Carbon nanotube hybrid electrodes for high performance Li-ion batteries

Introduction

LIBs are used in a variety of electronic devices such as mobile phones and smart watches to electric vehicles. The invention of LIB's has led to the creation of the smartphone, mainly due to the increased capacity and portability these batteries provide over older NiCd (nickel cadmium) batteries. This discovery has led to an explosion in portable consumer electronics, as they now have enough energy available to run high power intensive tasks that would not be possible without LIBs. In recent years, a spotlight has been shun on LIBs because these batteries can be used in the new foldable and flexible electronics of the future, due to the inclusion of carbon nanotubes (CNTs) into the electrodes. CNTs possess increased mechanical strength and improved conductivity over older conductive agents while still remaining cost-effective. Their properties provide the support needed in freestanding electrodes. These electrodes contain no current collector and therefore require a strong material to hold their shape for the flexible electronics of tomorrow.

This project will focus on the use of CNTs in LIBs in order to make freestanding electrodes. Different conductive agents will be tested in order to compare to CNTs to investigate CNT conductivity and their mechanical strength in freestanding electrodes. Etching will be done to produce the freestanding electrodes as it is a simple and time effective solution with the materials at hand. Etched copper and aluminium current collector electrodes will be compared along with different binders in order to find the most suitable formulation of materials to withstand the freestanding conversion process. Aqueous and organic solvents will be used with their respective binder. Half cells will be built and undergo galvanostatic cycling in a potentiometer.

Method

The cathode was made by formulating a slurry. This involves adding active and inactive material together with a suitable binder and solvent which creates a thick slurry which is then spread onto the current collector, usually a thin sheet of aluminium, and dried in a vacuum oven. The slurry was mixed using a mortar and pestle. Once dry the electrode could be cut out using an electrode cutting tool which would then be assembled in a Swagelok cell and cycled at a rate of C/2. This general method was chosen as it was the simplest method to produce a cathode. Slurries of various ratios and of materials and thickness of cathode were made and tested throughout the project until an optimised slurry ratio was chosen. The freestanding electrodes were made by etching the current collector using $FeCl_3$, which were then washed, dried and cycled at C/2. As the project title pertains, CNTs were used as the conductive agent but carbon black (CB) was also used. Both were tested in separate cathodes and also a mixture of the two were used. $LiCoO_2$ (LCO) was used as the active material. Polyvinylidene fluoride (PVdF), sodium carboxymethyl cellulose (Na CMC) and polyvinylidene

fluoride-co-hexafluoropropylene (PVdF-HFP) pellets were used as binders. Water, N-Methyl-2-pyrrolidone (NMP) and acetone were used as solvents.

Results

A variety of materials were tested but it was found during testing that cells made from organic binder and solvent outperformed aqueous binder and solvent in terms of capacity retention and overall capacity. In cells that used Na CMC as a binder and water as a solvent it was found that the capacity would quickly reduce meaning irreversible reactions were occurring with the lithium in the cathode that was preventing them from cycling. It was theorised that this was due to the water present during the formation of the slurry and could have been trapped in the cathode once spread and dried. Trapped water can benefit the cell in terms of increased conductivity but too much will lead to unwanted side reactions as was probably the case in cells using Na CMC and water.

Seven freestanding electrodes were made however only five of those could be cycled. This is due to the materials used in these cells, LCO, CNTs and PVdF, whereas the failed cell contained CB, Na CMC and LCO and the other failed cell contained CB, CNTs, Na CMC and LCO. The CB did not have the mechanical strength that the CNTs in the other cells possessed, which lead to the electrode to disperse once the current collector was removed. This highlights the importance of CNTs in freestanding electrodes as they can build stronger and tougher cells that are also flexible with impressive conductivity. For the other failed cell it is possible not enough CNTs were present, but also the Na CMC may have made the cell too flexible whereas PVdF made more rigid cells. Na CMC could be more useful in other freestanding electrode production processes other than etching.

Conclusion

To conclude, the cathode of a lithium ion battery was made into a slurry using LCO, conductive material, binder and solvent that was then spread on a current collector and dried in a vacuum oven. These cathodes were cycled via galvanostatic cycling in a potentiometer with freestanding electrodes being produced later by etching the current collector. It was found that the ratio of 80:10:10 of NMC:CNT:PVdF with NMP solvent on an aluminium (Al) sheet current collector gave the best results. Capacity loss from unstable solid electrolyte interphase (SEI) layer formation with irreversible reactions with Li ions was a major problem for each cell cycled but the effect it had could be lessened by eliminating as much water from the cell as possible and using CNTs, PVdF and NMP.

Freestanding electrodes widen the application of Li ion batteries for use in lighter electronics like smartwatches and flexible electronics like fordable smartphones, however they are limited by lower capacity due to the lower conductivity levels due to the lack of current collector. Future work should revolve around improving the conductivity of the electrodes to increase the capacity and lifetime of the cell. Etching is a viable technique although environmental concerns would be raised because of the waste compounds produced and its use of harsh solvents.