Investigation of Organic Materials for Lithium Batteries

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Certificate of original authorship

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as fully acknowledged within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

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Jinqiang Zhang

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Abstract

The performances of lithium-based batteries can be significantly influenced by the electrolyte and cathode materials. In this PhD project, functional organic materials were synthesised and applied as electrolyte and cathode components for lithium-ion (Li-ion) and lithium-oxygen (Li-O_2) batteries to improve overall performances. Theoretically, organic materials can be tailored with functional groups to fit various purposes, making them suitable for battery applications. Post-synthesis techniques such as field emission scanning electron microscopy, X-ray diffraction, and Fourier transform infrared spectroscopy were used to characterise the physical properties. Electrochemical analyses including galvanostatic discharge-charge method, cyclic voltammetry, linear sweep voltammetry, and impedance spectroscopy were conducted to determine the electrochemical performance of the materials.

Porous polymer membranes based on poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) are prepared using the breath-figure method. The as-prepared PVDF-HFP porous membrane showed a highly ordered honeycomb-like structure. The highly porous structure could absorb large quantities of liquid electrolyte, resulting in a high ionic conductivity. Moreover, the non-combustible PVDF-HFP membrane could significantly enhance safety properties of Li-ion batteries compared to the one using a conventional Celgard separator. The combination of the PVDF-HFP membrane with liquid electrolyte resulted in a higher capacity and prolonged cycle life.

Further investigation on coating poly(methyl methacrylate) (PMMA) on PVDF-HFP porous membranes to achieve hierarchical structures with sandwich-like morphology was

carried and studied. By the combination of porous PVDF-HFP and PMMA with higher affinity towards liquid electrolyte, the ionic conductivity was further improved. As a result, the electrochemical performance of Li-ion battery was significantly enhanced.

A bi-functional organic catalyst poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl methacrylate) (PTMA) was synthesized by a two-step method. The unique properties of PTMA during n-doping and p-doping could facilitate the discharge and charge processes, respectively. It was discovered that the discharge capacity increased and the charge over-potential was reduced. The mechanism investigation showed that it was the functional N-O radical interacting with oxygen and Li_2O_2 to catalyse the battery reactions. As a result, the cycling life of the Li-O_2 battery was significantly prolonged.

Further investigation of employing co-polymers as binder in the cathode for Li-O_2 batteries was carried out. The binder was synthesized by co-polymerizing methyl methacrylate (MMA) and 2,2,6,6-tetramethylpiperidinyloxy-4-yl methacrylate (TMA) monomers. The ratio between both monomers was also studied. The results indicated that the direct contact of co-polymer binder and liquid electrolyte would transfer it into a gel polymer electrolyte membrane which enabled the catalytic N-O radical group to function as restricted redox mediator. The electrochemical performance of Li-O_2 batteries can be further enhanced by employing PTMA.

An investigation of the mechanism when tetrathiafulvalene (TTF) was used in Li-O_2 batteries in the presence of LiCl was studied. It is revealed that the addition of LiCl in the electrolyte completely changed the functional mechanism of TTF in Li-O_2 batteries. Instead of functioning as a solution-based redox mediator, the combination of TTF and LiCl resulted in a deposition of an organic conductor on the surface of Li_2O_2, providing additional ways for electron transference. As a result, the cycling efficiency was improved, and with the use of porous graphene as cathode material the cycle life was prolonged.

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1. **Zhang, J**.; Sun, B.; Zhao, Y.; Kretschmer, K.; Wang, G., Modified tetrathiafulvalene as an organic conductor for improving performances of Li-O_2 batteries, *Angewandte Chemie International Edition* **2017**. Accepted, in press. DOI: 10.1002/ange.201703784, and DOI: 10.1002/anie.201703784.

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