

The invention relates to an electrochemical secondary cell having a positive electrode, a negative electrode and a non-aqueous electrolyte, the electrode material in each case forming an open lattice or skeletal structure which enables it, as host substance, to absorb, and to release again, electrochemically active cations with charging and discharging alternating.

An important impetus towards this invention was provided by the recent marked increase in demand for batteries affording high energy density and low weight, such as those which have already become a reality, in particular with the lithium systems, yet with the additional requirement of rechargeability. For this to be achieved, the electrodes must be chemically stable in contact with the electrolyte.

Lithium electrodes are unable to meet such demands on a long-term basis, even in organic electrolytes having aprotic solvents, because of the known narrow limits to their cyclic stability.

This shortcoming can be remedied by alloying lithium with an alkaline earth metal or earth metal, preferably aluminium. The advantages of this in terms of superior rechargeability and greater mechanical strength counterbalance a reduction in the energy content of the alloy electrode.

A different approach to improving the reversibility of the lithium electrode, which has been adopted in recent years, is by way of intercalation compounds. In this case, the electrodes of a cell are of a material of defined structure, which forms a suitable host lattice for an electrochemically active ionic species present in the electrolyte, by which lattice this species - in the current instance Li^+ - is either included or excluded, depending on polarity, when an external voltage is applied. During discharge, the electromotive power generated, which manifests itself in the tendency to reverse the imposed intercalation or de-intercalation,

is used to draw current.

From the outset, carbon having defined structural conditions has proved to be an electrode material which can be doped in this sense with Li^+ ions, and which can be used for both electrode polarities. The electrodes of an electrochemical battery known from DE-OS 32 31 243 are, for example, electrodes of activated carbon moulded products; according to EP-A 165 047 the carbon material is a pseudographite of defined crystallite size and having a lattice which is expanded in the direction of the c-axis, and which is obtained by pyrolysis of aromatic hydrocarbons. In the case of a secondary battery disclosed by EP-A-201 038, having as electrolyte the solution of an Li salt in a non-aqueous solvent, such a pseudographite forms the negative electrode material, and a similarly dopable metal chalcogenide forms the positive electrode material.

The intercalatability of metal chalcogenides, for example of WO_3 or TiS_2 , and furthermore of certain synthetic mixed oxides according to US-PS 4 668 595, results from the pronounced layer lattices thereof. The same publication also discloses a chemically stable n-type material in the form of a carbon product, which is obtained from high molecular weight constituents of petroleum by means of a controlled coking process, with a certain defective organisation of the fine structure being sought after in this product, with a view to the incorporation of metal cations, in particular Li^+ .

Finally, according to US-PS 4 507 371, host oxides or host sulphides such as may, in terms of their crystal chemistry, be allocated to the spinels, may be utilised in rechargeable cells, as cathode, as anode and, if no electron conductivity is present, even as electrolyte, according to choice. The said spinel structures show a high degree of stability or they may be stabilised optionally by the introduction of certain cations such as Mg^{2+} , Zn^{2+} , Cd^{2+} .

In particular, according to DE-OS 37 36 366, by reacting manganese dioxide, MnO_2 , with lithium salts at only moderately high temperatures of from 300 to 400°C, pure lithium manganese spinels can be produced, in the lattice whereof the Li^+ ions are highly mobile, which is why such spinels are usable as active cathode material in particular for rechargeable galvanic cells. They can be formulated in the charged state as LiMn_2O_4 and in the discharged state as LiMnO_2 . Acid treatment enables the lithium manganese spinel to be converted into a low-lithium compound, without changing its spinel structure, merely with slight contraction of the cubic lattice.

In the case of all secondary cells known to date whereof the cathode is of a material having a spinel structure, the anode coupled therewith is either a lithium alloy, an electrically conductive polymer such as polyacetylene or polyparaphenylene doped with lithium ions, an intermediate layer compound of the TiS_2 type, which exhibits lithium ions in the cavities of the intermediate layer, or, like the cathode, it is formed from a spinel.

The object of the invention is to provide an electrochemical secondary cell of high energy density, whereof the charge/discharge mechanism relies on a reciprocal intercalation and de-intercalation of preferably Li^+ ions in the positive and negative electrode materials, the electrode structures being intended to ensure good chemical resistance to the electrolyte and a high cyclic stability.

The object is achieved according to the invention with a secondary cell such as is defined in Claim 1.

It has been found that the requirements are to a high degree met by a secondary cell whereof the positive electrode includes as host substance an oxidic material which exhibits a fine structure such as that of the spinels and whereof the composition corresponds to the general formula $\text{M}_x\text{Mn}_y\text{O}_z$,

where

M = cation of at least one metal taken from the groups IIa, IVa, Va, IVb, Vb, VIb or VIIb;

x = a number between 0 and 0.6;

y = a number between 1.4 and 2.0, the ratio y : z being between 0.3 and 0.6,

absorption of a guest A, comprising the cation of a group Ia element, into the host structure resulting in an electrode of the general composition $A_qM_xMn_yO_z$ of the spinel type, in which A varies in accordance with an operating parameter q, and in that the host substance of the negative electrode is a carbon product formed from organic compounds by controlled thermal decomposition.

The electrochemically active cation A which is intercalatable by both electrode structures is preferably Li^+ .

According to the invention, the positive electrode of the novel secondary cell is in terms of composition substantially a lithium-manganese spinel, $Li_qM_xMn_yO_z$, in which, as determined by the parameters $0 < x < 0.6$ and $1.4 < y < 2.0$, up to approximately 30% of the manganese may be replaced by other metals M. Replacement metals are, specifically, the major elements Mg, Sn, Pb, Sb and Bi from groups IIa, IVa and Va of the Periodic Table and the transition elements Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Fe, Co and Ni from groups IVb, Vb, VIb and VIIb, respectively.

Partial replacement of Mn ions with M cations in the spinel lattice gives rise under certain conditions to certain structural defects in the lattice, as a consequence of which the host oxide is by no means always, in fact is even only exceptionally, a stoichiometric compound, and the M cations are also incorporated into the lattice

with valencies which differ from those of the Mn ions. The parameters x , y and z accordingly have a certain range of variation, yet are fixed in respect of each individual compound. If now the electrochemically active ionic species A diffuses into the spatial or skeletal structure of the host oxide under the influence of an electromagnetic field, the concentration of A or Li^+ , respectively, may vary over a broad range.

The preferred numerical value of q should be between 0 and 1.3 according to the invention. This limit characterises cathodes according to the invention - by contrast, for example, with the $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ phase (x corresponds here to q) disclosed in US-PS 4 507 371 - as low-lithium manganese spinels, which excel, however, by the very fact that by far the preponderance of their inherent capacity can be drawn off at potentials of > 3 V vs. Li/Li^+ . Furthermore, intercalation of the Li^+ ions occurs with a high degree of reversibility. A cobalt-containing lithium-manganese spinel of the composition $\text{LiCo}_{0.24}\text{Mn}_{1.76}\text{O}_{4.065}$ has proved to be a particularly favourable material for the positive electrode of a secondary cell according to the invention, as will be demonstrated.

A carbon product prepared from selected organic compounds by means of a coking or pyrolytic process serves according to the invention as a skeleton material for the negative electrode, which material is here assigned the role of host substance for the electrochemically active cationic species A.

A process which is of some interest in this context is the process known as "delayed coking". In this, petroleum refining residues are fed into a furnace as feedstock and are heated to approximately 500°C , the throughput rate or residence time in the furnace being, however, adjusted such that coke deposition takes place only in a coke chamber downstream which is operated alternately with a second chamber. The coke is removed from the chambers with the aid of a hydraulic cutting device after volatile hydrocarbons occurring as

by-products have been expelled by a vapour current.

One carbon product which is particularly suitable for the purpose according to the invention is that known as needle coke, a speciality coke already in use in the steel industry for making high-quality graphite electrodes for electrical smelting furnaces. Needle coke is also a product of the delayed coking described, however using feedstocks - such as thermal tars, decantation oils or coaltar pitches - which are based on highly aromatic hydrocarbon compounds.

For more detailed information on process engineering and typical needle coke specifications, the reader is referred to H.M. Feintuch, J.A. Bonilla and R.L. Godino "Handbook of Petroleum Refining Processes", R.A. Meyers, ed. McGraw Hill, New York, p. 7.1 - 7.61 (1986).

The non-aqueous electrolyte of a secondary cell according to the invention may be liquid, of paste consistency or solid. It preferably includes an Li salt with an organic solvent, and is preferably present in liquid form.

The Li salts are known electrolytic salts having one of the anions ClO_4^- , BF_4^- , AsF_6^- , CF_3SO_3^- , PF_6^- , I^- or AlClO_4^- . An organic solvent taken from the group comprising tetrahydrofuran, 2-methyltetrahydrofuran, acetonitrile, propionitrile, 4-methyl-2-pentanone, butyronitrile, valeronitrile, benzonitrile, 1,2-dichloroethane, γ -butyrolactone, dimethoxyethane, methyl formate, propylene carbonate, ethylene carbonate, vinylene carbonate, dimethylformamide, sulpholane, 3-methylsulpholane, trimethyl phosphate, whether alone or in mixture with others, may serve as a water-free solvent for the said salts.

In an advantageous embodiment of the secondary cell according to the invention, the electrolyte is immobilised by inorganic oxygen

compounds such as SiO_2 , Al_2O_3 , TiO_2 , MgO , B_2O_3 , Na_2SO_4 or AlPO_4 , which gel with the solvent in forms having a large surface area. Aprotic solvents such as propylene carbonate, acetonitrile, γ -butyrolactone, nitromethane, tetrahydrofuran, methyltetrahydrofuran, dimethoxyethane or dioxolane are in particular suitable for this purpose.

The electrolytes formed are of a paste to semi-solid consistency. Another possible route to fixing the electrolytes is afforded by the fact that alkali metal salts form with polyethylene oxide polyether complexes which have the characteristic of a solid ionic conductor. The Li salt as electrolyte component is in this case a constituent of a polymeric electrolyte matrix, having polyethylene oxide as the basic skeleton.

Ceramic alkali metal ionic conductors are furthermore contemplated as solid electrolytes.

Finally, the electrolyte of the secondary cell according to the invention may comprise molten salts. LiAlCl_4 , which melts at 150°C , or a eutectic mixture of LiCl and KCl , which has a melting point of 352°C , are examples of the latter. Particularly advantageous electrolytes are, however, so-called room temperature molten salts, which function in this instance as solvent for a conventional Li conductor salt. Examples which might be named are the following salt mixtures: 1-methyl-3-ethyl imidazolium chloride/ AlCl_3 , N-butyl pyridinium chloride/ AlCl_3 , phenyltrimethylammonium chloride/ AlCl_3 .

Neither the electrode materials nor the electrolyte of the secondary cell according to the invention imposes particular conditions on the design of practical cells which can also be operated as a battery complex. The electrodes may, for example, be present in compacted form, thus making for ease of handling during installation, and may optionally also be stiffened by a binder. In

close installation and when used in conjunction with liquid electrolytes, the electrodes may be electrically insulated from one another by a separator material which is generally conventional in lithium cells, such as, for example, polypropylene.

However, it is highly advantageous to reinforce the electrodes with electrically conductive metal carrier structures, in particular if the latter also simultaneously assume the function of charge eliminator. In a particularly favourable embodiment of the secondary cell according to the invention, the negative electrode has a charge eliminator of nickel or special steel, and the positive electrode one of aluminium or special steel.

The advantages of the invention, determined on the basis of electrical function tests, are highlighted with the aid of three Figures.

Figure 1 shows the voltage progression during a charge/discharge cycle in respect of a positive spinel electrode, measured against Li/Li^+ as counter-electrode.

Figure 2 shows the development in capacity of two positive spinel electrodes according to the invention during cyclic charge/discharge over 15 cycles, also against an Li/Li^+ electrode.

Figure 3 shows the characteristic voltage progression during a charge/discharge cycle in respect of a complete secondary cell according to the invention.

The voltage curve in Figure 1 was plotted for a pure lithium-manganese spinel of the composition LiMn_2O_4 , which is derived from the general formula $\text{Li}_q\text{M}_x\text{Mn}_y\text{O}_z$, where $q = 1$, $x = 0$ and $y = 2$. The low lithium content according to the invention ($0 < q < 1.3$) is responsible here for the unusually high voltage level of about 4 V during discharge.

According to Figure 2, spinel cathodes according to the invention are distinguished in cyclic operation by only a slight loss of capacity (capacity C in mAh) in cyclic operation (n = no. of cycles). At the same time the LiMn_2O_4 spinel is still out-performed in terms of cyclic stability by the aforementioned $\text{LiCo}_{0.24}\text{Mn}_{1.76}\text{O}_{4.065}$ modification. This favourable behaviour is a direct result of the almost unimpeded absorption and release of the Li^+ guest by the spinel host lattice, that is to say it results from a virtually reversible intercalation.

Figure 3 shows a typical charge/discharge voltage curve for a secondary cell according to the invention having a positive LiMn_2O_4 electrode and a negative Li^+ intercalating carbon electrode. According to this Figure, by far the majority of the capacity - as in the cases just described at a current $i = 0.1$ CA (for 10 hours) - can be discharged at a cell voltage which falls from 4 V to 3 V.

A 1.0 normal solution of LiAsF_6 in propylene carbonate was in each case utilised as electrolyte.

Claims

1. Electrochemical secondary cell having a positive electrode, a negative electrode and a non-aqueous electrolyte, the electrode material in each case forming an open lattice or skeletal structure which enables it, as host substance, to absorb, and to release again, electrochemically active cations with charging and discharging alternating, characterised in that the host substance of the positive electrode is an oxidic material having a spinel-type structure, whereof the composition corresponds to the general formula $M_xMn_yO_z$, where

M = cation of at least one metal taken from the groups IIa, IVa, Va, IVb, Vb, VIb or VIIb;

x = a number between 0 and 0.6;

y = a number between 1.4 and 2.0, the ratio $y : z$ being between 0.3 and 0.6,

absorption of a guest A, comprising the cation of a group Ia element, into the host structure resulting in an electrode of the general composition $A_qM_xMn_yO_z$ of the spinel type, in which A varies in accordance with an operating parameter q, and in that the host substance of the negative electrode is a carbon product formed from organic compounds by pyrolysis.

2. Electrochemical secondary cell according to Claim 1, characterised in that A is formed from Li^+ .

3. Electrochemical secondary cell according to Claim 2, characterised in that the operating parameter q is between 0 and 1.3.

4. Electrochemical secondary cell according to one of Claims 1



to 3, characterised in that the carbon product forming the host substance of the negative electrode is a needle coke.

5. Electrochemical secondary cell according to one of Claims 1 to 4, characterised in that the electrolyte includes an Li salt with an organic solvent.

6. Electrochemical secondary cell according to Claim 5, characterised in that the electrolyte is immobilised by a polymer matrix as solvent or by addition of inorganic substances which gel in the solvent.

7. Electrochemical secondary cell according to Claim 6, characterised in that the polymeric basic skeleton is polyethylene oxide.

8. Electrochemical secondary cell according to Claim 6, characterised in that the gelling agents are selected from the group comprising SiO_2 , Al_2O_3 , TiO_2 , MgO , B_2O_3 , Na_2SO_4 and AlPO_4 .

9. Electrochemical secondary cell according to one of Claims 1 to 4, characterised in that the electrolyte comprises a high-temperature molten salt containing a lithium salt.

10. Electrochemical secondary cell according to one of Claims 1 to 4, characterised in that the electrolyte comprises the solution of a lithium salt in a room temperature molten salt.

