



(19) **United States**

(12) **Patent Application Publication**

Van Heuveln et al.

(10) **Pub. No.: US 2004/0089540 A1**

(43) **Pub. Date: May 13, 2004**

(54) **MIXED OXIDE MATERIAL, ELECTRODE AND METHOD OF MANUFACTURING THE ELECTRODE AND ELECTROCHEMICAL CELL COMPRISING IT**

Publication Classification

(51) **Int. Cl.⁷ C25D 17/00**
(52) **U.S. Cl. 204/293; 29/592.1; 204/242**

(76) **Inventors: Frederik Henddrik Van Heuveln, Alkmaar (NL); Lambertus Plomp, Alkmaar (NL); Gerard Douwe Elzinga, Schagen (NL)**

(57) **ABSTRACT**

The invention relates to a mixed oxide material with a high electron conductivity of empirical formula ABO_y , where $y \neq 3$ and where A comprises at least one metal selected from Na, K, Rb, Ca, Ba, La, Pr, Sr, Ce, Nb, Pb, Nd, Sm and Gd, and B comprises at least one metal selected from the group consisting of Cu, Mg, Ti, V, Cr, Mn, Fe, Co, Nb, Mo, W and Zr, where A and B cannot both be Nb and where the compound $SrVO_{2.5}$ is excluded. The material may be a perovskite-type material, in which $y=3-\delta$ and $\delta \neq 0$, with values for δ in the range from approximately -0.2 to approximately -0.05 or in the range from $+0.05$ to $+0.7$. The material may also be a Brown-Millerite-type material, for which $y=2.5-\xi$ and ξ has a value in the range from approximately -0.2 to approximately -0.05 or in the range from $+0.05$ to approximately 0.3 . The invention also describes an electrode for an electrochemical cell which can be produced from a mixed oxide material of this type, a method for producing an electrode from a mixed oxide material and an electrochemical cell which comprises at least one electrode of this type made from mixed oxide material according to the invention.

Correspondence Address:

THOMAS, KAYDEN, HORSTEMEYER & RISLEY, LLP
100 GALLERIA PARKWAY, NW
STE 1750
ATLANTA, GA 30339-5948 (US)

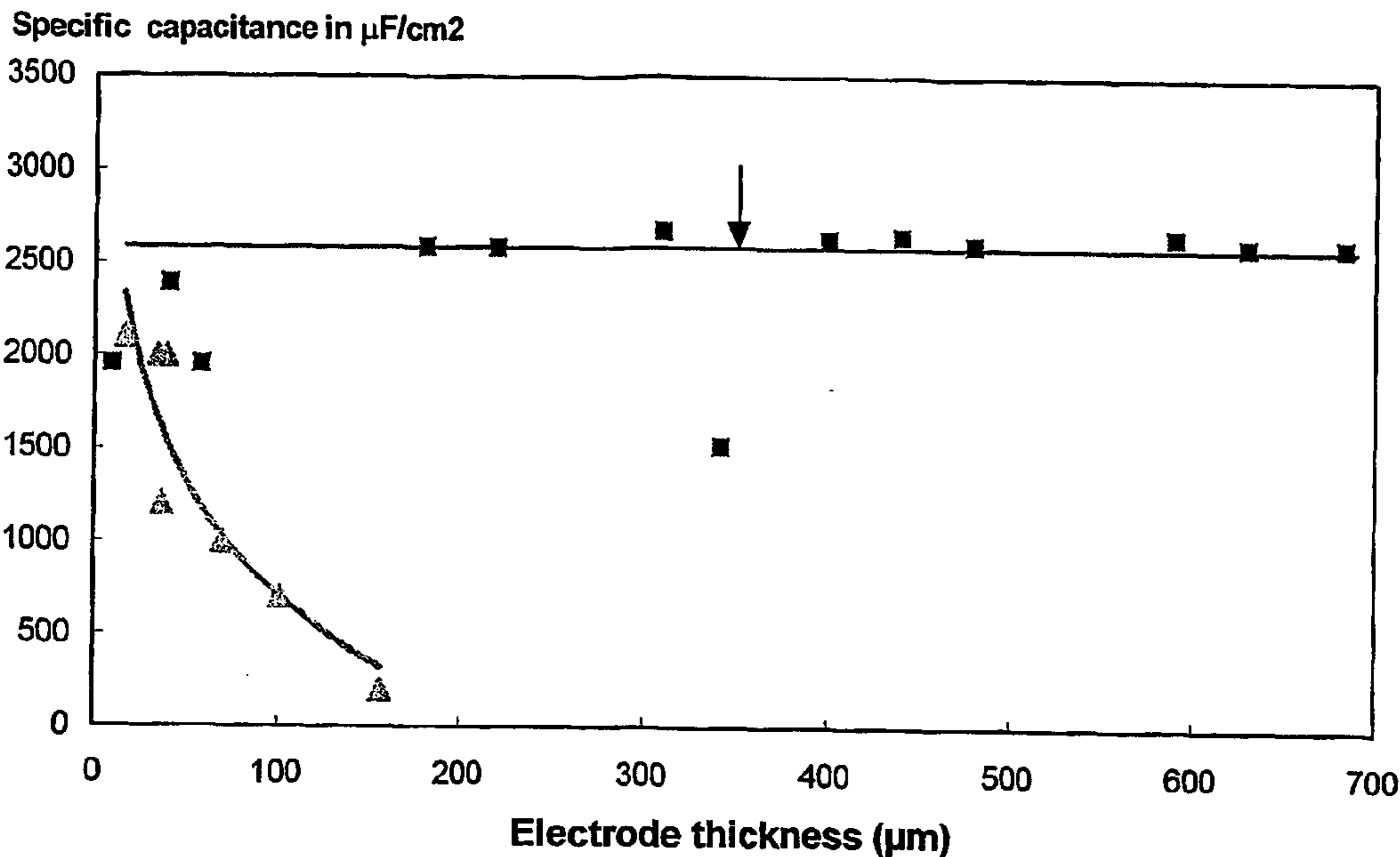
(21) **Appl. No.: 10/344,083**

(22) **PCT Filed: Jul. 26, 2001**

(86) **PCT No.: PCT/NL01/00621**

(30) **Foreign Application Priority Data**

Aug. 7, 2000 (NL)..... 1015886
Mar. 19, 2001 (NL)..... 1017632
Jun. 12, 2001 (NL)..... 1018266



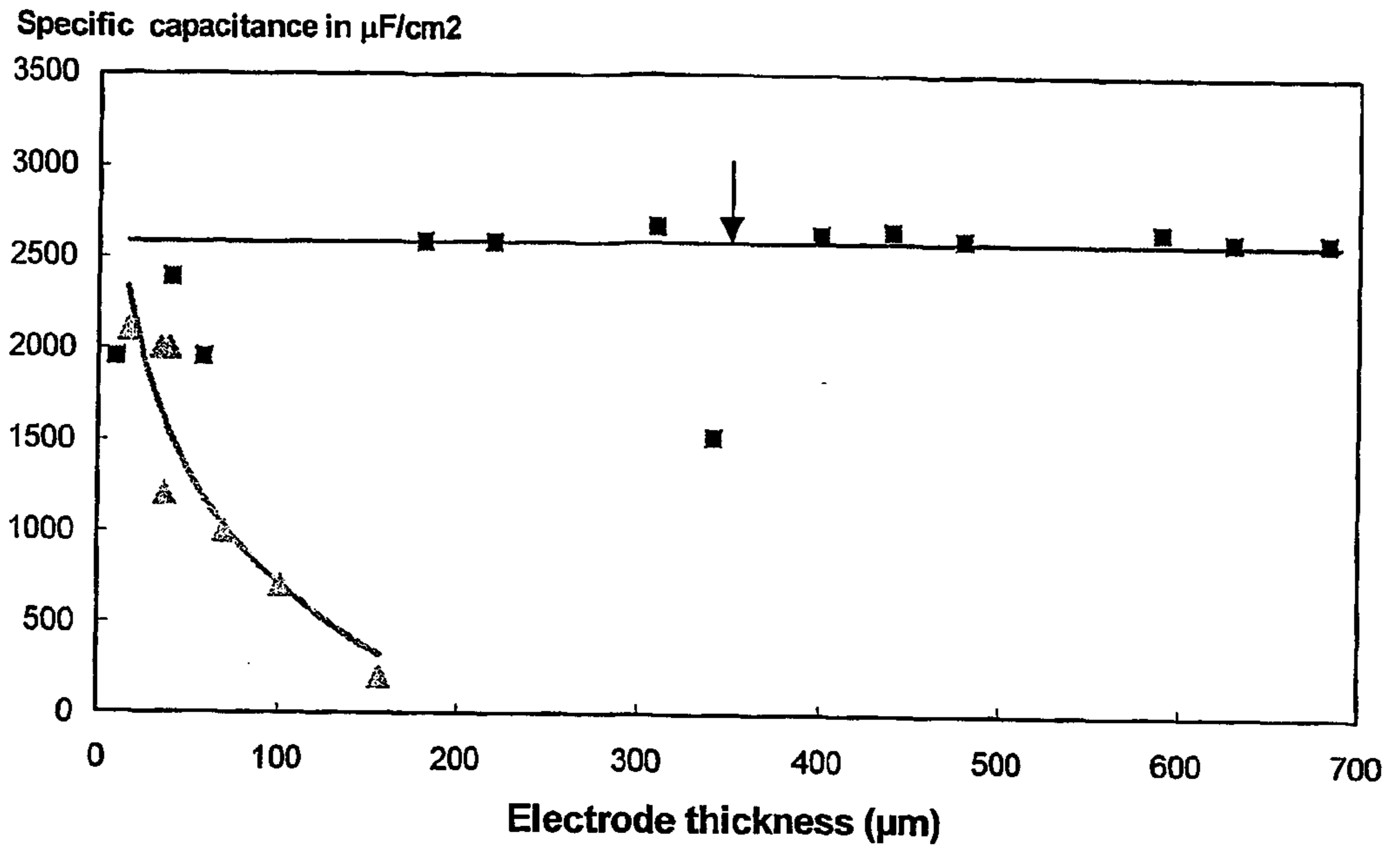


FIG. 1

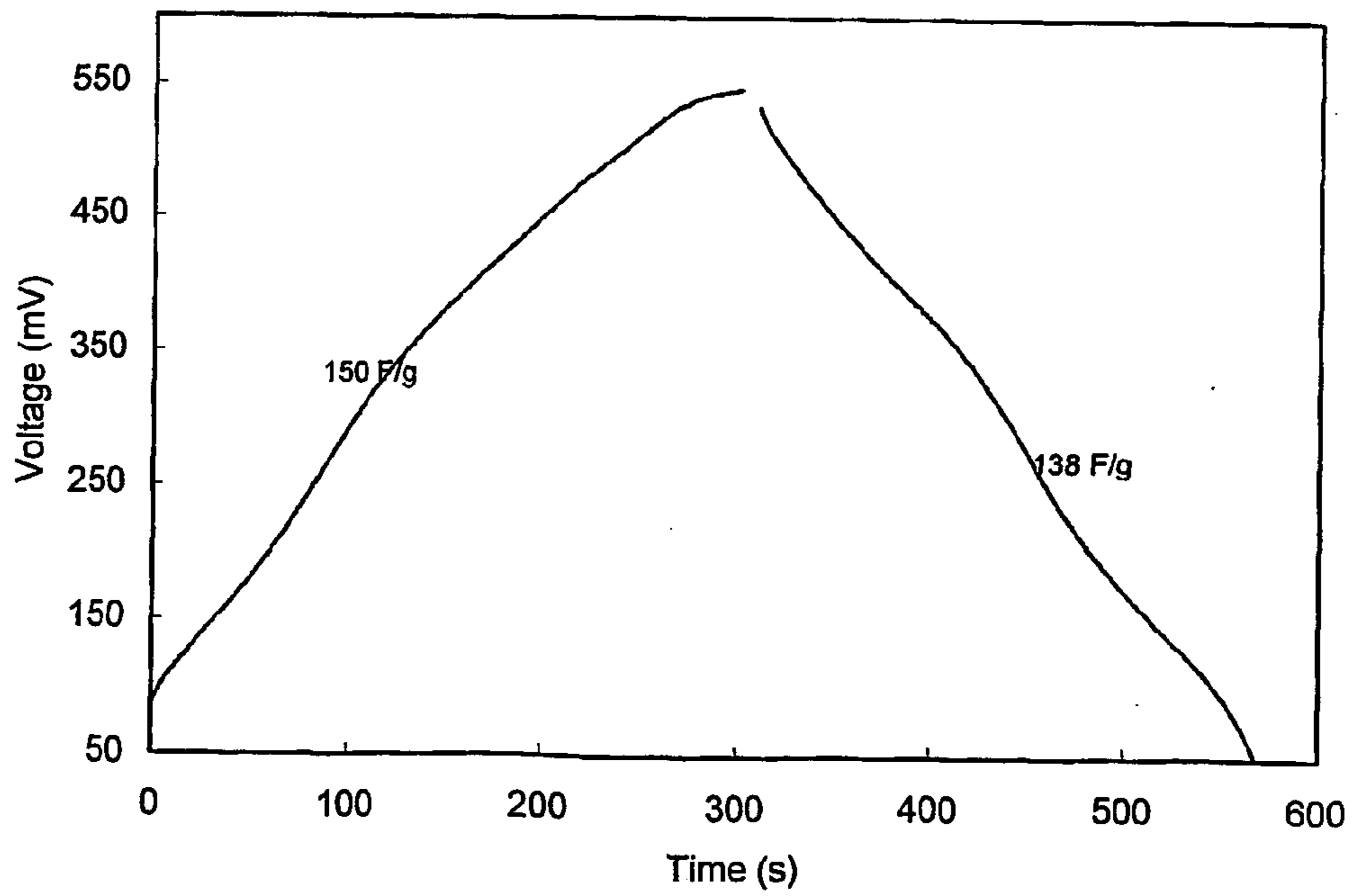


FIG. 2

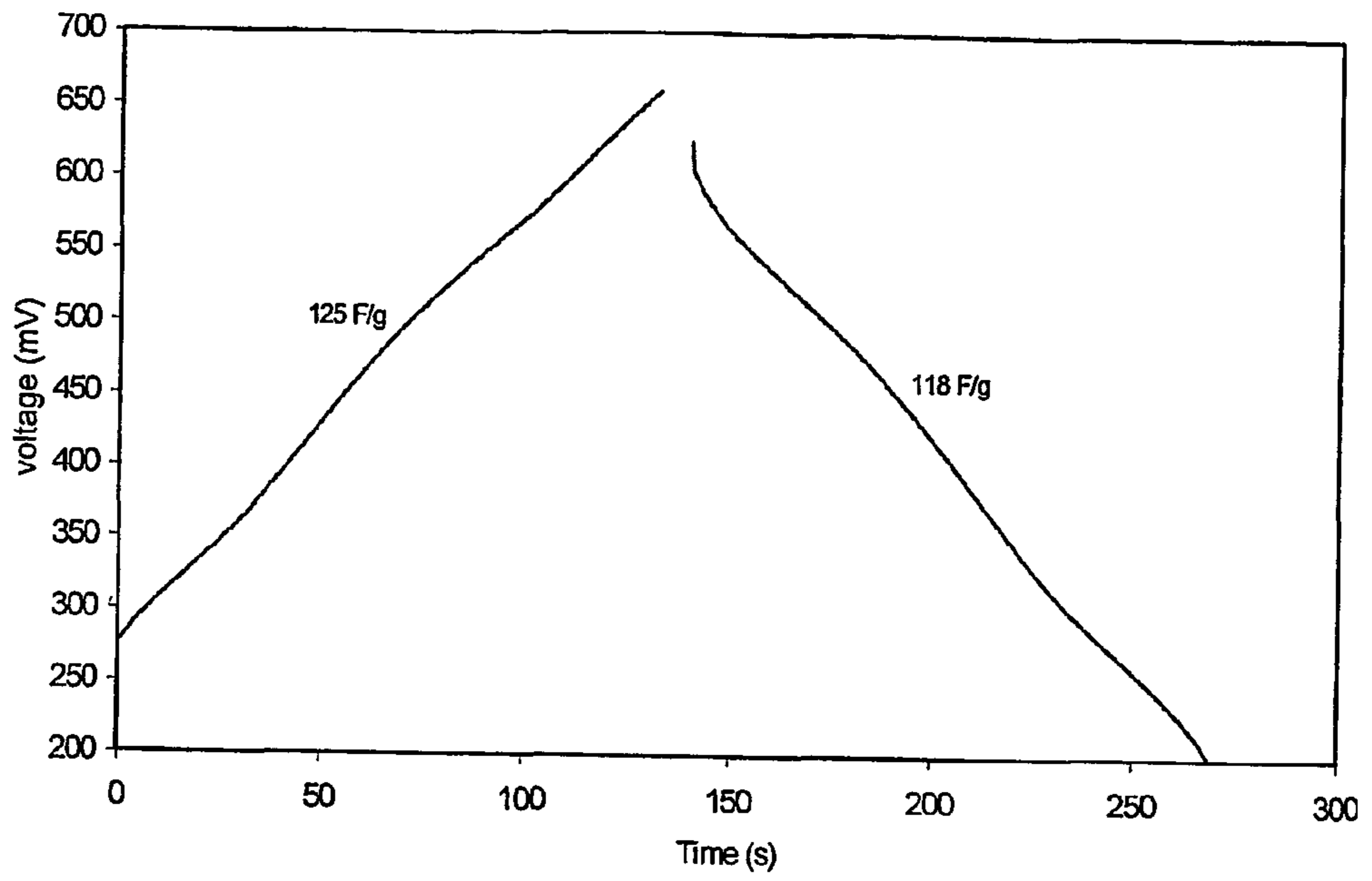


FIG. 3

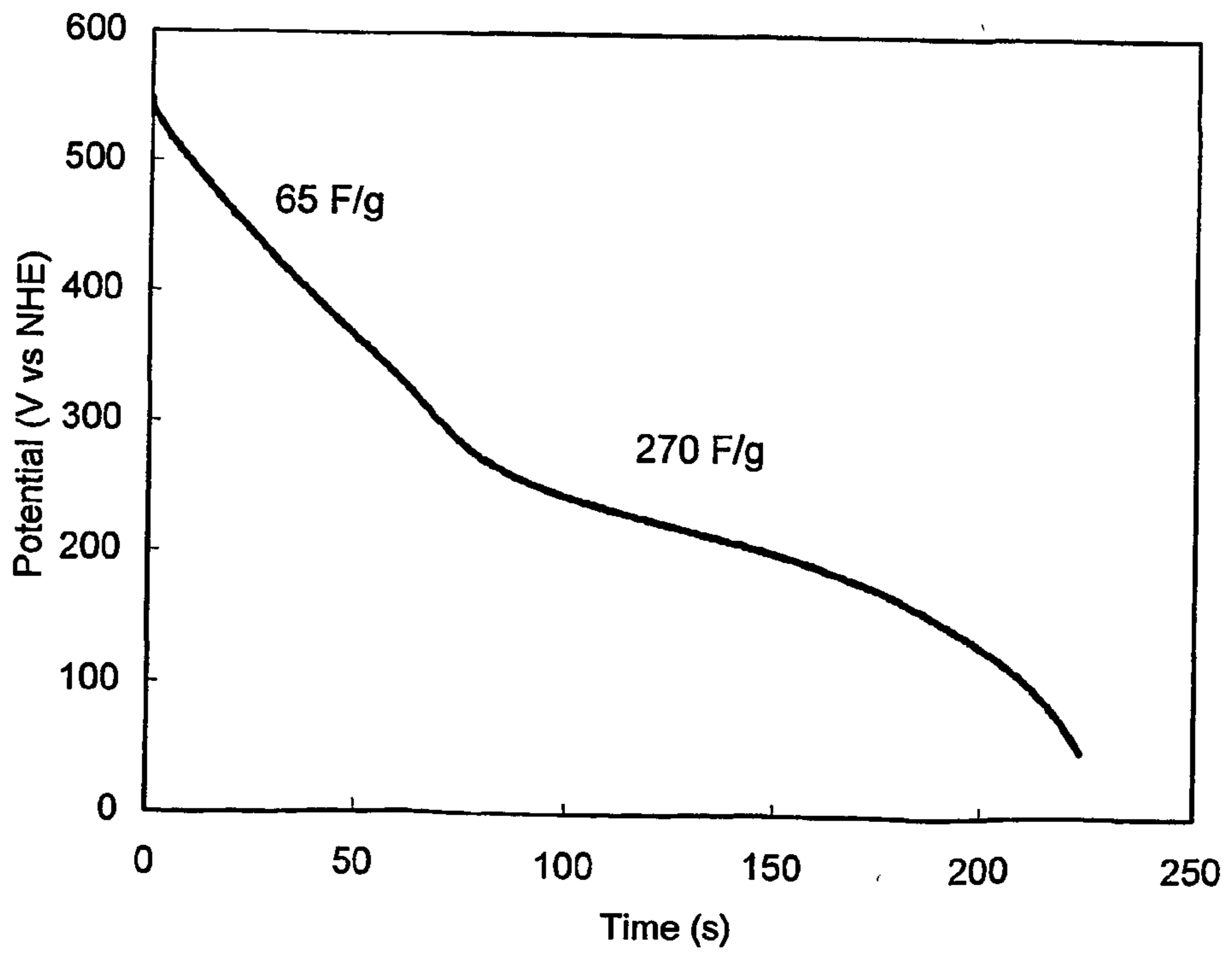


FIG. 4

MIXED OXIDE MATERIAL, ELECTRODE AND METHOD OF MANUFACTURING THE ELECTRODE AND ELECTROCHEMICAL CELL COMPRISING IT

[0001] The invention relates firstly to a mixed oxide material with a high electron conductivity.

[0002] A material of this type is known from DE-C-196 40 926.

[0003] The said publication describes compounds of the type $A(B_{1-x}C_x)O_3$, where $0 \leq x < 1$; materials of this type are used to produce electrodes for an electrochemical cell. A denotes a metal cation selected from group IIa (alkaline-earth metals) or from the lanthanides from the Periodic System, or a mixture thereof; B represents a platinum metal cation, while C represents a metal cation selected from groups IVb, Vb, VIb, VIIb, VIIIb and IIb of the Periodic System of the Elements, or a mixture thereof.

[0004] The applicant has carried out extensive research into mixed oxide materials of this type, investigating in particular whether a mixed oxide material of this type could also be made without using elements from the platinum group, i.e. without using metals from the group consisting of Pt, Ru, Ir, Rh, Ni and Pd.

[0005] Metals of this type make a mixed oxide of this type expensive, and consequently the use of mixed oxides of this type for such applications is unattractive.

[0006] Surprisingly, it has been found that, to obtain a mixed oxide material with a high electron conductivity, it is not necessary to use metals from the platinum group if a mixed oxide material of this type is provided with an empirical formula ABO_y , where $y \neq 3$ and where A comprises at least one metal selected from Na, K, Rb, Ca, Ba, La, Pr, Sr, Ce, Nb, Pb, Nd, Sm and Gd, and B comprises at least one metal selected from the group consisting of Cu, Mg, Ti, V, Cr, Mn, Fe, Co, Nb, Mo, W and Zr, where A and B cannot both be Nb and where the compound $SrVO_{2.5}$ is excluded.

[0007] This is because it has been found that the above-mentioned type of compounds, if deviating from oxygen stoichiometry, have an excellent conductivity for electrons, while the absence of metal components from the platinum group means that the cost price of the material is relatively low.

[0008] The above claim has included a disclaimer with regard to the compound $SrVO_{2.5}$. This exclusion is accounted for by the publication Hochleistungs-Doppelschichtkondensatoren auf Metalloxidbasis [High-performance double-layer capacitors based on metal oxide], J. Wind, A. Koch, A. Löffler, O. Schmid, Daimler Chrysler Forschung, 88039 Friedrichshafen in Anwenderforum Doppelschichtkondensatoren, 99, in ISET 99 dated 10 Nov. 1999, in particular pages 18-23, in which $SrVO_{2.5}$ is mentioned as a possibility worthy of investigation; no actual results with a material of this type are given.

[0009] In particular, the invention relates to a mixed oxide material which is characterized in that the material is a perovskite-type material, for which $y=3-\delta$, where $\delta=0$ and δ has values in the range from approximately -0.2 to approximately -0.05 or in the range from approximately $+0.05$ to approximately $+0.7$.

[0010] In another expedient embodiment, the mixed oxide material according to the invention is characterized in that the material is a Brown-Millerite-type material, for which $y=2.5-\xi$ and ξ has values in the range from approximately -0.2 to approximately -0.05 or in the range from approximately $+0.05$ to approximately $+0.3$.

[0011] The mixed oxide material according to the invention as described above may be such that both A and B are a single material; expediently, A and/or B comprise(s) a metal which is doped with another metal, the doping metals for A and B being selected from the options given above for A and B.

[0012] In an expedient embodiment, in the mixed oxide according to the invention, A is $Sm_xSr_{(1-x)}$, with x lying in the range from approximately 0.4 to approximately 0.6.

[0013] In another advantageous embodiment, in the mixed oxide material according to the invention, A is $Nd_xSr_{(1-x)}$, with x lying in the range from approximately 0.4 to approximately 0.6.

[0014] On the other hand, it is, of course, also possible for the composition of B to be composed of a plurality of metals, such as, in an advantageous embodiment, Co and/or Fe.

[0015] In particular, in the mixed oxide material according to the invention, B comprises $Co_{(1-x)}Fe_x$, with x lying in the range from approximately 0.2 to approximately 0.6.

[0016] The invention also relates to an electrode for an electrochemical cell which can be produced from a material with a high electron conductivity which is characterized in that the electrode comprises a mixed oxide material according to the invention as defined above.

[0017] The invention also relates to a method for producing an electrode for an electrochemical cell, comprising the steps of providing a suitable substrate, and forming a cohesive layer of a mixed oxide thereon by applying a mixture of a mixed oxide, one or more binders and at least one solvent, followed by removal of the solvent and, if appropriate, followed by a heat treatment, which is characterized in that a cohesive layer which includes a mixed oxide material as defined above in accordance with the invention is formed on the substrate. The substrate may be a strip of thin metal or an (optionally conductive) plastic.

[0018] In general, the mixed oxide material according to the invention, using a suitable binder and a solvent, will be brought into the form of a suspension or paste, after which a layer of the suspension or paste can be applied to the substrate by spreading, dipping, brushing or screen printing.

[0019] After removal of the solvent (drying), it is optionally also possible for a heat treatment to take place, in order to provide the mixed oxide with the desired activity and/or to form the mixed oxide into a cohesive structure.

[0020] The method can also be carried out by the substrate being a matrix and by the mixed oxide being accommodated in the matrix and forming a cohesive unit therewith. The paste or suspension described above can also be used to fill the matrix.

[0021] The substrate may also have a release property, so that the layer which comprises the mixed oxide material, after application on the substrate, is removed and is subjected to a heat treatment if appropriate. In all cases, a layer

of mixed oxide material, optionally on a substrate, is obtained, the mixed oxide material being a material according to the invention with a high electron conductivity.

[0022] Finally, the invention also relates to an electrochemical cell which comprises at least two electrodes and an electrolyte and which is characterized in that at least one electrode is an electrode as defined above in accordance with the invention.

[0023] Both electrodes may be an electrode according to the invention; it is also possible for one of the electrodes to be selected from a carbon electrode, an RuO_2 electrode and an $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ electrode.

[0024] On account of its electrical conductivity, the mixed oxide material according to the invention can be used for numerous purposes, such as electrodes in electrochemical cells, heating elements and the like. When used as an electrode in an electrochemical cell, this is understood, in its broadest sense, as meaning use of an electrode in combination with an electrolyte and other electrodes. Electrodes of this type are used in processes for the electrochemical conversion and storage of electricity, as are found in electrochemical capacitors, also known as supercapacitors or ultracapacitors, batteries, in particular including rechargeable batteries of the alkaline type or the metal/air type, fuel cells, such as the polymer electrolyte fuel cell, electrolysis equipment and sensors.

[0025] An electrochemical capacitor (or supercapacitor or ultra-capacitor) is a device in which electricity can be stored and then removed again, in particular with a high power density (in W/kg and W/l), by using electrical double-layer capacitance or what is known as pseudo-capacitance which is linked to Faraday processes, such as redox reactions or intercalation processes. Applications include, inter alia, the (short-term) storage and/or emission of peak power levels and the reduction of duty cycles of batteries, as arises, inter alia, in battery or hybrid or fuel-cell vehicles, in installations or equipment which ensure the quality of central or local power networks or supplies, and in optionally portable electronic equipment, such as laptops and mobile telephones. An electrochemical capacitor of this type has two electrodes, an anode and a cathode, at which electrons are respectively released and collected. Furthermore, the capacitor includes an electrolyte, for example an aqueous or organic solution, and a separator, and the entire assembly can be fitted in a metal or plastic housing. At least one of the two electrodes may be an electrode according to the invention. The charge, which is positive at one electrode and negative at the other, is stored in the electrical double-layer capacitance at the interface of electrode and electrolyte, in the pseudo-capacitance resulting from highly reversible redox reactions or intercalation processes at this interface or in the bulk of the electrode material, or in a combination of double-layer capacitance and pseudo-capacitance. In this case, important properties are the specific capacitance (in $\mu\text{F/cm}^2$), which is determined by the type of electrode material and the electrolyte used, the specific surface area of the electrode material (in cm^2/g) and the resulting effective capacitance (in F/g). Furthermore, the type of electrolyte is important for the acceptable potentials on the electrodes. These determine, in the case of pseudo-capacitance together with the effective potential range around the Nernst equilibrium potentials of the related reactions or processes, the

operational voltage range of the capacitor, which should preferably be as high as possible. The composition and microstructure of the electrode materials, the microstructure of the separator and the composition of the electrolyte partly, but not completely, determine the internal resistance R_i (in Ω) of the capacitor, which should preferably be as low as possible. The quantities described partly, but not completely, determine the energy density of the capacitor (in Wh/kg and Wh/l) and the power density (in W/kg and W/l). For known technologies these are typically, respectively, a few Wh/kg and a few thousand W/kg . For the energy E (in J) and the power P (in W) of the capacitor with capacitance C (in F) and charged to voltage V (in V), $E = CV^2/2$ and $P = V^2/4R_i$, respectively, approximately apply.

[0026] Inter alia, electrochemical capacitors with electrodes which have activated carbon as the most important constituent and which predominantly use electrical double-layer capacitance are known. It is important that the activated carbon forms a porous structure with a high specific surface area which is accessible to the electrolyte, in order to form a capacitance which is as high as possible, and with an electron conductivity which is as high as possible, in order to produce a resistance which is as low as possible and to utilize as much electrode material as possible. The highest energy and power densities are obtained in this way, which is a requirement for most applications. Carbon electrodes which predominantly use double-layer capacitance can be used as anodes and as cathodes; in this way, it is possible to make symmetrical capacitors. Carbon electrodes can be used in combination with an aqueous electrolyte, the permissible capacitor voltage being at most approx. 1.2 V and a low internal resistance being obtained, or in combination with an organic electrolyte, in which case the maximum voltage is approx. 2.4 V, but the internal resistance which can be obtained is generally less low.

[0027] For many applications, but in particular for use in vehicles, a higher energy density than that which is known in the prior art when using carbon electrodes is desirable. Particularly when attempting to achieve a higher energy density, the use of pseudo-capacitance is useful, since in this case generally much higher specific values are achieved than with double-layer capacitance. It is known to use ruthenium oxide RuO_2 and hydrated ruthenium oxide $\text{RuO}_2 \cdot x\text{H}_2\text{O}$, inter alia from U.S. Pat. Nos. 5,550,706, 5,851,506, 5,875,092 and 6,025,020. In combination with aqueous electrolytes, such as for example KOH solutions, these compounds have a high effective capacitance in F/g based on redox reactions and can be used as anodes and as cathodes. They also have a good electrical conductivity. Drawbacks of these compounds when used in (symmetrical) electrochemical capacitors are the limited operational voltage range and the very high costs of material of the desired purity. Considerable research is being undertaken into alternative pseudo-capacitance materials which are able to counteract these drawbacks while still allowing the desired higher capacitance and energy density to be achieved.

[0028] In the prior art, it is generally accepted that the use of compounds containing precious-metal elements, such as for example precious-metal oxides, is necessary in order to obtain a sufficiently high storage capacitance and/or a sufficiently high conversion rate or catalytic activity of the electrode, and a sufficiently high electrical conductivity.

[0029] As has already been indicated above, the costs of such compounds are high. Therefore, it has been proposed to reduce the quantity of precious metal in such compounds by using compositions which partially comprise inexpensive, non-precious metals. Compounds having the pyrochlore structure, such as $\text{Pb}_2\text{Ru}_2\text{O}_7$ (U.S. Pat. No. 5,841,627), perovskites $\text{A}(\text{B}_{1-x}\text{C}_x)\text{O}_3$, where $0 \leq x < 1$, and B is selected from the series consisting of Pt, Ru, Ir, Rh and Pd (the abovementioned DE 196 40 926), CaRuO_{3-x} and LaNiO_3 etc., are known. These compounds contain the expensive (semi-)precious-metal elements or are not oxygen-deficient (or both). For the first category, it has been found that, calculated on the basis of the capacitance or activity obtained for the quantity of (semi-)precious metal, scarcely any reduction in cost is achieved. For the second category, the capacitance or activity obtained per gram is so low that there is no improvement compared to carbon materials.

[0030] Furthermore, it has been proposed to use metal hydroxides, which may change into metal oxyhydroxides, such as in particular $\text{Ni}(\text{OH})_2$. Although this compound is attractive in view of its low cost, its high specific capacitance and its favourable potential range, its conductivity is low and is dependent on the charge state. The reversible charge/discharge reaction at an electrode of this material in an alkaline electrolyte can be represented by $\text{Ni}(\text{OH})_2 + \text{OH}^- \rightarrow \text{NiOOH} + \text{H}_2\text{O} + e$, in which $\text{Ni}(\text{OH})_2$ has a poor conductivity and NiOOH has a significant electrical conductivity, provided it is in the correct phase (the P phase). These restrictions in terms of the electrical conductivity require the use of additives, such as for example graphite, and the use of conductive matrices, such as for example foamed metals or metal mats, in order to enclose the material with additive. This restricts the electrode thickness which can be utilized beneficially and entails additional costs, weight and volume. This also makes the production of electrodes more complicated and more expensive. The occurrence of $\text{Ni}(\text{OH})_2$ in a plurality of phases (α, β, γ) limits the acceptable operational conditions for the electrode to the conditions in which the desired β phase is stable. Furthermore, an $\text{Ni}(\text{OH})_2$ electrode can only be used as an anode, and consequently it is impossible to make symmetrical capacitors and, by way of example, a carbon counterelectrode is required. This limits the improvements in capacitance and energy density which can be achieved compared to the symmetrical carbon capacitor. $\text{Ni}(\text{OH})_2$, and in particular the nickel constituent and, if appropriate, the nickel required for the preparation, are also believed to have disadvantageous properties for the environment and health. Consequently, requirements and regulations apply with regard to its treatment and processing, which entail additional costs. These also impose limitations on its application areas, for example to the applications and markets for which collection and/or reuse are regulated.

[0031] A (rechargeable) battery is a known item of equipment. It can be used to store electricity and then to release it again, in particular with a high energy density (in Wh/kg and Wh/l), by using electrochemical conversion of electrical energy into chemical energy and vice versa. The structure of batteries of this type corresponds to the structure of electrochemical capacitors described above, although their design and operation may differ. Inter alia, (rechargeable) batteries of the nickel-cadmium, nickel-zinc and nickel-iron type, of the nickel-hydrogen type, of the nickel-metal hydride type, and of the metal/air type, such as iron/air, zinc/air, aluminium/air and lithium/air, are known. At least

one of the two electrodes of batteries of this type can now profitably be replaced by an electrode according to the invention. In particular, but not exclusively, the nickel electrodes, the cadmium electrode and the air electrodes are suitable for this purpose.

[0032] Inter alia, (rechargeable) batteries of the NiCd, NiZn, NiFe, NiH_2 and NiMH type are known, in which the "nickel electrode" consists of the same $\text{Ni}(\text{OH})_2$ compound and has the same action as that described above for electrochemical capacitors. In this case, the same drawbacks in terms of the restrictions in electrical conductivity and the same problems with regard to the environment and health apply.

[0033] Batteries of the Fe/air, Zn/air, Al/air and Li/air types are also known, in which during the discharge oxygen is consumed at the air electrode by electrochemical reduction; batteries of this type are "mechanically recharged" by renewal of the anode. Bidirectional air electrodes which, as well as reducing oxygen, are also able to evolve oxygen in the reverse process and therefore allow electrically rechargeable metal/air batteries, are also known. The compounds which have been described above only enable moderate performance to be achieved, on account of limited conductivity and catalytic activity, and are often expensive.

[0034] The materials according to the invention make it possible to produce high-performance electrodes which do not have the above drawbacks, i.e. which are inexpensive to produce, do not have any restrictions in terms of the thickness which can be beneficially utilized, and do not cause any environmental problems.

[0035] In a first embodiment, an electrode for an electrochemical cell can be produced by using a compound comprising a perovskite of the type $\text{ABO}_{3-\delta}$, in which $\delta \neq 0$, where A comprises a metal selected from the group consisting of Na, K, Rb, Ca, Ba, La, Pr, Sr, Ce, Nb, Pb, Nd, Sm and Gd, and B comprises a metal selected from the group consisting of Cu, Mg, Ti, V, Cr, Mn, Fe, Co, Nb, Mo, W and/or Zr, and in which there is no metal from the group consisting of Pt, Ru, Ir, Rh, Ni and Pd, and in which A and B cannot both be Nb, and $\text{SrVO}_{2.5}$ is excluded. Surprisingly, it has been found that, when using such a perovskite of the type $\text{ABO}_{3-\delta}$ in which there are no (semi-)precious metals or nickel, and in which δ is selected in particular between -0.2 and -0.05 or between $+0.05$ and $+0.7$, a particularly good storage capacitance (in F/g or Ah/kg) and/or a particularly good conversion rate or catalytic activity is obtained, and the electrical conductivity (in S/cm) is also good. Surprisingly, it has also been found that utilization of the electrode material comprising a compound of this type is virtually independent of the electrode thickness. A property of this type is altogether unknown in the prior art. It should be understood that the term perovskites of the type $\text{ABO}_{3-\delta}$ is also understood as meaning perovskites of the type either $\text{A}_1\text{A}_2\text{BO}_{3-\delta}$ or $\text{AB}_1\text{B}_2\text{O}_{3-\delta}$ or $\text{A}_1\text{A}_2\text{B}_1\text{B}_2\text{O}_{3-\delta}$, where $\delta \neq 0$ and δ in particular is within the limits indicated above. Examples include $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$, $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ and $\text{Nd}_{0.4}\text{Sr}_{0.6}\text{CoO}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$, although the invention is not restricted to these examples.

[0036] In a second embodiment, it is possible to produce an electrode for an electrochemical cell by using a compound comprising a Brown-Millerite $\text{ABO}_{(2.5-\xi)}$, where $\xi \neq 0$, and A and B are selected from the groups described

above. A high capacitance and/or conversion rate or catalytic activity and a good electrical conductivity can be achieved in particular for values for ξ of between -0.2 and -0.05 or between $+0.05$ and $+0.3$. One example of a compound of this type is $\text{SrCoO}_{(2.5-\xi)}$, although the invention is not restricted to this example.

Table 1. In particular, the electrical conductivity is of the same high level as that of $\text{Pb}_2\text{Ru}_2\text{O}_7$, and the capacitance in $\mu\text{F}/\text{cm}^2$ is of the same high level as that of $\text{Ni}(\text{OH})_2$. As well as the expensive ruthenium, it is also possible, with an electrode according to the invention, although not necessary, to avoid the heavy metal lead.

TABLE 1

Comparison of properties between electrodes*) according to the prior art and an $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ electrode*) according to the invention. C is the capacitance; σ is the electrical conductivity, A is the effective surface area. Maximum voltage V and maximum voltage drop ΔV apply to the entire cell.						
Property	Activated carbon	$\text{RuO}_2 \cdot x\text{H}_2\text{O}$	$\text{Pb}_2\text{Ru}_2\text{O}_7$	SrRuO_3	$\text{Ni}(\text{OH})_2$	$\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$
C ($\mu\text{F}/\text{cm}^2$)	10 ... 40	60	2200	2600
A (m^2/g)	<1200	120	10 ... 150	70	100	$\leq 5^{(0)}$
C (F/g)	<100	<720	72	20 ... 2000	220	>130 ⁽⁰⁾
σ (S/cm)	<1	...	500	>700
V (V)	1.2	1.3	...	1.2	1.6	1.6
ΔV (V)	1.0	1.0	0.9	0.7	0.8	1.2
Costs (Euro/kg)	2.25 ⁽¹⁾	3000 ⁽²⁾ ... 5000 ⁽³⁾	1000 ⁽²⁾ ... 23000 ⁽⁴⁾	>3000 ⁽²⁾	6 ... 10 ⁽⁵⁾	20 ⁽²⁾ ... 1200 ⁽⁶⁾

*)as working electrode in a supercapacitor with carbon counterelectrode and KOH electrolyte
In the compound according to the invention $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$, δ was 0.25 ± 0.05 .

⁽⁰⁾>2 600 F/g at > 100 m^2/g

⁽¹⁾purchase price based on 1000 kg

⁽²⁾raw material price

⁽³⁾purchase price based on 25 kg and depending on purity

⁽⁴⁾chemically pure and based on 5 grams

⁽⁵⁾based on NiO raw material price for > 1000 kg

⁽⁶⁾purchase price for one-off batch of 1 kg

[0037] It should be understood than an electrode may comprise more than one of the corresponding perovskites and/or Brown-Millerites.

[0038] The use of these compounds makes it possible to obtain electrodes with desired properties at low materials costs and using a simple manufacturing process. Furthermore, the invention makes it possible to beneficially utilize electrodes of up to great thicknesses without additions of extra materials or components being required, for example for electrical conductivity or current consumption. Expediently, electrodes of this type have a considerable porosity, in order to increase the active surface area with the electrolyte. Preferably, an electrode of this type, at least in the vicinity of the surface, comprises a porous structure which comprises at least 30% and preferably more than 70% of one or more of the abovementioned compounds. Surprisingly, in an electrochemical capacitor, it has been found that electrodes of this type have a high pseudo-capacitance. By way of example, when used as an anode in an asymmetric electrochemical capacitor with a carbon cathode and with KOH electrolyte, a high electrode capacitance was found, which, in view of the effective surface area, cannot be ascribed to double-layer capacitance. A high capacitance of the total cell was also found, with a low internal resistance, a favourable Nernst equilibrium potential E_0 and an appropriately useful voltage range. This leads to high energy and power densities for the cell. Separate measurements revealed high electrical conductivities for electrodes which comprise compounds according to the invention. A comparison with the properties of electrodes which are known from the prior art is given in

[0039] In addition to one or more of the abovementioned compounds according to the invention, the electrodes may also, although not necessarily, contain a binder for the purpose of forming a cohesive structure. A structure of this type may, but does not have to, be arranged in a matrix. It is also possible, although not necessary, for the electrodes to have undergone a heat treatment or calcining treatment or a sintering treatment.

[0040] FIG. 1 shows results of measurements carried out on electro-chemical capacitors with a carbon electrode and, respectively, an $\text{Ni}(\text{OH})_2$ (indicated by Δ) electrode which is known from the prior art and an $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ electrode (indicated by \square) according to the present invention. In the case of the $\text{Ni}(\text{OH})_2$ electrode, graphite was added in various percentages, in order to improve the electrical conductivity, while there was no addition used in the $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ ($\delta=0.25\pm 0.05$) electrode. It is clearly apparent that the electrode according to the invention can be used up to greater thicknesses without any loss in effective capacitance. It is therefore possible to use electrodes according to the invention up to greater thicknesses without employing additives, such as for example graphite, or conductive matrices, such as for example foamed metals. This allows cells and stacks of cells to be produced with less inactive material and therefore with higher energy and power densities. On account of the high conductivity, it is also possible to use a matrix with a lower conductivity than that of, for example, a foamed metal, for example a matrix of a conductive plastic or a conductive polymer, so that reductions in weight and costs can also be achieved. It is also possible to form

independent, relatively thick electrode layers, for example by printing, casting or dipping, optionally onto other (electrical or electronic) components, and which have a high capacitance and do not use expensive precious-metal elements.

[0041] None of this detracts from the fact that electrodes according to the invention can also be made as thin films, for example by printing, casting, dipping, painting or spraying, and can be used in this form.

[0042] In terms of the design and use, the electrodes according to the invention are not restricted to asymmetric capacitors or to capacitors with the structure indicated; they can also be put to good use in symmetrical electrochemical capacitors, in batteries and in fuel cells, reversible fuel cells, electrolysis equipment and sensors. By way of example, an electrode comprising one or more compounds according to the invention may replace the known $\text{Ni}(\text{OH})_2$ electrode in an alkaline battery, for example an NiCd or NiMH battery. For this purpose, the composition of the electrode according to the invention is then selected in such a way that the capacitance lies within the potential range which is desired for the battery.

[0043] An electrode according to the invention is characterized by a specific oxygen non-stoichiometry, i.e. a specific range of values for δ and/or ξ , and by the complete avoidance of precious-metal elements, in particular ruthenium and iridium, by a high pseudo-capacitance (of the same level as for $\text{Ni}(\text{OH})_2$) and/or a high catalytic activity and/or a high conversion rate, by a high electrical conductivity (of the same level as for $\text{Pb}_2\text{Ru}_2\text{O}_7$), virtually irrespective of the charge state or polarization, by a high stability, on account of the absence of undesired phases, and by a useful voltage range. In an electrode according to the invention, it is also possible to avoid the use of environmentally harmful elements, such as nickel and lead, which occur in electrodes according to the prior art. On account of the abovementioned properties, an electrode according to the invention, compared to those which are known in the prior art, can be less expensive, can have a higher round-trip efficiency, in particular at relatively high current intensities, can be produced more easily, can be used in the form of a thin film or a thick layer, and may optionally be enclosed in a matrix which may also comprise a lightweight, inexpensive plastic material of moderate conductivity. In this way, an electrode according to the invention also permits designs other than those which are known in the prior art for capacitors, supercapacitors, batteries, fuel cells, electrolyzers and sensors. For example, it is now possible for the electrode to be printed as a layer onto another component and, in this way, to add a function to this component. This component may, for example, form part of a photovoltaic solar cell or of an electrochromic window.

[0044] The present invention will be explained in more detail below with reference to a number of examples.

EXAMPLE 1

[0045] Electrode according to the invention produced by the application of a layer of suspension, ink or paste to a substrate. The substrate may, for example, be a metal foil or a plastic film. The suspension, ink or paste comprises one or more compounds according to the invention, a solvent, and possibly auxiliaries, such as dispersing agents, surfactants, wetting agents and the like. The compounds according to the

invention may in this case be added in the form of a powder with a high specific surface area. The suspension, ink or paste may if appropriate also contain a binder. The application is effected by means of spreading, painting, spraying, dipping, printing, casting, slip casting or rolling. After its application, the layer may firstly be dried, during which process solvent and auxiliaries are completely or partially removed. If appropriate, it is possible to use a heat treatment, calcining or sintering after the drying or as substitute for the drying. Then, the substrate bearing the layer, which may have characteristic thicknesses of between approx. $2\ \mu\text{m}$ and approx. $1\ 000\ \mu\text{m}$ and which may have a porosity of between approx. 5% and approx. 40%, is used in a supercapacitor or battery.

[0046] In this way, by way of example, an $1\ \text{cm}^2$ electrode according to the invention is made as follows. A quantity of 1 g of $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ ($\delta=0.25\pm 0.05$) powder with a low specific surface area of $\leq 5.0\ \text{m}^2/\text{g}$ was added to 1.5 ml of solution comprising 4 M KOH electrolyte and 0.1% by weight of surfactant. Agitation for 24 hours resulted in a homogeneous suspension, some of which was then applied to a $50\ \mu\text{m}$ thick nickel foil (the current collector). All of this was then dried for 4 hours at $80^\circ\ \text{C}$., in order in this way to obtain a $1\ \text{cm}^2$ electrode/current collector laminate, with an electrode layer which was approx. $15\ \mu\text{m}$ thick. Together with a separator and a counterelectrode made from activated carbon, this laminate was arranged in a Teflon® cell housing. Both electrodes were provided with approx. $50\ \mu\text{l}$ of electrolyte, after which the cell housing was sealed. Two stainless steel pins provide contact between the current collectors and the outside of the cell. The internal resistance ESR of the supercapacitor obtained in this way was measured with the aid of impedance spectroscopy. Then, charging and discharging cycles were carried out, cyclic voltammograms were recorded and charging and discharging cycles were carried out again at current densities of up to 500 mA per gram of $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ ($\delta=0.25\pm 0.05$) and between the cell voltages of 0 and 1.8 V. FIG. 2 shows the results for a cell in which a platinum reference electrode was also fitted in the separator. The potential curve of the electrode during charging and discharging with a current of 0.25 A/g leads to an effective capacitance for the compound according to the invention of $\geq 130\ \text{F/g}$.

EXAMPLE 2

[0047] Electrode produced by the application of a suspension, ink or paste in a matrix. The matrix may be foamed metal or a metal mat, metal gauze, polymer foam, polymer gauze or some other porous structure. The suspension, ink or paste comprises one or more perovskite and/or Brown-Millerite compounds according to the invention, and may furthermore contain constituents as described in Example 1. The perovskite and/or Brown-Millerite compounds may in this case be added in the form of a powder with a high specific surface area. The suspension, ink or paste may be applied using the methods described in Example 1. After the application, the steps as described in Example 1 may follow. Typical thicknesses of the electrode structure which is formed will lie between approx. $100\ \mu\text{m}$ and approx. $1\ 500\ \mu\text{m}$.

[0048] In this way, by way of example, a $1\ \text{cm}^2$ electrode according to the invention was made as follows. A quantity of 1 g of $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ ($\delta=0.25\pm 0.05$) powder with a

low specific surface area of $\leq 4.0 \text{ m}^2/\text{g}$ was added to 1.5 ml of solution comprising 4 M KOH electrolyte and 0.1% by weight of surfactant. By agitation for 24 hours, a homogeneous suspension was obtained, which was forced into a 900 μm thick nickel foamed metal. The filled foam was then dried for 12 hours at 80° C. In the same way as in Example 1, this was used to make a supercapacitor cell, and experiments were carried out. **FIG. 3** shows the results for a cell in which a platinum reference electrode is also incorporated in the separator. The potential curve of the electrode during charging and discharging with a current of 0.37 A/g reveals an effective capacitance for the compound according to the invention of $\geq 120 \text{ F/g}$.

EXAMPLE 3

[0049] Electrode produced by the application of a layer of suspension, ink or paste to a substrate. The suspension, ink or paste comprises one or more perovskite and/or Brown-Millerite compounds according to the invention, a solvent and possibly auxiliaries, such as dispersing agents, surfactants, wetting agents and the like. The perovskite and/or Brown-Millerite compounds may in this case be added in the form of a powder with a high specific surface area. If appropriate, the suspension, ink or paste may also contain a binder. The substrate is a smooth surface. The suspension is distributed over the surface by spreading, painting, printing or casting and is dried. Then, the tape which is formed is removed from the smooth surface as an independent electrode layer. If appropriate, for use in a capacitor, battery, fuel cell, electrolyser or sensor, it is also possible for heat treatments, calcining steps or sintering steps to be carried out on the tape.

EXAMPLE 4

[0050] Electrode produced by the application of a suspension, ink or paste comprising one or more compounds according to the invention to a substrate or in a matrix, this substrate or matrix forming part of or being intended to form part of another component or device, such as a photovoltaic solar cell or electrochromic window.

EXAMPLE 5

[0051] One or more compounds according to the invention are packaged in powder form in an envelope of porous plastic material, which is inert with respect to the electrolyte which is to be used and is electrically insulating. To close the envelope, powder material, envelope and a wire or strip of metal are pressed together in such a manner that there is contact between the powder particles themselves and between the wire or strip and the powder. The structure formed in this way is used as an electrode in an electrochemical cell.

EXAMPLE 6

[0052] In a similar manner to that described in Example 1, a 1 cm^2 electrode according to the invention was made from a low-surface area powder of the Brown-Millerite $\text{SrCoO}_{(2.5-\xi)}$, where $\xi=0.10\pm 0.05$. The electrode was likewise used in the same way as in Example 1 in a laboratory supercapacitor, fitted with a Pt reference electrode and a counterelectrode. The results of the charging and discharging experiments are shown in **FIG. 4**. At a charging and discharging current intensity of 200 mA/g, the mean capacitance is approx. 160 F/g.

[0053] The characterizing use of perovskites and/or Brown-Millerites in the electrodes according to the invention means that, compared to the known materials and electrodes, there are numerous possible ways of influencing the properties and adapting them to specific use requirements.

[0054] Although the invention has been described above with reference to preferred embodiments, it will be understood that, on reading the above description, variants which are obvious and lie within the scope of the appended claims will occur to the person who is skilled in the relevant art.

1. Mixed oxide material with a high electron conductivity, characterized by

an empirical formula ABO_y , where $y \neq 3$ and where A comprises at least one metal selected from Na, K, Rb, Ca, Ba, La, Pr, Sr, Ce, Nb, Pb, Nd, Sm and Gd, and B comprises at least one metal selected from the group consisting of Cu, Mg, Ti, V, Cr, Mn, Fe, Co, Nb, Mo, W and Zr, where A and B cannot both be Nb and where the compound $\text{SrVO}_{2.5}$ is excluded.

2. Mixed oxide material according to claim 1, characterized in that

the material is a perovskite-type material, for which $y=3-\delta$, where $\delta \neq 0$ and δ has values in the range from approximately -0.2 to approximately -0.05 or in the range from approximately +0.05 to approximately +0.7.

3. Mixed oxide material according to claim 1, characterized in that

the material is a Brown-Millerite-type material, for which $y=2.5-\xi$ and ξ has values in the range from approximately -0.2 to approximately -0.05 or in the range from approximately +0.05 to approximately +0.3.

4. Mixed oxide material according to one or more of claims 1-3, characterized in that

A and/or B comprise(s) a metal doped with another metal, the doping metals for A and B being selected from the options given for A and B.

5. Mixed oxide material according to claim 4, characterized in that

A comprises $\text{Sm}_x\text{Sr}_{(1-x)}$, with x lying in the range from approximately 0.4 to approximately 0.6.

6. Mixed oxide material according to claim 4, characterized in that

A comprises $\text{Nd}_x\text{Sr}_{(1-x)}$, with x lying in the range from approximately 0.4 to approximately 0.6.

7. Mixed oxide material according to one or more of the preceding claims 1-6, characterized in that

B comprises Co.

8. Mixed oxide material according to one or more of the preceding claims 1-6, characterized in that

B comprises Fe.

9. Mixed oxide material according to claims 7 and 8, characterized in that

B comprises $\text{Co}_{(1-x)}\text{Fe}_x$, with x lying in the range from approximately 0.2 to approximately 0.6.

10. Electrode for an electrochemical cell which can be produced from a material with a high electron conductivity, characterized in that

the electrode comprises a mixed oxide material according to one or more of claims **1-9**.

11. Method for producing an electrode for an electrochemical cell, comprising the steps of providing a suitable substrate, and forming a cohesive layer of a mixed oxide thereon by applying a mixture of a mixed oxide, one or more binders and at least one solvent, followed by removal of the solvent and, if appropriate, followed by a heat treatment, characterized in that

a cohesive layer which includes a mixed oxide material according to one or more of claims **1-10** is formed on the substrate.

12. Method according to claim 11, characterized in that the substrate is a matrix and the mixed oxide is accommodated in the matrix and forms a cohesive unit therewith.

13. Method according to claim 11, characterized in that the substrate has a release property, and the layer which comprises a mixed oxide material, after application on the substrate, is removed and is subjected to a heat treatment if appropriate.

14. Electrochemical cell which comprises at least two electrodes and an electrolyte, characterized in that

it comprises at least one electrode according to claim 10.

15. Electrochemical cell according to claim 14, characterized in that

it comprises a further electrode selected from a carbon electrode, an RuO_2 electrode and an $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ electrode.

* * * * *