as the carbon source. A correlation between temperature of synthesis and CNF properties was observed, with higher temperatures leading to increased SSA and total pore volumes, which reached the highest values at 550°C. However, the best electrochemical performance, defined by the highest first cycle discharge capacity, was achieved by CNF synthesized at 500°C and thus this temperature was selected for the study regarding nitrogen doping.

During the functionalization by *in-situ* methods, ammonia, acetonitrile, and melamine were added to the stream of raw materials in CVD synthesis. On the other hand, doping via *ex-situ* approach was conducted with ammonia by hydrothermal process or by subsequent ammonization. All of the conducted processes led to the incorporation of nitrogen into the structure of CNF, which was confirmed by elemental analysis and XPS measurements. Among *in-situ* methods, the combined use of ammonia and melamine resulted in the largest amount of N atoms build-into CNF. On the other hand, hydrothermal doping conducted at 180°C and the mass ration of 1:25 (CNF : NH_3) led to the highest nitrogen content in CNF from all *ex-situ* processes. Nitrogen doping significantly enhanced battery performance, especially in terms of discharge capacity, reversibility, and cycling life.

As an alternative to the standard catalyst, a novel approach using free-standing nickel oxalate was developed for CNF synthesis. Although CNFs were successfully synthesized at all tested temperatures, the process yields were lower compared to the standard catalyst system. Carbon nanofibers grown on nickel oxalate displayed lower SSA, total pore volume, and mesoporosity, and no consistent correlation between these physical parameters and battery performance was observed. Nevertheless, CNF obtained at 500°C demonstrated the best electrochemical performance, reinforcing the conclusion that 500°C is an optimal synthesis temperature across different catalyst systems.

In order to investigate the influence of porosity on the performance of cathode materials, activated carbons were prepared via chemical activation with potassium hydroxide and phosphoric acid, to obtain highly microporous and mesoporous materials. The obtained results clearly indicated that dominant mesoporosity of a material has a beneficial effect of its performance as cathode in lithium-oxygen battery.

Based on the obtained results, new catalyst composed of highly mesoporous AC and nickel oxalate was proposed. Such approach enabled the synthesis of CNF/AC composite that allowed to utilize the best properties of both group of materials – well-developed porosity of activated carbon and catalytic activity of carbon nanofibers. The influence of the nickel content in the initial catalyst on the properties of obtained composite was researched. The observed synergy of properties of AC and CNF improved the performance of $Li-O_2$ battery, especially visible in increased capacity, better reversibility, and superior cyclability in comparison to CNF or AC alone, or their simple physical mixture. The most promising composite, obtained on the catalyst containing 50 wt. % of Ni, was thoroughly investigated, by conducting electrochemical measurements at wide range of current densities and different cut-off capacities.

Additionally, a new route for the preparation of carbon aerogels was proposed. Presented method based on homogenization, freeze-drying, and lyophilization of aqueous dispersion of carbon nanotubes (CNT), enabled the synthesis of carbon aerogels in relatively straightforward approach, without the need of excessive amounts of cross-linkers or prior functionalization of carbon material. The concentration of CNT in the initial dispersion was found to critically influence the final aerogel structure and battery performance. Aerogels synthesized at a concentration of 4.5 mg ml^{-1} delivered the highest first-cycle discharge capacity and showed strong potential as free-standing cathode materials. Post-mortem analysis of the cathodes and electrochemical impedance spectroscopy provided further insight into the reaction mechanisms and resistive behavior of the battery system.

In conclusion, in this work, the extensive research was conducted on the preparation and characterization of various cathode material groups. Multiple strategies to enhance the performance of $Li-O_2$ batteries were proposed, including nitrogen doping, composite formation, and the development of free-standing cathodes. Among the tested materials, carbon aerogels achieved the highest first-cycle discharge capacities, while the CNF/AC composites demonstrated the most promising cyclability. Additionally, nitrogen doping was proven to improve the first-cycle discharge capacity, reversibility, and long-term cycling performance of carbon nanofibers, highlighting the potential of this functionalization technique to enhance cathode behavior. At the same time, the need to optimize synthesis parameters across all material groups in parallel with advancing lithium-oxygen battery operation was emphasized.