

the occurrence of hysteresis in the potential profile during the lithium intercalation and deintercalation.

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Effect of temperature on the performance of PMAN carbon anodes in 1 M LiPF₆/EC-DMC solution

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A considerable research effort is underway to utilize carbon and graphite materials as anodes for use in rechargeable lithium-ion cells. Graphitic materials can theoretically be charged to a composition of LiC₆ or 372 mAh g⁻¹. Some disordered carbons have been reported to reversibly store over 500 mAh g⁻¹.

During the first intercalation, however, solvent-reduction processes take place which irreversibly tie up part of the Li⁺ in a passive film. The nature and composition of the film is a function of the type of solvent and supporting electrolyte used. It is desirable to minimize the extent of passive-film formation while maintaining a high reversible capacity for intercalation. To gain an understanding as to the kinetics of passive film formation, the intercalation process was examined as a function of temperature for carbons derived from a polymethacrylonitrile (PMAN)-divinylbenzene (DVB) copolymer. Both the irreversible and reversible capacities of the PMAN carbons were measured during galvanostatic cyclic experiments with 1 M LiPF₆/ethylene carbonate (EC)-dimethyl carbonate solution between 2 V and 0.01 V versus Li/Li⁺ at temperatures of 5, 21 and 35°C. Cyclic voltammetric experiments between 3 V and 0.01 V were used to obtain supplemental information. Complex impedance spectra were taken as a function of voltage during intercalation to derive kinetic information of the intercalation and passive-film processes.

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Bismuth compounds as cathodic material for lithium accumulators

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Several groups of bismuth-containing oxide compounds (BCOC) were investigated to use as cathodic materials in

lithium accumulators. Galvanostatic characteristics of composite BCOC-based electrodes have been obtained in PC, DME/1 M LiClO₄ electrolyte.

BiXO₃ (X = Eu, Sm) compounds have been assigned to the first group of BCOCs investigated.

The OCV of Li/BiXO₃ is 3.1 to 3.2 V. During cycling at a current density of 2 mA cm⁻² for six cycles, the following specific discharge capacities (Ah kg⁻¹) were obtained:

	Cycle number					
	1	2	3	4	5	6
BiEuO ₃	145	140	130	100	75	76
BiSmO ₃	320	315	200	158	140	148

At the first cycle of this BCOC group, the discharge curve is characterised by the voltage plateau of 1.7–1.4 V which increased up to 2.1–2.0 V in the subsequent cycles.

In the second group of BCOC, Aurivillius [1,2] phases, Li/Bi₄Ti₃O₁₂ and Bi₄V₂O₁₁ have been investigated. On discharge at 1 mA cm⁻² to 1.1 V, on the first cycle, bismuth titanate gave 325 Ah kg⁻¹ and 490 Wh kg⁻¹. During the next three cycles, capacity dropped to 175, 180 and 170 Ah kg⁻¹, over the voltage range 4 to 1.1 V.

Bi₄V₂O₁₁ was also investigated in monocrystalline form. The lithium/bismuth vanadate has the following characteristics: OCV = 3.1 V. Plateau voltage on first discharge at 0.1 mA cm⁻² was 1.8 V and the capacity to 1.1 V was 390 Ah kg⁻¹. Capacity decreased with cycling (Ah kg⁻¹). 2nd: 241, 3rd: 175, 4th: 108, 5th: 102, 6th: 103.

In the third group investigated, BCOC was a mixture of PbBi₂O₃ + Bi₄Ti₂O₃. The OCV was 3.1 to 3.15 V and capacity 575 Ah kg⁻¹ at 0.1 mA cm⁻² down to 1.1 V, or 260 Ah kg⁻¹ to 1.5 V.

These first results are encouraging. For practical accumulators, more investigations are necessary.

References

- [1] B. Aurivillius, *Ark. Kemi.*, (1949) 463.
- [2] B. Aurivillius, *Ark. Kemi.*, (1949) 499.

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Modelling and optimization of the parameters of the lithium/nonaqueous electrolyte interface in high energy power sources

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The problem of passivating film formation on lithium surfaces and the influence of the properties of this film is of

particular concern for the development of lithium accumulators. In this connection, it is very important to determine some of the dynamic characteristics of the lithium/non-aqueous electrolyte interface and to learn what governs these characteristics.

An equivalent circuit of systems studied is proposed. The parameters of the circuit were determined in different electrolytes by a grapho-analytical method based on impedance measurements. Experimental data were compared with the results of mathematical modelling of various equivalent circuits. The analysis carried out allows us to suggest the location of the growth zone of a passivating film and to a certain degree to predict a system's behaviour and its dynamic properties.

Changing the composition, volume and surface of binary and ternary lithium alloys allows us to change significantly the parameters of the passivating film, which affects both system storage and cycling efficiency.

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Lithium cobaltite. A supplier's point of view

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This paper reviews different aspects linked with the production of LiCoO_2 and its use as cathode material in secondary lithium batteries. As the electrochemical performances of LiCoO_2 are now well established, the poster focusses on other aspects that have been less addressed in the past.

Correlations between particle size, surface area and tap densities are presented. The influence of the conditions of synthesis and of the nature of the starting products on these properties are also discussed.

In a second part of the poster, economic aspects are reviewed. The structure of the cost of LiCoO_2 is shown and compared to that of other lithiated oxides.

Forecasts are given for total production, share of each type of oxide and market price.

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Analysis of lithium manganese oxide for lithium rechargeable batteries

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Introduction

Lithium manganese oxide (LiMn_2O_4) is the favoured cathode material in the long term for lithium rechargeable batteries because it can be produced from cheap and readily available starting materials and it is non-toxic. At present, lithium cobalt oxide is used in rechargeable lithium-ion batteries but is expensive and somewhat toxic. However the synthesis of LiMn_2O_4 , particularly in large quantities, is difficult to control, as there are many different chemical phases in the lithium/manganese/oxygen system. This led to difficulty in specifying LiMn_2O_4 , as nominally similar materials in practice show very different performance in batteries.

A programme of analyses has been carried out to characterise lithium manganese oxide using a range of techniques. Both commercial samples and materials we have synthesised have been analysed for lithium and manganese content by ICPAES (inductively coupled plasma atomic emission spectrometry), oxygen content by a LECO TC436 analyser and by thermogravimetric analysis. The valence state of manganese was determined by a titration method following reductive dissolution of iron (II) sulfate in sulfuric acid solution. X-ray diffraction patterns were used to monitor the presence of impurities.

Results

The results obtained indicate that samples of lithium manganese oxides prepared at lower temperatures are the so called oxygen-rich, defect spinel and those prepared at higher temperatures contain less oxygen and have formulae closer to those of the regular stoichiometric spinel. Furthermore, the LECO oxygen analyser gave poor results because this technique is only suitable for trace amounts of oxygen in alloys; the classical titration method gave better results for oxygen content. The average oxidation state of Mn in LiMn_2O_4 was found to be about 3.55 for samples examined. X-ray powder diffraction analyses of the prepared powders indicated a spinel structure with less impurities (LiMn_2O_4) at higher temperatures. The amount of these impurities appeared to increase with decrease in the calcining temperatures. In addition, the diffraction peaks were broader in the samples calcined at lower temperatures. Particle size characterisation of LiMn_2O_4 was carried out by a sieving technique and by a laser diffraction method. The results obtained by the two methods were very similar, but the spinel oxides calcined at higher temperatures have smaller surface area. The results discussed above are in agreement with previous findings, all relevant evidence for the above results being shown on the poster.

Conclusion

In summary it is difficult to control the reaction parameters such as uniform temperature, cooling time and oxygen flow