A lithium ion cell containing a non-lithiated cathode

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Abstract

Lithium ion cells have been constructed with a stabilised lithium metal powder incorporated in the anode. The powder can be used to compensate for the irreversible capacity of the anode, allowing anode materials with large reversible and irreversible capacities to be used. The powder also enables high capacity, non-lithiated cathode materials to be used in lithium ion cells. The stabilised lithium metal powder is safe to use in dry air, provided reasonable safety precautions are followed.
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1. Introduction

Lithium ion battery technology has been very successful in the decade or so since it was introduced. Improvements in electrode materials and cell manufacturing techniques have doubled the capacity of the standard 18,650 cell size. However, there is a perception that there is little scope for further increases in capacity with the existing electrode materials, typically graphite and lithium cobalt oxide. There are promising new cathode materials like $LiFePO_4$ [1] and $LiMn_xNi_xCo_{1-2x}O_2$ [2]. These are safer and potentially cheaper than $LiCoO_2$, but they do not offer a big increase in cell capacity. Therefore, the two main prospects for higher cell capacities are anode materials like tin and silicon, and non-lithiated cathode materials.

Tin and silicon have the high theoretical capacities of 990 and 4200 mAh g^{-1}, respectively, based on $SnLi_{4.4}$ and $SiLi_{4.4}$. Despite many years of development, the commercial adoption of any of these potentially large capacity materials remains elusive. The problem of the large volume expansion associated with lithium intercalation can be managed to some extent with inactive frameworks and control of the particle size [3]. However, the large irreversible capacity on the first cycle requires a secondary source of lithium available within the cell.

Non-lithiated cathode materials were widely investigated for use with lithium metal anodes, in cells based on polyethylene oxide electrolytes. Vanadium oxides such as V_6O_{13} and LiV_3O_8 have capacities of at least double that of lithium cobalt oxide, though at a lower average discharge voltage [4,5]. These materials are inherently safer than lithiated cathode materials because they cannot be overcharged. To be used in a lithium ion cell, an alternative source of lithium must be provided. The lower voltage is not necessarily a problem, given reduction in the operating voltage of electronic circuits.

Even for graphites with low irreversible capacity, methods of adding extra lithium to lithium ion cells to compensate for the irreversible capacity have been investigated. These include chemical and electro-chemical pre-lithiation [6,7], and the use of sacrificial third electrodes, typically lithium foils [8]. An alternative approach has recently been introduced, using a stabilised lithium metal powder [9]. The stabilising layer allows the powder to be handled in a dry room, unlike normal lithium powder, which can only be used safely in an argon filled glove box. This paper describes experiments to prove the usefulness of the powder, to compensate for the anode irreversible capacity, or to allow non-lithiated cathodes to be used, or both.

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2. Experimental

The stabilised lithium metal powder is not compatible with various solvents, including *N*-methyl pyrrolidinone (NMP), 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. Ten percent stabilised lithium metal powder content means the lithium:carbon molar ratio was 1:60, to compensate for the irreversible capacity. One hundred and ten percent content means the lithium:carbon molar ratio was 11:60, to compensate for the irreversible capacity and fully lithiate the graphite.

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 cm². The soft pack cell was based on folded stack technology [10], but with only two single sided electrodes. The area of each electrode was around 14 cm². The electrolyte in all the tests was 1.2 mol dm⁻³ LiPF₆ 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. Impedance measurements used a Solartron 1250 frequency response analyser and 1286 potentiostat.

Although the stabilised lithium metal powder is safe to use in a dry room, its safety should never be taken for granted. The key principle for safe use is good housekeeping. The powder should be kept in sealed bottles. Coating residues, and powder incorporated in electrodes, should be de-activated before disposal.

3. Results and discussion

3.1. Initial tests

The aim of the initial experiments was to prove that the stabilised lithium metal powder could be coated in a composite anode, and that the lithium was electro-active. When the powder and liquid electrolyte come into contact, the following coupled reactions are expected to occur:

$$Li\,(s) \rightarrow Li^+ + e^- \tag{1}$$

$$ROCOOR' + 2Li^+ + 2e^- \rightarrow Li_2CO_3\,(s) + RR'\,(g) \tag{2}$$

$$ROCOOR' + 2Li^+ + 2e^-$$
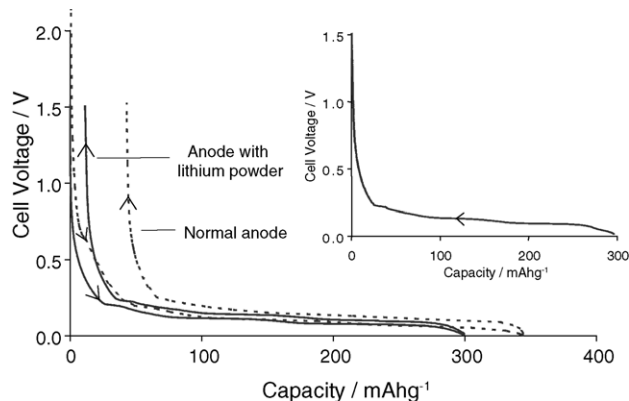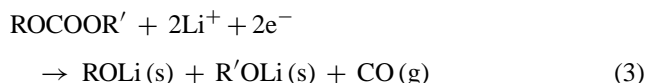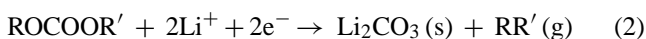$$\rightarrow ROLi\,(s) + R'OLi\,(s) + CO\,(g) \tag{3}$$

Fig. 1. Initial intercalation and de-intercalation sweep of graphite anode (inset shows de-intercalation of anode with lithium powder before full sweep).

$$6C + xLi^+ + xe^- \rightarrow Li_xC_6 \tag{4}$$

Reactions (2) and (3) are typical of the reactions that create the SEI layer. Any surplus lithium is then intercalated into the carbon. These reactions are exothermic, so it is important that they do not occur too quickly. However, it is also expected that the powder reacts more quickly than lithium foils, which can take several days to dissolve completely.

Three-electrode cells were prepared with stabilised lithium metal powder incorporated in the anode, and lithium metal counter and reference electrodes. For some cells, the ac impedance was recorded periodically with the cell at open circuit. Other cells were tested using slow sweeps. Fig. 1 shows the first lithium intercalation and de-intercalation sweeps of two anodes at ±0.2 mA, a normal graphite anode and a graphite anode containing around 110% stabilised lithium metal powder. For the normal anode, the initial cell voltage was around 3 V versus Li/Li⁺, there was a shoulder at around 0.8 V versus Li/Li⁺, and the irreversible capacity was around 12%. For the anode with lithium powder, the initial voltage was around 0.01 V versus Li/Li⁺, and there was substantial de-intercalation capacity. The shoulder at 0.8 V was not present, and the irreversible capacity was less than 4%.

Fig. 2 shows a series of impedance plots recorded at different times after filling, for an anode containing 110% stabilised lithium metal powder. The curves are offset in the Imag {*Z*} direction for clarity. The high frequency semi-circle increased in size up to around 4 h, and then stabilised. The data was fitted to a simple equivalent circuit, with a series resistor, two resistor/constant phase element (CPE) combinations and a low frequency constant phase element. This is illustrated in Fig. 3. A third resistor/CPE pair is sometimes required, if the spectrum contains three semi-circles [11]. Some fitted values for the three resistors (*R*ₛ, *R*₁ and *R*₂) as a function of elapsed time are also shown in Fig. 3. The series resistance (*R*ₛ) is the sum of the resistances of the electrolyte, current collectors and leads. The higher frequency semi-circle (*R*₁/CPE1) is usually attributed to a film on the electrode particles, and
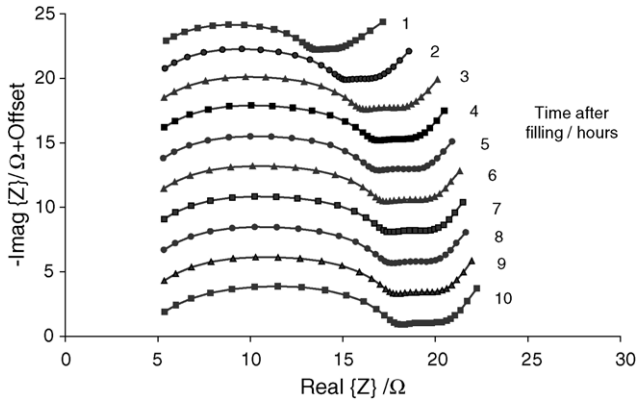
Fig. 2. Cell impedance spectra at rest following filling with electrolyte.

the lower frequency semi-circle (R_2/CPE2) to charge transfer kinetics [11].

From these results, it is evident that the stabilised lithium metal powder is present in the anode and electro-active. The shoulder at 0.8 V in the conventional anode is usually associated with the formation of the SEI layer. This consumes the lithium that leads to the irreversible capacity. For the anode containing 110% stabilised lithium metal powder, the absence of this shoulder, and the low initial voltage, indicate that an SEI layer has formed on the graphite through localised corrosion reactions of the lithium. The impedance results suggest that film formation stabilises after around 4 h, which is a convenient timescale.

3.2. Tests with lithiated cathodes

One of the properties of graphite electrodes, particularly those using meso carbon micro beads (MCMB), is their low irreversible capacity. This means that using the stabilised lithium metal powder only gives a small increase in cell capacity. However, three-electrode cells were prepared using different quantities of stabilised lithium metal powder in the anode, and cathodes based on lithium cobalt oxide. Table 1 shows the Coulombic efficiencies during the first and second cycles. All the tests were at ±0.3 mA, with voltage lim-
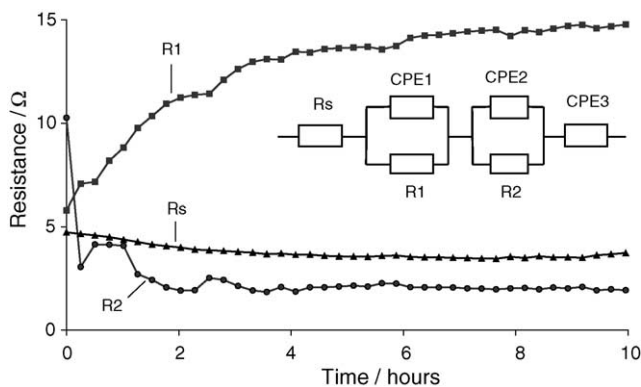
Table 1
First and second cycle efficiency for cells with lithiated cathodes

Cell	First cycle efficiency (%)			Second cycle efficiency (%)		
	0% lithium	10% lithium	20% lithium	0% lithium	10% lithium	20% lithium
#1	89.5	93.5	94.6	96.2	96.4	98.0
#2	86.5	93.0	94.4	93.4	96.6	97.5
#3	87.9	92.6	95.4	98.2	97.0	98.5

its of 4.2 and 2.75 V. The first cycle efficiencies clearly increased with increasing stabilised lithium metal powder content. However, the second cycle efficiencies were generally similar.

It is clear that the stabilised lithium metal powder can compensate for the irreversible capacity of the anode when used with a lithiated cathode. This three-electrode cell construction never gives 100% efficiency, because of the relatively thick separator layer. However, some of the remaining capacity loss on the first cycle was due to structural changes in the cathode; lithium cobalt oxide typically has a first cycle irreversible capacity of 2–3%.

3.3. Tests with non-lithiated cathodes

The success of lithium ion technology has moved attention away from non-lithiated cathode materials, and it is difficult to procure battery grade materials in bulk at present. However, samples of V_6O_{13} and LiV_3O_8 were obtained, and coated as composite cathodes with carbon and a PVDF binder. These cathodes were then used to make two-electrode soft pack cells, with graphite anodes containing stabilised lithium powder. Fig. 4 shows the first discharge and charge cycle for one cell with each type of cathode, at ±2 and ±8 mA, respectively. The LiV_3O_8 cathode gave reasonable cycle performance, with 70% of initial capacity after 80 cycles.

The successful operation of lithium ion cells with non-lithiated cathode materials is the best proof of the concept of using the stabilised lithium metal powder, because there

Fig. 3. Fitted resistance values from impedance spectra following filling.
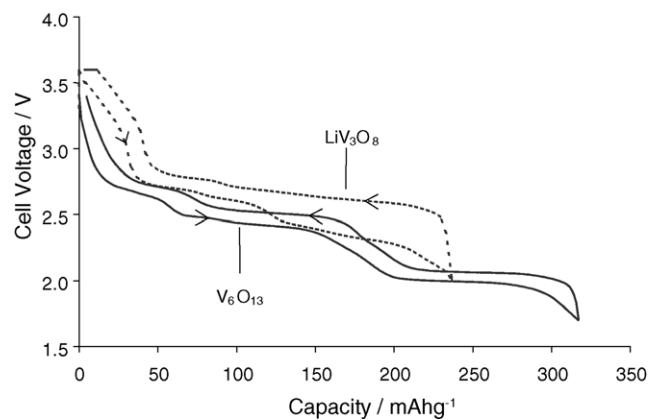

Fig. 4. First cycle for stabilised lithium metal powder anode with non-lithiated cathodes.

is no other source of lithium within the cell. Experimentally, the mixing and coating of cathodes containing non-lithiated materials has been found to be a non-trivial exercise. It cannot be assumed that processing conditions that work well for lithium cobalt oxide will produce good electrodes with different active materials.

4. Conclusions

The results described in this paper demonstrated some of the potential advantages of using stabilised lithium metal powder in lithium ion cells. The powder can be incorporated into anodes using standard slurry coating techniques. The powder is activated by contact with the liquid electrolyte, and provides the lithium both to form the SEI layer and to lithiate the carbon. The process is fast and yet controlled, typically over a 4 h timescale.

The stabilised lithium metal powder can be used with lithiated cathodes, to offset the irreversible capacity of the anode. This is most useful with anode materials with large reversible and irreversible capacities, such as tin and silicon containing materials. In addition, it means that carbons can be optimised for properties other than low irreversible capacity. Finally, the powder can be used to create lithium ion cells with non-lithiated cathodes, which opens up a much wider choice of

cathode material. Overall, we believe that use of the stabilised lithium metal powder can be considered an enabling technology, opening the door to lithium ion cells with significantly higher capacities.

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