

Short communication

A prelithiated carbon anode for lithium-ion battery applications

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Abstract

A prelithiated carbon anode has been produced incorporating stabilised lithium metal powder. Electrodes have been fabricated which are partially lithiated, to compensate for the irreversible capacity of the anode material and combined with conventional Li-ion cathode materials. Fully lithiated anodes have also been fabricated and combined with non-lithiated cathode materials to produce a Li-ion cell.

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1. Introduction

With current Li-ion technology, the lithium in the cell is provided by the cathode, which leads to limitations in performance. Lithiated cathode materials tend to have lower specific capacities than non-lithiated cathode materials. For example, LiCoO_2 has a capacity of around 155 mAh g^{-1} . In comparison, a non-lithiated cathode material like V_6O_{13} has a theoretical capacity of 417 mAh g^{-1} . It would be much more efficient to supply the lithium in the cell as lithium metal rather than LiCoO_2 .

We have developed a method of fabricating a lithiated carbon electrode, using a stabilised lithium metal powder [1] (SLMP) developed by FMC Corporation. This technology can be used to produce a Li-ion cell in two ways:

1. A partially lithiated anode can be fabricated with SLMP added, to compensate for the first cycle irreversibility. This is used with a conventional Li-ion cathode.
2. A fully lithiated anode can be produced, to use with a non-lithiated cathode.

As the irreversible capacity of the anode material can be compensated by addition of the lithium powder, the range of

potential anode materials that can be considered is increased, as the irreversible capacity of the anode material is no longer a limiting factor. This opens up a wide range of materials with higher reversible and irreversible capacities that can be considered.

There have been previous attempts to add lithium to the anode, such as by chemical lithiation [2] or the use of a sacrificial lithium electrode [3]. However, there are several advantages of using the stabilised lithium metal powder incorporated into the electrode:

1. The quantity of lithium powder added can be adjusted and controlled.
2. The lithium powder is uniformly distributed throughout the electrode.
3. The stabilised lithium metal powder can be handled safely in dry air.
4. The powder reacts when electrolyte is added to the cell, producing an SEI layer and lithiated carbon.
5. After formation, there is no residual lithium metal—a Li-ion cell is produced.

2. Experimental

The stabilised lithium metal powder is not compatible with some solvents, including *N*-methyl pyrrolidinone (NMP),

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dimethyl formamide (DMF) and dimethyl acetamide (DMA). Unfortunately, these are the only three common solvents for PVDF, the most widely used binder in lithium-ion cells. However, the powder is compatible with most hydrocarbons and some ethers, which allows a range of alternative binders to be used. All the tests described in this paper used anodes that were coated on a standard two zone industrial coater. The coater was located in a dry room, with a typical dew point of -40°C . Electrode slurries containing the stabilised lithium metal powder were made using standard mixing equipment.

Two types of cell were used in the experiments, a three electrode “half” cell and a two electrode soft pack cell. The three electrode cell had a working electrode area of 1.2 cm^2 . The soft pack cell was based on folded stack technology [4], but with only two single sided electrodes. The area of each electrode was around 14 cm^2 . The electrolyte in all the tests was $1.2\text{ mol dm}^{-3}\text{ LiPF}_6$ in EC/EMC (Merck). The three electrode cells were tested at ambient temperature with a Macpile II rig. The two electrode cells were tested in an environmental chamber set to 20°C , using a Maccor 4200 rig with multi-range capability.

Composite cathodes containing LiCoO_2 or LiV_3O_8 were made in the conventional way using PVDF binder and carbon additive, and coated onto an aluminium foil current collector.

3. Results and discussion

3.1. Partial lithiation to compensate for irreversible capacity

Three electrode cells were prepared with stabilised lithium metal powder incorporated in the anode, and a LiCoO_2 counter electrode and lithium reference electrode. Fig. 1 shows the first charge curves for two anodes with respect to the lithium reference electrode; a normal graphite anode and a graphite anode containing 1.93 wt% SLMP as a percentage of carbon and lithium content, tested at 0.3 mA. From

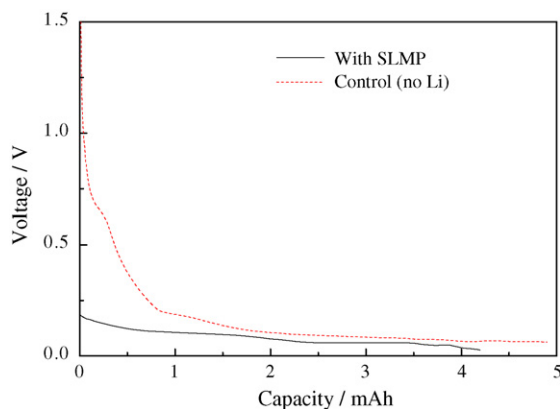


Fig. 1. First charge curves of two anodes with respect to a lithium reference electrode; a normal graphite anode and a graphite anode containing 1.93 wt% SLMP as a percentage of carbon and lithium content.

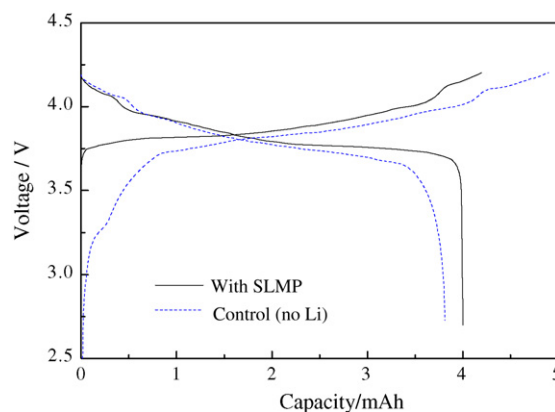


Fig. 2. Comparison of first charge and discharge curves of a cell containing a partially lithiated electrode and a control cell.

this figure, it can be seen that the initial voltage of the partially lithiated carbon electrode is much lower than that of the control cell, at less than 0.2 V, indicating that the partial lithiation reaction has occurred. In addition, the capacity due to SEI formation, around 0.6 V wrt Li/Li^+ , is not present for the cell containing the partially lithiated anode.

The first charge and discharge curves for a three electrode cell containing a partially lithiated electrode and a control cell, are shown in Fig. 2. The initial OCV of the cell containing the partially lithiated anode was 2.86 V. This cell required less capacity on charge and provided more capacity on discharge leading to increased first cycle efficiency. The first cycle efficiency of the cell containing the partially lithiated electrode was 95.4%, compared to 77.9% for the control cell. These cells were not fully optimised and we would predict an improvement of 5–15% for an optimised system, depending on the irreversible capacity of the carbon material.

Two electrode soft packaged cells have been fabricated containing either non-lithiated or partially lithiated carbon electrodes and LiCoO_2 cathodes. An improvement in first cycle efficiency was observed for cells containing partially lithiated carbon electrodes. Fig. 3 shows the cycle perfor-

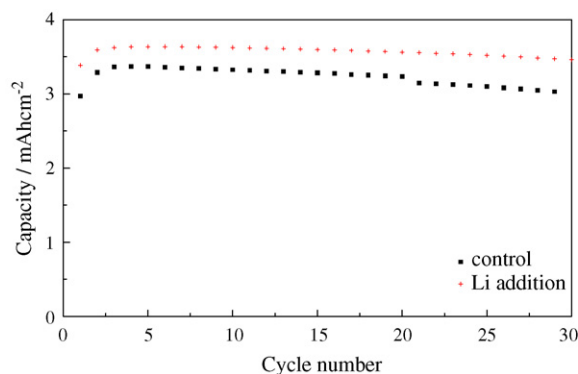


Fig. 3. Comparison of cycle performance of a cell containing a partially lithiated anode with a control cell.

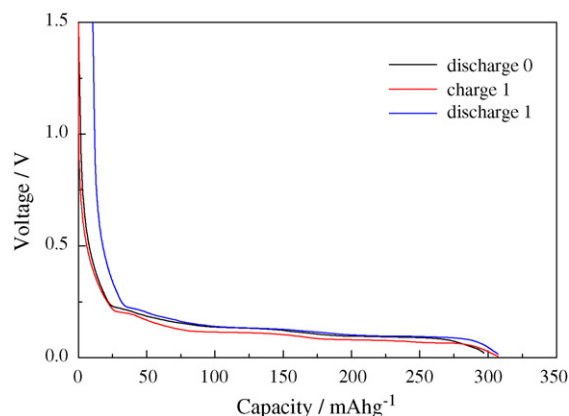


Fig. 4. Initial discharge curve and first cycle data for a cell containing a fully lithiated anode.

mance of two cells. The data is plotted in terms of capacity per unit area of cathode, indicating the improvement in utilisation of the cathode if compensation for the irreversible capacity of the anode is accounted for. This demonstrates that an improvement in cell capacity can be achieved if the specific capacity of the cathode is maintained and combined with an increased capacity anode, or, if the specific capacity of the cathode is reduced to match the anode, an improvement in energy density is achieved as the cathode weight is reduced.

3.2. Fully lithiated anode combined with a non-lithiated cathode

This electrode combination opens up a much wider range of possibilities in terms of improvement in energy density, due to the higher specific capacities of non-lithiated cathode materials compared to LiCoO_2 .

Small three electrode test cells were fabricated containing a fully lithiated carbon anode and lithium counter and reference electrodes. These were tested at 0.164 mA cm^{-2} between voltage limits of 0.005–1.50 V. Such cells had initial open circuit voltages close to 0 V, indicating the formation of LiC_x . The initial discharge curve and following cycle data of one cell are shown in Fig. 4.

We have previously reported initial cell data for a Li-ion cell containing a lithiated carbon anode and a V_6O_{13} cathode [5]. Further evaluation has been carried out using a LiV_3O_8 cathode material. The lithium contained in this structure is not removable on charge. Two electrode soft packed cells have been produced containing a fully lithiated graphite anode and a LiV_3O_8 cathode. Fig. 5 shows the first discharge and charge curves for one cell at C/20 rate. The data are plotted in terms of utilisation of LiV_3O_8 . An initial capacity of 256 mAh g^{-1} for LiV_3O_8 was measured. The cycle performance of this cell is shown in Fig. 6.

This data confirms the concept proposed in this paper that Li-ion cells can be produced using non-lithium providing

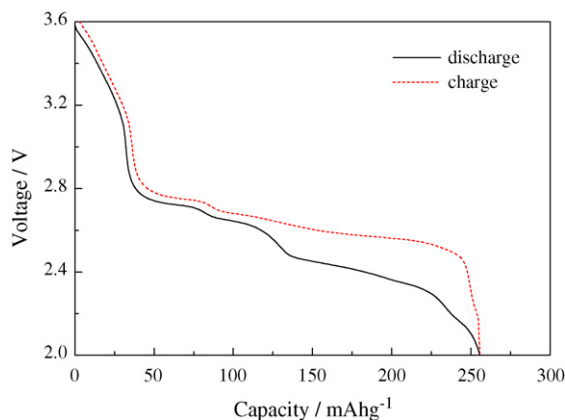


Fig. 5. First discharge and charge curves of a cell containing a fully lithiated graphite anode and a LiV_3O_8 cathode.

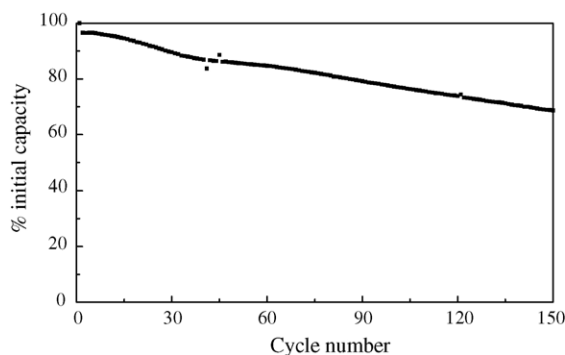


Fig. 6. Cycle performance of a cell containing a fully lithiated graphite anode and a LiV_3O_8 cathode.

cathode materials and incorporating stabilised lithium metal powder as the source of lithium for the cell.

4. Conclusions

The use of stabilised lithium metal powder to produce a fully lithiated carbon anode which can be combined with a non-lithiated cathode to form a Li-ion cell has been demonstrated. The powder can also be used to compensate for the irreversible capacity of the anode in a conventional Li-ion cell to give an improvement in cell capacity.

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