Abstract

Lithium-sulphur (Li-S) battery system has been investigated since the 1970s, but it has not been possible to commercialise them yet. Due to its complicated working mechanism and poor understanding of these mechanisms, has led to underperforming Li-S battery.

This thesis was devised as a fundamental study to understand different properties of battery components, which influence the performance of Li-S system. To develop new types of analytical techniques to acquire more knowledge about the properties of redox intermediates formed during battery operation.

In the first part of the thesis we successfully study the parameters of the composites, electrolytes and separators that highly influence the performance of Li-S battery. We demonstrated that surface area of the host matrix has a very important role in encapsulating the sulphur and its redox intermediates. However with proper design of a relatively low surface area graphene/cellulose composite, a high electrochemical performance along with good cyclability can be achieved. This, points out the importance of proper engineering of cathode, which along with selection of binder and electrolyte can have large influence on the cycling stability of Li-S batteries.

We demonstrate that Li-S battery cycling can be stabilised using catholyte solutions (electrolytes with dissolved polysulphides) or solvent-in-salt (SIS) electrolytes system which prevents cathode dissolution and polysulphides migration. Finally, we clearly showed the importance of effective separation between the sulphur cathode and the lithium anode in Li–S batteries, which was achieved with the use of Li ion selective separators that block lithium polysulphides from diffusing away from the cathode electrode but allow only lithium ions to diffuse through them.

In the second part of the thesis our focus was on the development and use of several different analytical tools, which helped us to understand the working mechanism of Li-S battery, and the redox intermediates that were produced in the electrode during battery operation. We developed new types of in operando mode and ex-situ mode analytical techniques with the help of UV-Visible spectroscopy (UV-Vis), X-ray Absorption Near-Edge Structure (XANES), MAS NMR and 4-electrode Swagelok cell to get an insight of Li-S battery system.

For the very first time in operand UV-Vis spectroscopy was successfully used to understand the formation of lithium polysulphides at different potentials. Measurements of catholyte

solutions with chemically synthesised polysulphides enabled us to develop procedure where polysulphide can be determined in quantitative and qualitative way. Based on calibrations we had the possibility to compare different Li-S battery systems and evaluate influence of components on the polysulphide diffusion and shuttling mechanism

XANES measurements were successfully conducted at Elettra-Synchrotron Trieste, on in operando mode cell, chemically synthesised lithium, sodium polysulphides (which were used as standards) and ex-situ battery components and electrodes. The results reveal the detailed understanding of the mechanism of polysulphide formation and knowledge about the interactions of sulphur and polysulphides with a host matrix and electrolyte. Complementary information about the lithium species within the cathode and chemically synthesis polysulphide intermediates are obtained by using ^{7}Li MAS NMR spectroscopy.

A modified 4-electrode Swagelok cell was successfully used as an in situ analytical tool for the detection of soluble polysulphides in the electrolyte during Li-S battery operation. The cell was also used as an effective and a reliable in situ analytical tool to study how different electrolytes and electrode architectures impact the stability of the Li-S battery.

The setups that were developed for the in operando UV-Vis, XANES and 4-electrode measurements can be viewed as valuable analytical tools that can be used further to understand the sulphur environment in Li–S batteries.