

A composite carbon anode for use in a polymer electrolyte battery

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Abstract

A composite carbon anode has been developed for a room temperature polymer electrolyte cell using poly(ethylene oxide) (PEO). By means of half-cells the charge/discharge process has been studied and the specific capacity of the Li_xC_6 electrode as a function of cycle number determined. This has been supported by impedance analysis which has been carried out at various electrode compositions. Data on the effect of carbon content on performance and the influence of elevated temperature (40 °C) are reported. Good cycleability of a polymer electrolyte cell comprising a carbon anode, PEO-based electrolyte and a high voltage intercalating cathode LiMn_2O_4 has been demonstrated.

Keywords: Anodes; Composite carbon; Polymer electrolyte cells

1. Introduction

Commercial cells based on the principle of transferring lithium ions back and forth between the anode and cathode have recently appeared on the market [1,2]. These cells use a carbon anode in combination with a high-voltage intercalating cathode and a liquid electrolyte. Replacement of this liquid by a thin-film polymer electrolyte should in principle permit development of cells that retain the high cycle life (>1000 cycles) and energy density (>100 Wh kg^{-1}) associated with liquid electrolyte cells and, at the same time, increase safety and provide greater flexibility to the shape of the final battery.

An integral part of any lithium-ion polymer cell development programme is the need to formulate composite electrodes capable of functioning in a non-liquid environment. In addition to the presence of the active material, electronic conductor and binder that are all essential electrode components for liquid electrolyte cells, a proportion of polymer electrolyte has to be incorporated in both the anode and cathode for use in polymer cells to facilitate lithium-ion migration. In this paper, we report our results on the development of a composite carbon anode suitable for use in a room temperature polymer electrolyte cell.

2. Experimental

Composite carbon electrodes were prepared from a pitch coke. X-ray analysis of the anode material yielded the following parameters; interlayer spacing $d_{(002)}$ (Å) = 3.48, stack height L_c (Å) = 23.4, stack width L_a (Å) = 52.7. Electrodes were fabricated by coating a mix consisting of carbon of the type referred to above, poly(ethylene oxide), ethylene carbonate, propylene carbonate and lithium perchlorate on to a copper foil (12 μm) to give electrode thicknesses in the range from 50 to 70 μm . These electrodes were characterised electrochemically by fabricating lithium/polymer electrolyte/carbon half-cells of cross-sectional area 10 or 16 cm^2 . The cells were sealed in a suitable moisture-proof packaging to permit testing outside of a dry room environment.

Electrochemical testing was carried out on computer-controlled cycling equipment (Bitrode, USA). Impedance analysis performed on the cells at various states of discharge used a Solatron frequency response analyser (Model No. 1174) coupled with a Solatron electrochemical interface (Model No. 1186).

3. Results and discussion

The initial cycling behaviour of a lithium/polymer electrolyte/carbon cell at room temperature is shown

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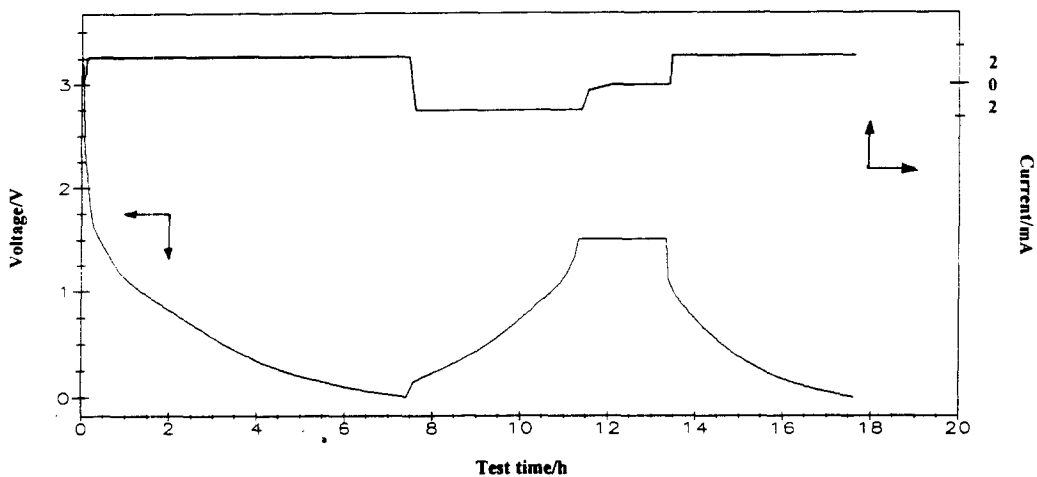


Fig. 1. Initial voltage vs. current curves for a composite carbon electrode.

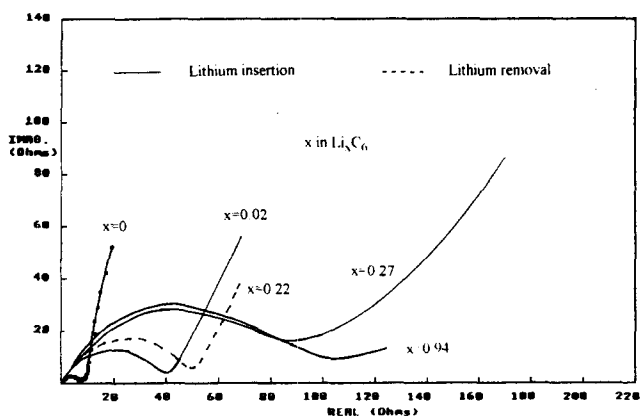


Fig. 2. Changes to the impedance spectra of a carbon electrode as lithium ions are inserted and removed from the structure; electrode area = 16 cm², charge/discharge current = 2.5 mA.

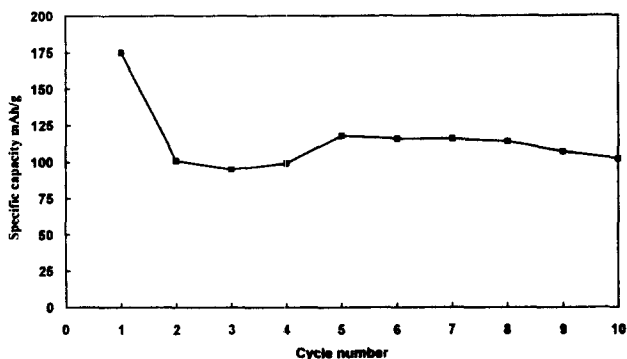


Fig. 3. Capacity of carbon electrode as a function of cycle number; electrode area = 16 cm², voltage range 1.50-0.02 V, charge/discharge current = 2.5 mA.

in Fig. 1. As lithium ions are inserted into the carbon structure the voltage falls rapidly until it approaches the cutoff voltage of 0.02 V versus Li. It can be seen that lithium ions are readily removed from the structure by increasing the voltage to around 1.5 V versus Li. As reported by other authors using similar types of

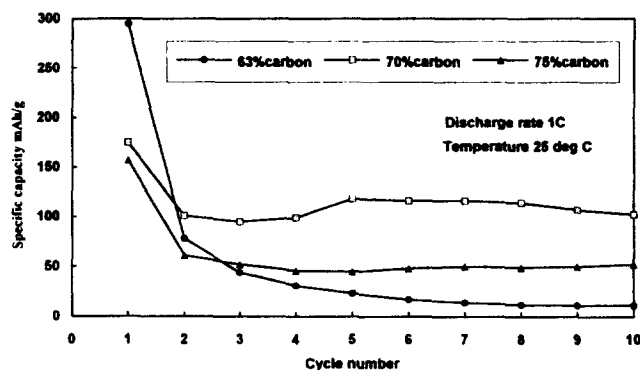


Fig. 4. Carbon content vs. performance of the carbon electrode; electrode area = 16 cm², charge/discharge current = 2.5 mA.

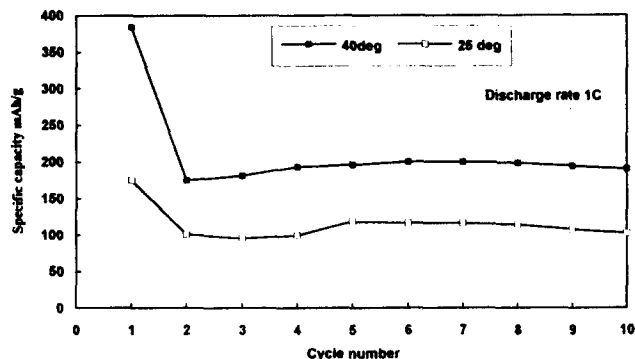


Fig. 5. Temperature vs. performance of the carbon electrode. Electrode area = 16 cm², charge/discharge current = 2.5 mA.

carbon mentioned in Refs. [3,4], a significant amount of available capacity is lost after the first cycle (about 30%) possibly as a result of solvent decomposition.

The intercalation of lithium into the composite carbon electrode during the first discharge process and its subsequent removal was investigated by recourse to impedance analysis. This was performed by arresting the discharge of the cell at a selected voltage followed by carrying out an impedance sweep before resuming

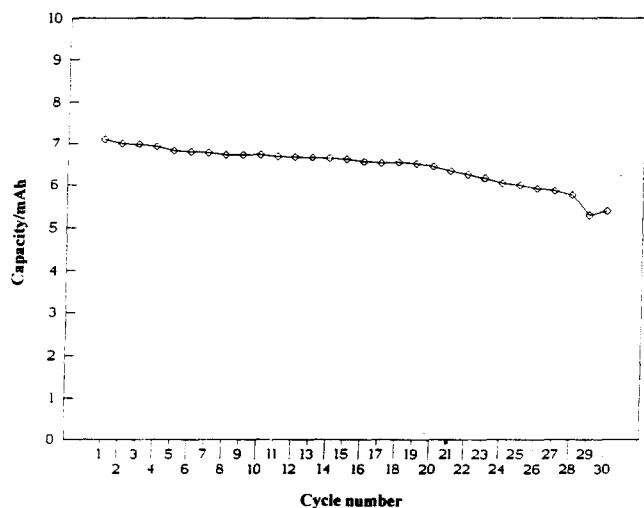


Fig. 6. Cycling performance of a carbon/polymer electrolyte/LiMn₂O₄ cell; electrode area = 10 cm², charge/discharge current = 1.5 mA.

the discharge and repeating the exercise. Fig. 2 shows the results obtained at various levels of intercalation. The spectra are all characterised by a single semi-circle that increases in diameter and height as lithium ions are inserted into the structure. As the lithium ions are de-intercalated from the carbon, the reverse is true but the size of the semi-circle does not reduce to its original dimensions. This behaviour is attributed to an increase in the impedance of the carbon electrode with progressive increase in lithiation.

The specific capacity of the composite carbon electrode as a function of cycle number is illustrated in Fig. 3. Following the fall off in capacity over the early cycles the stage is reached where the decline becomes much more gradual. Thus after ten cycles a respectable level of reversible capacity is achieved, namely 102 mAh g⁻¹. At all cycle numbers good charge efficiency was observed this being >90%. As will be seen below we have established that this value is dependent upon the electrode formulation. This clearly demonstrates that it is possible to construct a composite carbon electrode that functions in combination with a thin polymer electrolyte.

In order to optimise the performance of the composite carbon electrode the effect of varying the carbon content in the range from 50 to 85 wt.% was studied. It was found that at the lower extreme the mixes became too viscous to coat whilst at the upper limit insufficient

poly(ethylene oxide) was present to adequately bind the material. Attention was therefore confined to the range from 63 to 75%. Fig. 4 shows the cycling performance of the carbon electrode as a function of the carbon content. As can be seen from this plot the specific capacity was strongly dependent on the amount of carbon present. Performance was superior for the 70% carbon formulation with both smaller and greater proportions of carbon leading to a reduction in capacity.

The behaviour of the carbon electrode at elevated temperature has been studied briefly. Increasing the operating temperature from 25 to 40 °C had a significant beneficial effect on performance. Fig. 5 shows that an increase in capacity of around 70% was observed at 40 °C compared with room temperature behaviour.

To establish if the composite carbon anode would exhibit satisfactorily performance when combined with an intercalating cathode in a lithium-ion polymer cell, cells were constructed as described above but with the lithium metal replaced with a composite LiMn₂O₄ cathode. Fig. 6 shows the cycling performance of a carbon/polymer electrolyte/LiMn₂O₄ cell. This cell was cycled at room temperature between the voltage limits 4.25 to 2.50 V and gave good performance over the first 30 cycles. The behaviour compares favourably with results reported elsewhere [5].

4. Conclusions

It is concluded that a composite carbon anode based on a pitch coke exhibits promise as an anode for a lithium-ion polymer electrolyte battery. In combination with a LiMn₂O₄ cathode good cycling performance has been achieved.

References

- [1] T. Nagaura, A lithium-ion battery, paper presented at the 4th Int. Rechargeable Battery Seminar, Deerfield Beach, FL, USA, 1990.
- [2] Lithium-Ion Cells from AT Battery Corporation, *Nikkei Sangyo (Industry) Newspaper, Japan*, 19 July 1993.
- [3] R. Fong, U. von Sacken and J.R. Dahn, *J. Electrochem. Soc.*, 137 (1990) 2009.
- [4] J.M. Tarascon and D. Guyomard, *J. Electrochem. Soc.*, 138 (1991) 2864.
- [5] K.M. Abraham, *Electrochim. Acta*, 38 (1993) 1233.