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(54) **Secondary battery and method for its manufacturing**

(57) The present invention relates to secondary battery which comprises

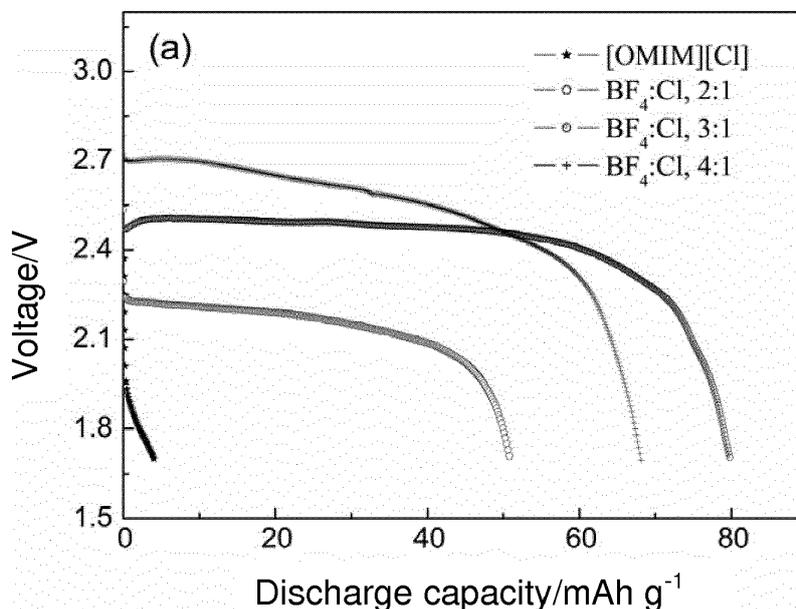
- A negative electrode (anode) having a first metal or a first alloy or a host material capable of reacting with or intercalating a chloride ion as anode material,
- A positive electrode (cathode) having a chloride of a second metal or of a second alloy or a chloride intercalation compound as cathode material,
- A separator to separate the cathode from the anode, and

- An electrolyte which exhibits an chloride ionic conductivity.

The present invention further relates to a method for manufacturing such a secondary battery.

The present invention refers to a safe and energetic rechargeable battery which is based on the transfer of chloride ions. The main advantage of such a battery is attributed to the fact that chloride ions are environmentally friendly and abundant at the same time.

Fig. 1a



Description

[0001] The present invention relates to a secondary battery and a method for its manufacturing.

[0002] High energy density, abundant material resources, high safety, and environmental friendliness are important features for secondary, i.e. rechargeable, batteries which are receiving particular attention in the areas of portable electronic devices, electric vehicles and other energy storage systems.

[0003] Electrochemical cells, also denoted as *batteries*, based on a cation shuttle, including H^+/OH^- , Li^+ , Na^+ , K^+ , Mg^{2+} , Al^{3+} , and Zn^{2+} , have been known for a long time. A rechargeable battery which uses a fluoride anion as an anion shuttle was reported in US 7,722, 993 B2 as well as in M.A. Reddy and M. Fichtner, J. Mater. Chem., 2011, 21, 17059-17062. In the latter, the battery is operated at 150 °C by employing a solid electrolyte of a LaF_3/BaF_2 composite which exhibits a fluoride conductivity of 0.2 mS cm^{-1} at about 150 °C. The overall reaction for the metal fluoride/metal secondary battery is expressed as



where M_a represents a first metal employed as anode, M_c denotes a second metal employed as cathode, and m, n gives the number of respective fluoride ions.

[0004] Similar to metal fluoride/metal batteries, batteries based on various metal chloride/metal systems theoretically exhibit a large Gibbs free energy change which should yield a high electro motoric force (EMF) during the phase transition which is effected by a chloride ion transfer. Calculated data of specific capacities and energy densities for a number of metal chloride/metal couples are listed in **Table 1** and **Table 2**. There, C_c and C_a denote the theoretical capacities of the cathode and anode materials, respectively. The specific capacity of the battery is calculated based on both cathode and anode materials. The Gibbs free energy $\Delta_r G$ data are derived from known standard thermodynamic properties of the selected materials.

Table 1: Specific gravimetric capacities and energy densities for metal chloride/metal couples

Battery reaction	$\Delta_r G$, kJ/mol	n	EMF, V	Theoretical capacity C , mAh/g	Specific capacity of battery, Ah/kg	Energy density, Wh/kg
$CoCl_2(c) + 2Li(a) \rightarrow 2LiCl + Co$	-499.0	2	2.58	$C_c = 412.8; C_a = 3861$	372.9	962.1
$VCl_3(c) + 3Li(a) \rightarrow 3LiCl + V$	-642.0	3	2.21	$C_c = 511.1; C_a = 3861$	451.3	997.3
$BiCl_3(c) + 3Li(a) \rightarrow 3LiCl + Bi$	-838.2	3	2.89	$C_c = 255.0; C_a = 3861$	239.2	691.3
$2BiCl_3(c) + 3Mg(a) \rightarrow 3MgCl_2 + 2Bi$	-1145.4	6	1.98	$C_c = 255.0; C_a = 2205$	228.6	452.6
$BiCl_3(c) + Ce(a) \rightarrow CeCl_3 + Bi$	-669.8	3	2.31	$C_c = 255.0; C_a = 573.8$	176.5	407.7
$CuCl_2(c) + Ca(a) \rightarrow CaCl_2 + Cu$	-573.1	2	2.97	$C_c = 398.7; C_a = 1340$	307.2	912.5
$CuCl_2(c) + Mg(a) \rightarrow MgCl_2 + Cu$	-416.1	2	2.15	$C_c = 398.7; C_a = 2205$	337.6	725.9
$CuCl_2(c) + 2Na(a) \rightarrow 2NaCl + Cu$	-592.5	2	3.07	$C_c = 398.7; C_a = 2330$	297.0	911.9
$CuCl_2(c) + 2Li(a) \rightarrow 2LiCl + Cu$	-593.1	2	3.07	$C_c = 398.7; C_a = 3861$	361.3	1109
$CuCl(c) + Li(a) \rightarrow LiCl + Cu$	-264.5	1	2.74	$C_c = 271.7; C_a = 3861$	252.9	693.1
$FeCl_2(c) + 2Na(a) \rightarrow 2NaCl + Fe$	-465.9	2	2.41	$C_c = 425.9; C_a = 2330$	311.9	751.6

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(continued)

Battery reaction	$\Delta_r G$, kJ/mol	n	EMF, V	Theoretical capacity C , mAh/g	Specific capacity of battery, Ah/kg	Energy density, Wh/kg
$\text{NiCl}_2(\text{c}) + 2\text{Na}(\text{a}) \rightarrow 2\text{NaCl} + \text{Ni}$	-509.2	2	2.64	$C_c = 413.5; C_a = 2330$	305.2	805.7
$\text{FeCl}_3(\text{c}) + \text{Ce}(\text{a}) \rightarrow \text{CeCl}_3 + \text{Fe}$	-650.8	3	2.25	$C_c = 495.6; C_a = 573.8$	265.9	598.2
$2\text{FeCl}_3(\text{c}) + 3\text{Mg}(\text{a}) \rightarrow 3\text{MgCl}_2 + 2\text{Fe}$	-1107.4	6	1.91	$C_c = 495.6; C_a = 2205$	404.7	773.0
$\text{MnCl}_2(\text{c}) + 2\text{Li}(\text{a}) \rightarrow 2\text{LiCl} + \text{Mn}$	-328.3	2	1.70	$C_c = 425.9; C_a = 3861$	383.6	652.1

Table 2: Specific volumetric capacities and energy densities for metal chloride/metal couples

Battery reaction	$\Delta_r G$ kJ/mol	n	EMF, V	Theoretical capacity C , mAh/g	Specific capacity of battery, Ah/L	Volumetric energy density, Wh/L
$\text{CoCl}_2(\text{c}) + 2\text{Li}(\text{a}) \rightarrow 2\text{LiCl} + \text{Co}$	-499.0	2	2.58	$C_c = 412.8; C_a = 3861$	827.9	2136.0
$\text{VCl}_3(\text{c}) + 3\text{Li}(\text{a}) \rightarrow 3\text{LiCl} + \text{V}$	-642.0	3	2.21	$C_c = 511.1; C_a = 3861$	891.4	1970.0
$\text{BiCl}_3(\text{c}) + 3\text{Li}(\text{a}) \rightarrow 3\text{LiCl} + \text{Bi}$	-838.2	3	2.89	$C_c = 255.0; C_a = 3861$	761.0	2199.3
$2\text{BiCl}_3(\text{c}) + 3\text{Mg}(\text{a}) \rightarrow 3\text{MgCl}_2 + 2\text{Bi}$	-1145.4	6	1.98	$C_c = 255.0; C_a = 2205$	920.8	1823.2
$\text{BiCl}_3(\text{c}) + \text{Ce}(\text{a}) \rightarrow \text{CeCl}_3 + \text{Bi}$	-669.8	3	2.31	$C_c = 255.0; C_a = 573.8$	923.4	2133.1
$\text{CuCl}_2(\text{c}) + \text{Ca}(\text{a}) \rightarrow \text{CaCl}_2 + \text{Cu}$	-573.1	2	2.97	$C_c = 398.7; C_a = 1340$	818.1	2429.8
$\text{CuCl}_2(\text{c}) + \text{Mg}(\text{a}) \rightarrow \text{MgCl}_2 + \text{Cu}$	-416.1	2	2.15	$C_c = 398.7; C_a = 2205$	998.6	2147.0
$\text{CuCl}_2(\text{c}) + 2\text{Na}(\text{a}) \rightarrow 2\text{NaCl} + \text{Cu}$	-592.5	2	3.07	$C_c = 398.7; C_a = 2330$	614.5	1886.5
$\text{CuCl}_2(\text{c}) + 2\text{Li}(\text{a}) \rightarrow 2\text{LiCl} + \text{Cu}$	-593.1	2	3.07	$C_c = 398.7; C_a = 3861$	813.3	2496.8
$\text{CuCl}(\text{c}) + \text{Li}(\text{a}) \rightarrow \text{LiCl} + \text{Cu}$	-264.5	1	2.74	$C_c = 271.7; C_a = 3861$	724.7	1985.7
$\text{FeCl}_2(\text{c}) + 2\text{Na}(\text{a}) \rightarrow 2\text{NaCl} + \text{Fe}$	-465.9	2	2.41	$C_c = 425.9; C_a = 2330$	611.7	1474.2
$\text{NiCl}_2(\text{c}) + 2\text{Na}(\text{a}) \rightarrow 2\text{NaCl} + \text{Ni}$	-509.2	2	2.64	$C_c = 413.5; C_a = 2330$	637.9	1684.0
$\text{FeCl}_3(\text{c}) + \text{Ce}(\text{a}) \rightarrow \text{CeCl}_3 + \text{Fe}$	-650.8	3	2.25	$C_c = 495.6; C_a = 573.8$	1048.7	2359.8
$2\text{FeCl}_3(\text{c}) + 3\text{Mg}(\text{a}) \rightarrow 3\text{MgCl}_2 + 2\text{Fe}$	-1107.4	6	1.91	$C_c = 495.6; C_a = 2205$	1045.3	1996.5
$\text{MnCl}_2(\text{c}) + 2\text{Li}(\text{a}) \rightarrow 2\text{LiCl} + \text{Mn}$	-328.3	2	1.70	$C_c = 425.9; C_a = 3861$	782.9	1330.9

[0005] From both **Table 1** and **Table 2** it is apparent that a metal chloride/metal secondary battery would exhibit high energy densities. For practical applications the volumetric energy densities given in **Table 2** are usually of higher importance compared to the gravimetric energy densities given in **Table 1** since volume is often a larger problem than weight, e.g. in cellular phones. Despite these attractive features presented in **Table 1** and **Table 2**, secondary batteries, which work on the basis of a transfer of chloride ions, have not been reported so far.

[0006] It is noteworthy to mention that a large volume change, especially for the selected cathode materials, occurs during the phase transition between a metal chloride and its corresponding metal. As an example, a drastic volume expansion of 482.3 % from Co to CoCl_2 was observed. Values for other couples are presented in **Table 3**.

Table 3: Volume change between some metals and their chlorides

Metal/metal chloride	Volume change, %	
	Metal to metal chloride	Metal chloride to metal
Li/LiCl	56.5	-36.1
Na/NaCl	13.6	-12.0
Mg/MgCl ₂	197.5	-66.3
Ca/CaCl ₂	100.0	-50.0
Ce/CeCl ₃	221.8	-68.9
Cu/CuCl	216.2	-68.3
Co/CoCl ₂	482.3	-82.8
Cu/CuCl ₂	460.0	-82.1
Fe/FeCl ₂	464.5	-82.3
Ni/NiCl ₂	453.5	-81.9
Mn/MnCl ₂	472.4	-82.5
V/VCl ₃	480.0	-82.7
Bi/BiCl ₃	210.6	-67.8

[0007] This feature has to be considered in a real battery setup since it easily causes an interruption of a mass transfer when an electrode material is contacted with a mechanically rigid solid electrolyte.

[0008] Little attention has been paid to anionic conductors with chloride conductivity so far. I. V. Murin, O. V. Glumov, and N. A. Mel'nikova, *Russ. J. Electrochem.*, 2009, 45, 411-416, and N. Imanaka, K. Okamoto and G. Adachi, *Angew. Chem. Int. Ed.*, 2002, 41, 3890-3892, reported that solid inorganic compounds such as PbCl_2 , SnCl_2 , and LaOCl show a fast chloride transfer at very high temperatures.

[0009] Furthermore, I. V. Murin, O. V. Glumov, and N. A. Mel'nikova, *Russ. J. Electrochem.*, 2009, 45, 411-416, and K. Yamada, Y. Kuranaga, K. Ueda, S. Goto, T. Okuda, and Y. Furukawa, *Bull. Chem. Soc. Jpn.*, 1998, 71, 127-134, demonstrated that cubic CsSnCl_3 shows a high ionic conductivity of 1 mS cm^{-1} at about 100°C where, however, its electrochemical stability turns out to be a problem due to a weak Sn-Cl bond.

[0010] L. C. Hardy and D. F. Shriver, *Macromolecules*, 1984, 17, 975-977, P. C. Huang and K. H. Reichert, *Angew. Makromol. Chem.*, 1989, 165, 1-7, as well as N. Ogata, *J. Macromol. Sci. Polymer. Rev.*, 2002, 42, 399-439, reported that chloride ionic liquids which are cross-linked in polymers also possess fast ionic conduction. As an example, a composite of poly(diallyl-dimethylammonium chloride)/tetramethylammonium chloride shows an ionic conductivity of 0.22 mS cm^{-1} at 25°C .

[0011] The main object of the present invention is therefore to provide a secondary battery on the basis of a metal chloride/metal transition and a method for its manufacturing, which overcome the limitations known from the state of the art.

[0012] In particular, it is an object of the present invention to provide a secondary battery which comprises an electrolyte which exhibits high chloride ionic conductivity.

[0013] It is a further object of the present invention to provide a secondary battery which is safely rechargeable.

[0014] The solution of this problem is provided by a secondary battery according to claim 1 and a method for its manufacturing according to claim 13. The dependent claims describe preferred features.

[0015] According to the present invention, a metal chloride/metal secondary battery having at least the following composition is provided:

- a negative electrode (anode) which comprises a first metal or a first alloy or a host material, which is capable to react with or to intercalate a chloride ion Cl^- , as anode material,
- a positive electrode (cathode) which comprises a chloride of a second metal or of a second alloy or a chloride intercalation compound as cathode material,
- 5 - a separator which physically separates the cathode from the anode in order to prevent any touching, and
- an electrolyte, preferably in the form of a solid, a gel or a liquid, which exhibits a chloride ionic conductivity, preferably of at least 0.1 mS cm^{-1} , more preferably of at least 1 mS cm^{-1} .

[0016] Hereby, a *chloride intercalation compound* describes a complex material where a chloride ion Cl^- is reversibly inserted between at least a single other chemical compound, which is generally denoted as *host material*.

[0017] In a preferred embodiment, the anode material includes

- an alkali metal, preferably Li or Na, or
- an alkaline earth metal, preferably Mg or Ca, or
- 15 - a rare earth metal, preferably La or Ce, or
- an alloy which includes at least one of these metals.

[0018] In a further preferred embodiment, finely dispersed metal powder is used as anode material in a composite with carbon black or porous nanocarbon or non-porous nanocarbon, including graphene, or other electrically conductive materials, including a metal powder or a metal foam.

[0019] In a preferred embodiment, the cathode material includes a chloride of a transition metal or a post-transition metal, preferably of Co or of V or of Bi, or of a mixture of these chlorides.

[0020] In a further preferred embodiment, the cathode material is constituted by a composite which includes carbon black or porous nanocarbon or non-porous nanocarbon, including graphene, or other electrically conductive materials, including a metal powder or a metal foam, in addition to the chloride of a transition metal or of a post transition metal. In a most preferred embodiment, a composite of CoCl_2 or of VCl_3 or of BiCl_3 , respectively, with carbon black is employed as cathode material.

[0021] In a preferred embodiment, the electrolyte is selected from

- 30 - a chloride ionic liquid, i.e. a chloride salt which is in the liquid state at operation temperature of the battery. In general, ionic liquids consist of a salt where one or both the ions are large, and the cation has a low degree of symmetry. These factors tend to reduce the lattice energy of the crystalline form of the salt, and hence lower the melting point,
- a complex anion which contains a chloride ion, and an organic solvent.
- an organic chloride salt, or
- 35 - an inorganic chloride salt.

[0022] Particularly for operation temperatures of the secondary battery above 100°C , the electrolyte is selected from an inorganic chloride salt, either in its solid or in its molten form, preferably from

- 40 - a solid solution of a PbCl_2 /alkali-metal chloride, preferably with KCl,
- a solid solution of a SnCl_2 /alkali-metal chloride, preferably with KCl,
- CsSnCl_3 , CsPbCl_3 ,
- K_2NiCl_4 , or
- LaOCl , or from $\text{La}_{1-x}\text{Ca}_x\text{OCl}_{1-x}$.

[0023] In a further preferred embodiment, particularly for operation temperatures of the secondary battery within a temperature range from 25°C to 100°C , the electrolyte is selected from an organic chloride salt or from a chloride ionic liquid.

[0024] Preferred organic chloride salts include poly(diallyldimethyl-ammonium chloride) or organic chlorides with cations of imidazolium, pyrrolidinium, piperidinium, or pyridinium without or with side chains. In a specific embodiment, solid chlorides with cations of ammonium, imidazolium, pyrrolidinium, piperidinium or pyridinium are employed as additives in polymer electrolyte.

[0025] Preferred chloride ionic liquids are pure ionic liquids, binary ionic liquids or ternary ionic liquids.

[0026] Preferred *binary ionic liquids* include chloride ionic liquids with cations of imidazolium, pyrrolidinium, piperidinium, pyridinium, and quaternary ammonium. Since the imidazolium species shows the lowest electrochemical window, large side chains are preferred. The *electrochemical window* of a material is the voltage range between which the material does neither become oxidized nor reduced. In a particularly preferred embodiment, ionic liquids with different anions, preferably with BF_4^- , PF_6^- , or $[\text{N}(\text{CF}_3\text{SO}_2)_2]^-$, are added as solvents to the selected binary ionic liquid.

[0027] In a specific embodiment, *ternary ionic liquids*, e.g. imidazolium tetrafluoroborate [BMIM][BF₄], are employed as additives in order to increase the ionic conductivity of a specific binary ionic liquids electrolyte.

[0028] In a further embodiment, the electrolyte is selected from a chloride ionic liquid to which an organic solvent, preferably polycarbonate (PC), a mixture of polycarbonate and dimethyl carbonate (PC/DMC), or a mixture of ethylene carbonate and dimethyl carbonate (EC/DMC), has been added.

[0029] In a further embodiment, the electrolyte is selected from a mixture of a complex anion which contains a chloride ion and an organic solvent or an ionic liquid. In order to obtain a complex anion, a transition metal chloride including FeCl₃, FeCl₂, NiCl₂, or CoCl₂ which reacts with a chloride ion to form a corresponding complex anion [FeCl₄]⁻, [FeCl₄]²⁻, [NiCl₄]²⁻ or [CoCl₄]²⁻ which is stable in the electrolyte and cannot be reduced to the corresponding metals in the electrochemical window of the electrolytes, is employed. In contrast with these findings, [AlCl₄]⁻ and [CuCl₄]²⁻ can be reduced to metals.

[0030] Another aspect of the invention concerns a method for manufacturing such a secondary battery. According to the present invention, such method comprises the following steps (a) to (d).

[0031] According to step (a), an anode material having a first metal or a first alloy or a host material, which is able to react with or to intercalate a chloride ion Cl⁻, is provided and a negative electrode (anode) is formed therewith.

[0032] According to step (b), a cathode material having a chloride of a second metal or of a second alloy or a chloride intercalation compound is provided and a positive electrode (cathode) is formed therewith.

[0033] According to step (c), an arrangement is composed by arranging a separator in such a way that, while the cathode stays physically separated from the anode in order to avoid any touching between the cathode and the anode, a flow of chloride ions is generated during the operation of the secondary battery.

[0034] According to step (d), an electrolyte is added to this arrangement in such a way that, while the cathode still remains physically separated from the anode, an electrically conducting connection between the anode and the cathode results during the operation of the battery.

[0035] In a preferred embodiment, the cathode material is provided during step (b) in the form of a dried powder. The cathode is subsequently formed by ball milling this powder with carbon black or porous nanocarbon or non-porous nanocarbon, including graphene, in order to form a composite thereof.

[0036] In an alternative embodiment, the cathode material is provided during step (b) in the form of a dried powder, which is first dissolved by a suitable solvent in a solution, which is then added to carbon black or porous nanocarbon or non-porous nanocarbon, including graphene, in such a way that it delivers a wet composite. The cathode itself is formed by firstly freeze-drying the wet composite and subsequently heating it to a temperature, which is preferably between 100 °C and 200 °C.

[0037] The present invention refers to a safe and energetic rechargeable battery which is based on the transfer of chloride ions. The main advantage of such a battery is attributed to the fact that chloride ions are environmentally friendly and abundant at the same time.

[0038] The present invention will be more apparent from the following description of non-limiting specific embodiments with reference to the drawings.

[0039] High-purity (> 99.5 %) anhydrous CoCl₂, VCl₃, and BiCl₃ powders were dried under vacuum at appropriate temperatures. The positive electrodes (cathodes) were prepared by ball milling one of said metal chlorides and 20 wt% carbon black utilizing a silicon nitride vial with silicon nitride balls (20 and 10 mm in diameter) under an argon atmosphere. The ball to powder ratio was 20:1. The milling was performed in a planetary mill with a rotation speed of 300 rpm. The milling time was 1 h.

[0040] In an alternative route, a freeze-dry method was employed to prepare the CoCl₂/carbon black composite. The anhydrous CoCl₂ powders were dissolved in anhydrous methanol to form a blue solution which was then added dropwise into the active carbon in a beaker. The wet composite was cooled in a liquid nitrogen bath and subsequently freeze-dried under vacuum for 5 h, followed by 18 h of drying at 160 °C.

[0041] Ionic liquids of 1-Methy-3-Octylimidazolium chloride ([OMIM] [Cl], purity > 97%) and 1-Butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF₄], purity >98%) were both dried at 85 °C for 72 h under vacuum and with different volume ratios and subsequently employed as electrolyte.

[0042] A Glass fiber was utilized as separator.

[0043] The electrochemical measurements were conducted by utilizing two-electrode Swagelok-type cells with lithium metal as anode material. The cathode materials consisted of CoCl₂/C, VCl₃/C or BiCl₃/C powders, respectively, where C denotes carbon black. Discharge and charge tests were carried out galvanostatically at various current densities over a voltage range from 3.5 V to 1.6 V by using a multi-channel battery testing system at 298 K. Cyclic voltammetry (CV, 1.6 V to 3.5 or 4 V, 50 μV s⁻¹) spectra were taken by using an electrochemical workstation.

[0044] Powder X-ray diffraction (XRD) patterns were obtained with a diffractometer with Cu-K_α radiation. X-ray photoelectron spectroscopy (XPS) measurements were carried out by utilizing a K-Alpha spectrometer with Al-K_α radiation as X-ray source.

[0045] Fig. 1 shows discharge curves as well as XRD patterns of a CoCl₂/Li battery with a mixture of 1-Methy-3-

Octylimidazolium chloride ([OMIM][Cl]) and 1-Butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF₄]) as electrolyte. Since [OMIM][Cl] on one hand exhibits a melting point below 0 °C, and on the other hand shows a high viscosity, a battery in which [OMIM][Cl] is used as sole electrolyte will almost not be able to discharge as shown in **Fig. 1a**. The reason for this behaviour is found in a weak chloride mobility in pure [OMIM][Cl] at 298 K.

[0046] By adding [BMIM][BF₄] as second electrolyte component, the movement of the chloride ion could be significantly increased. Employing a volume ratio of [BMIM][BF₄] to [OMIM][Cl] at 3:1, a discharge capacity of about 80 mAh g⁻¹ was measured and a voltage plateau at 2.47 V for the CoCl₂ electrode was observed. At a molar concentration of about 1 M for [OMIM][Cl], the ionic conductivity was 0.91 mS cm⁻¹ at 298 K. After the discharge a transition from CoCl₂ to metallic Co at the cathode as well as a LiCl formation at the anode were evidenced by the XRD patterns shown in **Fig. 1b** which indicate that the chloride ion moves from the cathode to the anode during discharging.

[0047] Recharging tests were performed for several couples in the electrolyte with about 1 M [OMIM][Cl] at 298 K. The ball-milled CoCl₂ exhibited a charge capacity of 67.1 mAh g⁻¹ which is 84% of the first discharge capacity as shown in **Fig. 2a**.

[0048] In an alternative route, wet impregnation and the freeze-drying method were employed to prepare a CoCl₂/carbon composite, which contains finely dispersed CoCl₂ particles and which shows a further improvement of the capacity to 105.2 mAh g⁻¹.

[0049] However, this value is still considerably lower than the theoretical capacity of a CoCl₂ cathode with a value of 412.8 mAh g⁻¹ as mentioned in **Table 1**. This feature can be attributed to a partial dissolution of CoCl₂ into the electrolyte. It is known that transition metal chlorides are Lewis acids which react with a Lewis base containing a chloride ion, resulting in a formation of complex ions. For example, CoCl₂ reacts with Cl⁻ to form a blue CoCl₄²⁻ complex which readily dissolves into an electrolyte. Since this process consumes a part of the active material, it leads to a lower discharge capacity of the CoCl₂ electrode.

[0050] The CV spectrum for a CoCl₂/Li battery as shown in the inset in **Fig. 2a** exhibits a pair of cathodic and anodic peaks in the potential electrochemical window from 3.5 V to 1.6 V, which can be attributed to the chloride shuttle during discharge and charge. The single cathodic or anodic peak is caused by a one-step phase transformation of the reduction of CoCl₂ and also the subsequent oxidation during charging.

[0051] Multistep reversible reactions were observed in a VCl₃/Li secondary battery as presented in the inset in **Fig. 2b**. The first reduction peak in the CV spectrum appears at 2.86 V and a subsequent broad reduction peak is observed in the voltage range from 2.6 V to 1.5 V while three distinct oxidation peaks appear in a reverse scan. These redox couples can be ascribed to reactions among the vanadium species of V³⁺, V²⁺, V⁺ and V, which results in a discharge capacity of 111.8 mAh g⁻¹ of the VCl₃ electrode.

[0052] **Fig. 2c** shows a battery in which BiCl₃ is utilized as cathode material. BiCl₃ is a mild Lewis acidic chloride and therefore relatively non-toxic and has subsequently been employed as an eco-friendly catalyst system in synthetic green chemistry. In addition, it has been found that BiCl₃ is stable in the electrolyte even after more than 3 months of immersion. A flat voltage plateau of 2.34 V and a high discharge capacity of about 176.6 mAh g⁻¹ were observed, which corresponds to 69% of the theoretical capacity 255 mAh g⁻¹ (see **Table 1**). Moreover, its charge capacity of 165 mAh g⁻¹ shows that 93 % of the discharge capacity could be recovered. As shown in the CV pattern in the inset in **Fig. 2c**, a BiCl₃/Li battery presents multistep reversible reactions during discharge and charge.

[0053] A so-called *cycling test* for the BiCl₃/Li battery is presented in **Fig. 2d**. The BiCl₃ cathode shows a discharge capacity of 142.9 mAh g⁻¹ at a current density of 3 mA g⁻¹ and its capacity decreases in the subsequent cycles. Since the phase transformation of Bi metal to BiCl₃ causes a large volume expansion of 210.6 %, electrical contacts between some BiCl₃ particles and carbon at the cathode seem to be interrupted which would result in the observed capacity decay. A similar reason is applicable to the observations at the anode.

[0054] Stable multistep reactions in the BiCl₃/Li battery could be observed in the CV pattern as shown in the inset in **Fig. 2d**. L. Heerman and W. D'Olieslager, J. Electrochem. Soc., 1991, 138, 1372-1376, reported that two intermediate oxidation states, i.e. Bi₅³⁺ and Bi₅⁺ clusters, in the electrochemical reduction of Bi³⁺ to Bi from a room temperature molten salt exist. Here the CV spectrum shows that the major electrical charge is derived from the redox reaction at a low voltage. It is assumed that two ways of a solid phase transformation occur at the cathode, a multistep process including the mentioned intermediate oxidation states and a direct transformation between BiCl₃ and Bi metal.

[0055] **Fig. 3** presents XRD patterns of various cathode materials after discharge and charge. For the CoCl₂/Li battery, Co metal is formed by a reduction of CoCl₂ during discharge and its diffraction peaks almost disappear during charging, which may be reflected by a combination of Co metal and a chloride ion Cl⁻. However, no diffraction peaks corresponding to CoCl₂ were observed in the XRD pattern according to **Fig. 3a** which is explained by a formation of amorphous and/or nanoscale chloride particles. Similar phenomena could be observed for conversion reactions of CoCl₂, CoF₂ or CoN as electrode in lithium ion batteries. The broad diffraction peak at 22.6° in **Fig. 3a** is assigned to a reflection of the electrolyte since it is rather difficult to remove the electrolyte from the surface of an active material without dissolving the active material.

[0056] **Fig. 3b** shows XRD patterns of a VCl₃ cathode. Only the diffraction peak of the electrolyte appears after

discharge, suggesting that V metal, which exhibits poor crystallinity being much weaker than that of Co, was formed by an electrochemical reduction of VCl_3 . On the contrary, Bi metal, which was formed after discharging, exhibits sharp diffraction peaks as shown in **Fig. 3c**. This is explained by a phase transition from the bismuth clusters Bi_5^{3+} and Bi_5^+ mentioned above. Similar to the charged state of the $CoCl_2$ electrode, $BiCl_3$ could also not be detected by XRD in the charged electrode. However, as presented in **Fig. 3d**, the intensity of the Bi metal peaks, especially the peak corresponding to the (012) plane, is drastically decreased and several diffraction peaks disappear in **Fig. 3c** by the reversible oxidation reaction shown in the CV patterns which again points to the formation of amorphous and/or nanoscale product phases.

[0057] **Fig. 4** directly demonstrates the operation of a metal chloride/metal secondary battery according to the present invention.

[0058] The XPS data in **Fig. 4a** show $4f_{7/2}$ und $4f_{5/2}$ signals of Bi which were generated at the surface of a $BiCl_3$ cathode material.

[0059] **Fig. 4b** exhibits that metallic Bi^0 was formed after discharging of the $BiCl_3$ cathode material. The oxide also found here is interpreted as partial surface oxidation of Bi during the transfer of the sample from glove box to XPS chamber.

[0060] **Fig. 4c** finally demonstrates that metallic Bi^0 , which had been formed during the discharging, was again reversed into $BiCl_3$ after a recharging of the battery.

Claims

1. A secondary battery which comprises
 - a negative electrode (anode) having a first metal or a first alloy or a host material capable of reacting with or intercalating a chloride ion as anode material,
 - a positive electrode (cathode) having a chloride of a second metal or of a second alloy or a chloride intercalation compound as cathode material,
 - a separator to separate the cathode from the anode, and
 - an electrolyte which exhibits a chloride ionic conductivity.
2. A secondary battery according to claim 1, where the chloride ionic conductivity equals or exceeds a value of 0.1 mS cm^{-1} .
3. A secondary battery according to claim 1 or 2, where the anode material includes an alkaline metal or an alkaline earth metal or a rare earth metal or an alloy which includes at least one of said metals.
4. A secondary battery according to one of the claims 1 to 3, where the cathode material includes a chloride of at least a single transition metal or at least a single post-transition metal.
5. A secondary battery according to one of the claims 1 to claim 4, where the anode material and/or the cathode material comprises a composite which further includes carbon black or a nanocarbon or a metal powder or a metal foam.
6. A secondary battery according to claim 5, where the cathode material includes a solid mixture of $CoCl_2$ or of VCl_3 or of $BiCl_3$ with carbon black.
7. A secondary battery according to one of the claims 1 to 6, where the electrolyte is selected from a chloride ionic liquid, a mixture of a complex anion which comprises a chloride ion and an organic solvent or an ionic liquid, an organic chloride salt, or an inorganic chloride salt.
8. A secondary battery according to claim 7, where the chloride ionic liquid is selected from a first binary chloride ionic liquid with a cation of imidazolium, pyrrolidinium, piperidinium, pyridinium, or of a quaternary ammonium.
9. A secondary battery according to claim 8, where an organic solvent or a second ionic liquid with an anion which differs from the first binary chloride ionic liquid is added as a solvent to the first binary chloride ionic liquid.
10. A secondary battery according to claim 7, where the complex anion includes $[FeCl_4]^-$, $[FeCl_4]^{2-}$, $[NiCl_4]^{2-}$, or $[CoCl_4]^{2-}$.
11. A secondary battery according to claim 7, where the organic chloride salt is selected from a poly(diallyldime-thyl-

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ammonium chloride) or an organic chloride with a cation of imidazolium, pyrrolidinium, piperdinium, or of pyridinium, without or with at least a single side chain.

5 12. A secondary battery according to claim 7, where the inorganic chloride salt is selected from a solid solution of a PbCl_2 /alkali-metal chloride, a solid solution of a SnCl_2 /alkali-metal chloride, Cs_5nCl_3 , CsPbCl_3 , K_2NiCl_4 , LaOCl , or $\text{La}_{1-x}\text{Ca}_x\text{OCl}_{1-x}$.

13. A method for manufacturing a secondary battery according to one of the claims 1 to 12, with the steps:

10 (a) Providing an anode material having a first metal or a first alloy or a host material capable of reacting with or intercalating a chloride ion and forming a negative electrode (anode) therewith,

(b) Providing a cathode material having a chloride of a second metal or of a second alloy or a chloride intercalation compound and forming a positive electrode (cathode) therewith,

15 (c) Arranging a separator such that the cathode is physically separated from the anode while a flow of chloride ions is allowed during operation of said battery, and

(d) Adding an electrolyte in such a way that the cathode is electrically connected with the anode.

20 14. A method according to claim 13, where the cathode material is provided during step (b) in form of a dried powder and the cathode is subsequently formed by ball milling said powder with carbon black or a nanocarbon.

25 15. A method according to claim 13, where the cathode material is provided during step (b) in form of a dried powder, which is dissolved in a solution and is then added to carbon black or a nanocarbon, such delivering a wet composite, and the cathode is formed by freeze-drying said wet composite and subsequently heating it.

Fig. 1a

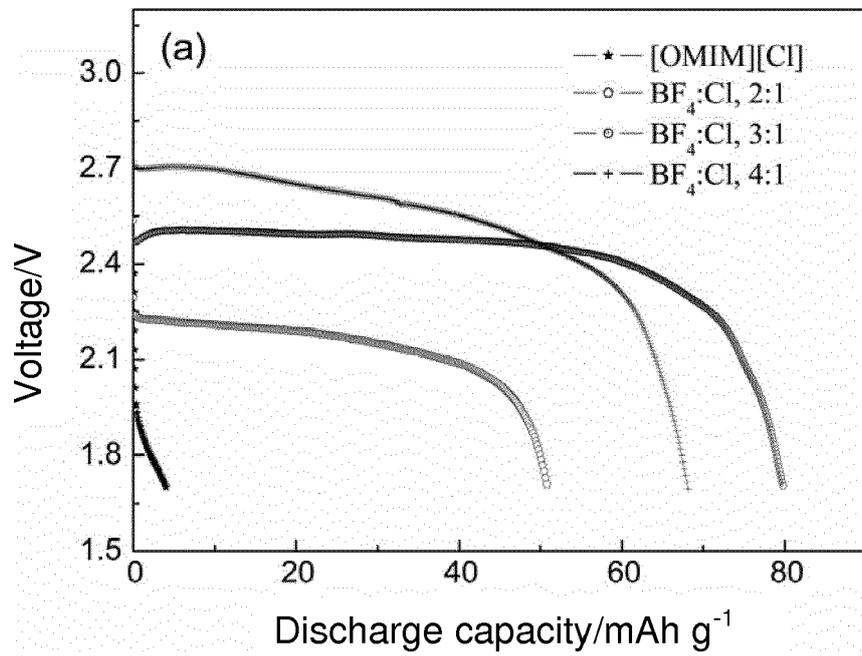


Fig. 1b

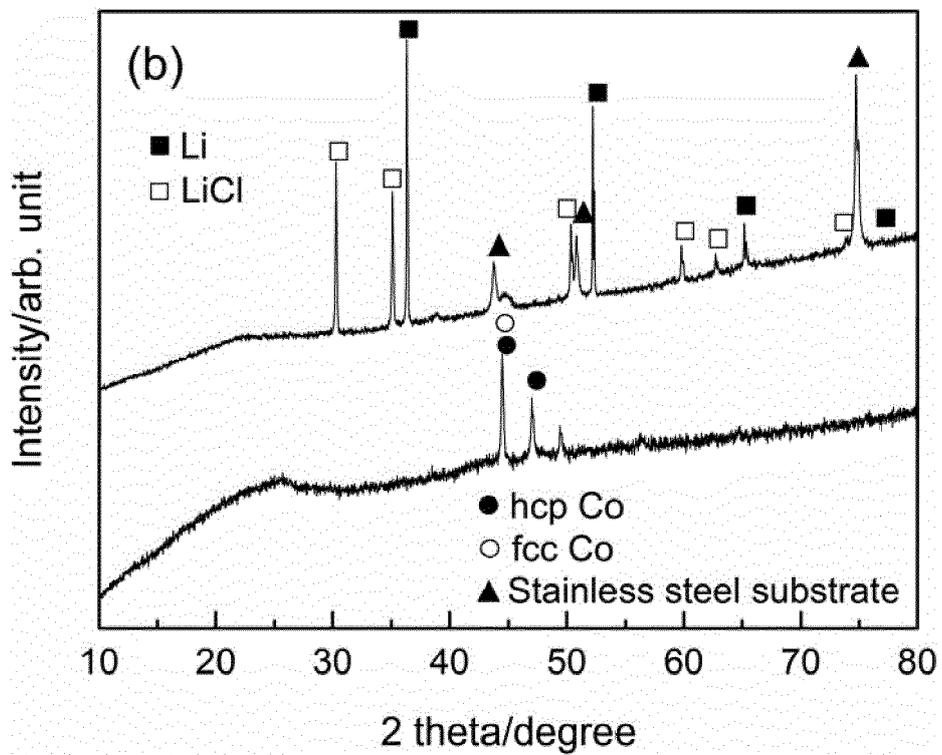


Fig. 2a

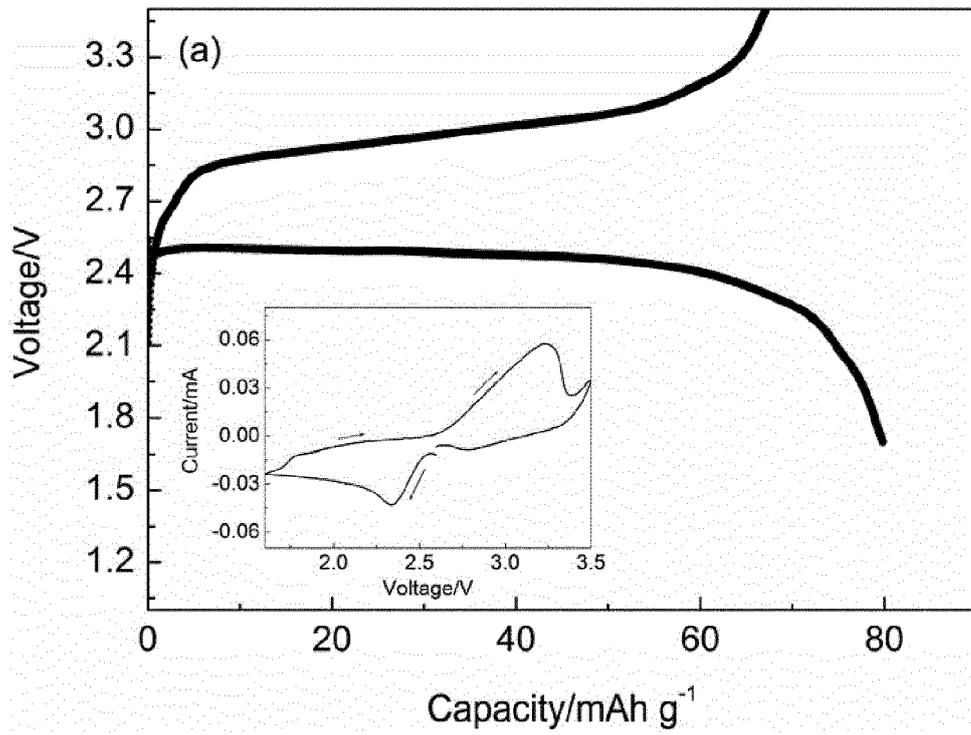


Fig. 2b

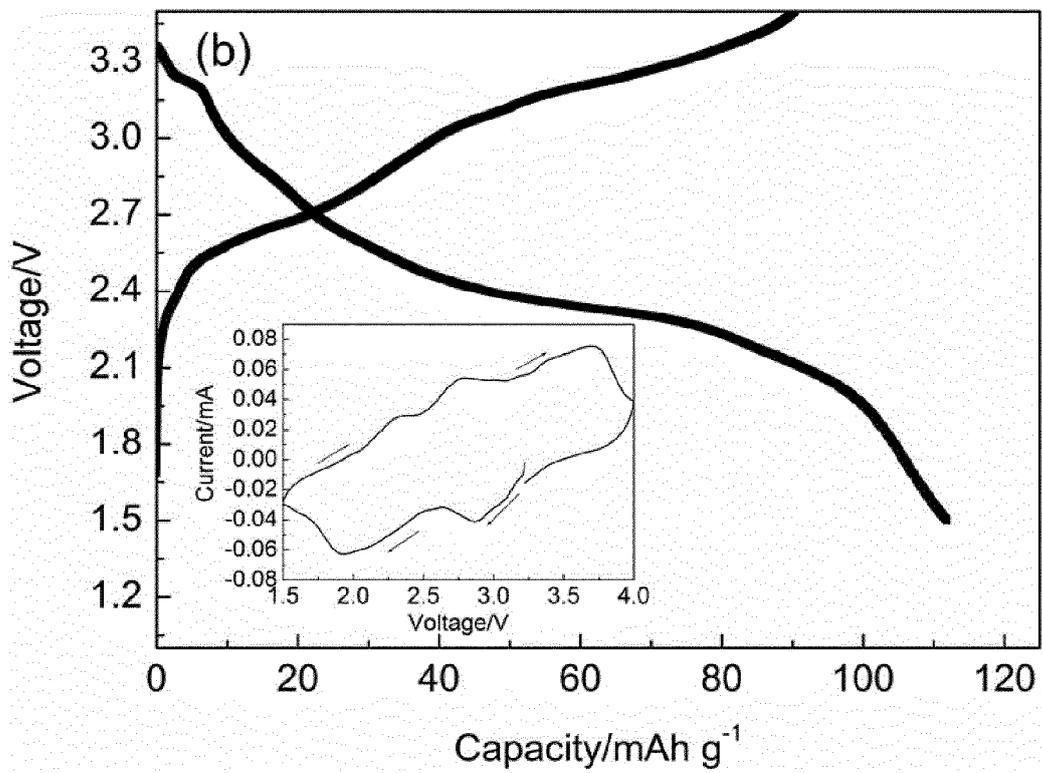


Fig. 2c

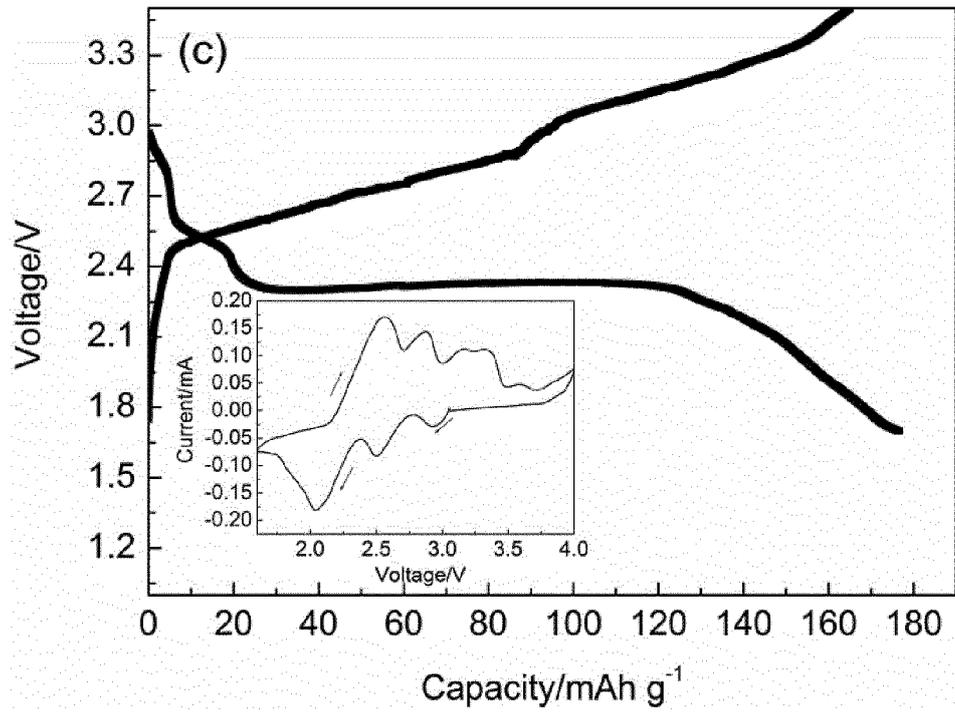


Fig. 2d

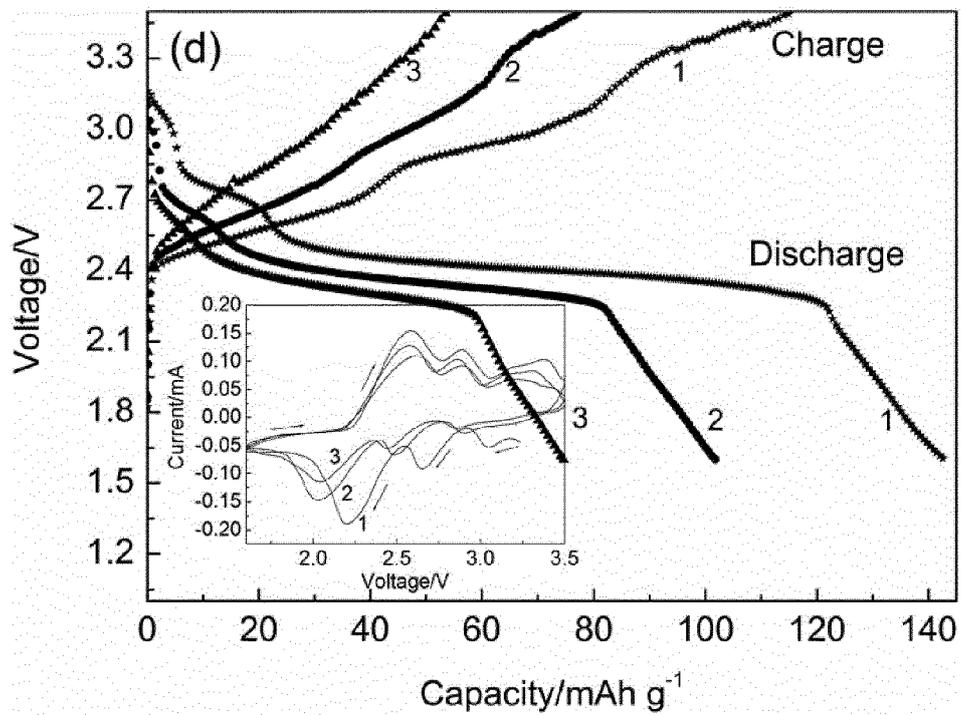


Fig. 3a

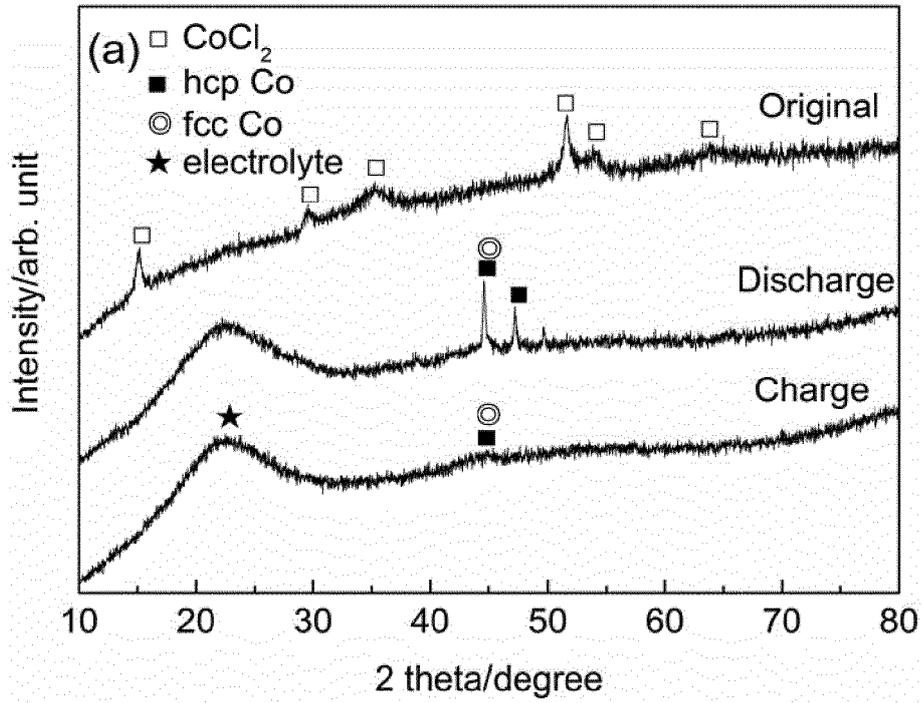


Fig. 3b

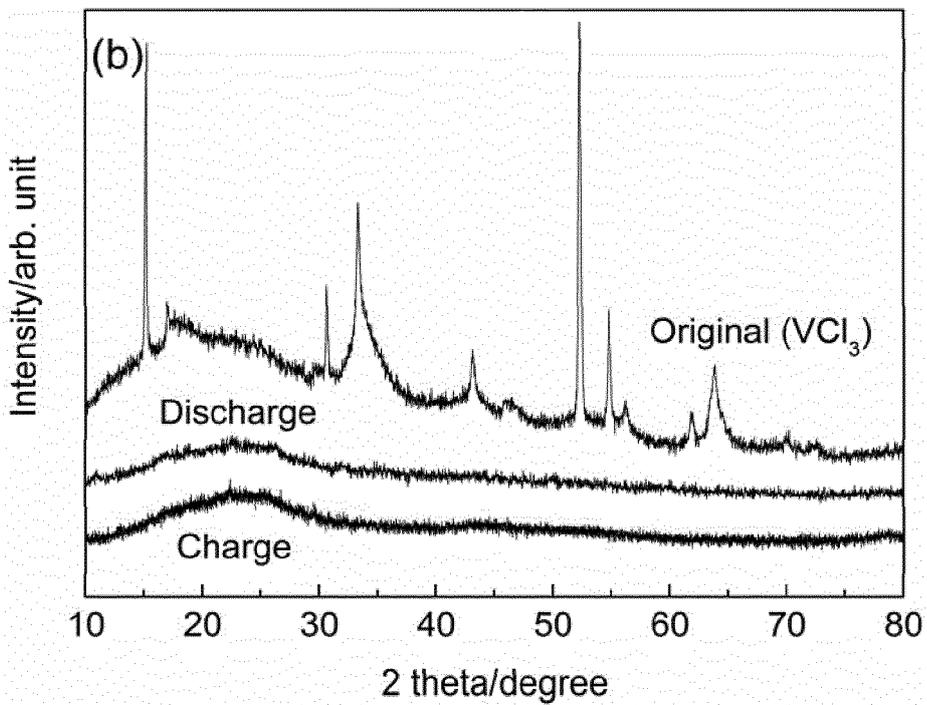


Fig. 3c

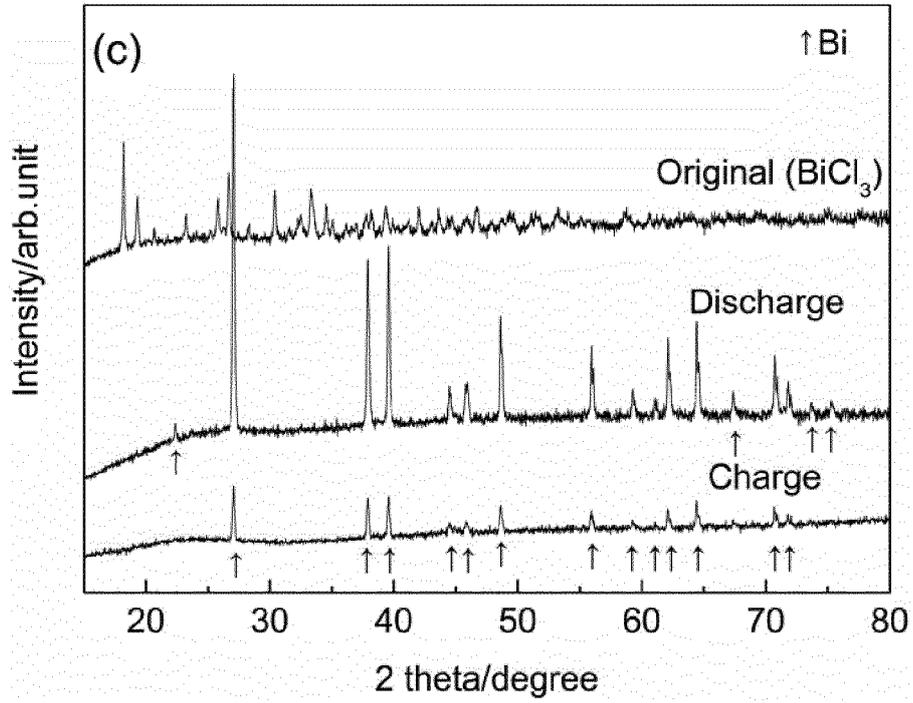


Fig. 3d

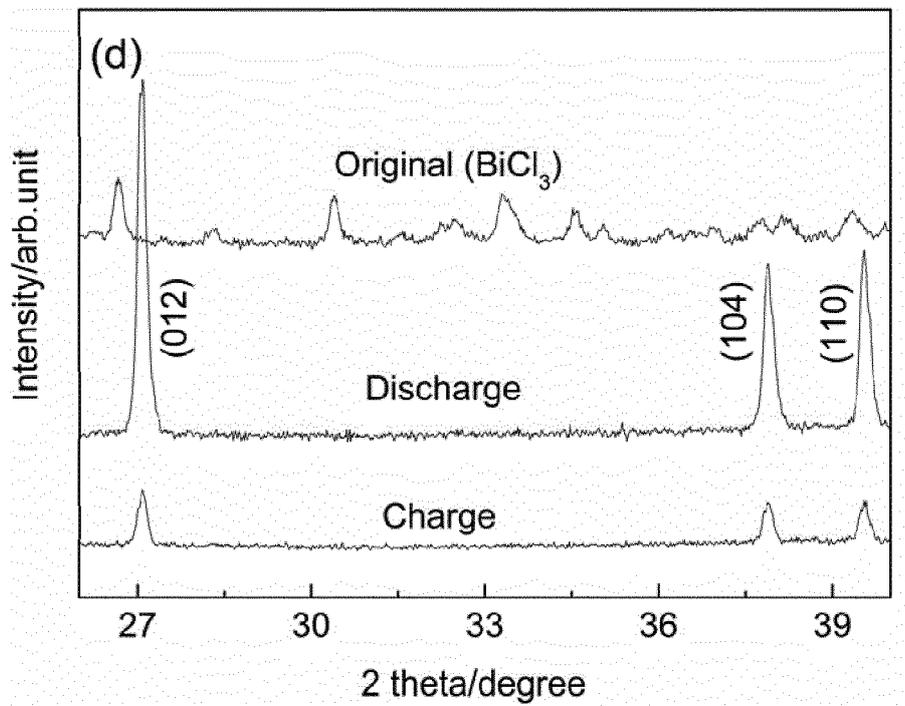


Fig. 4a

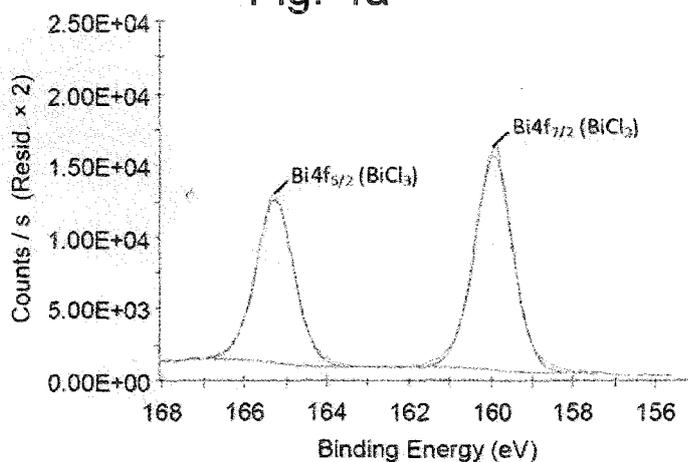


Fig. 4b

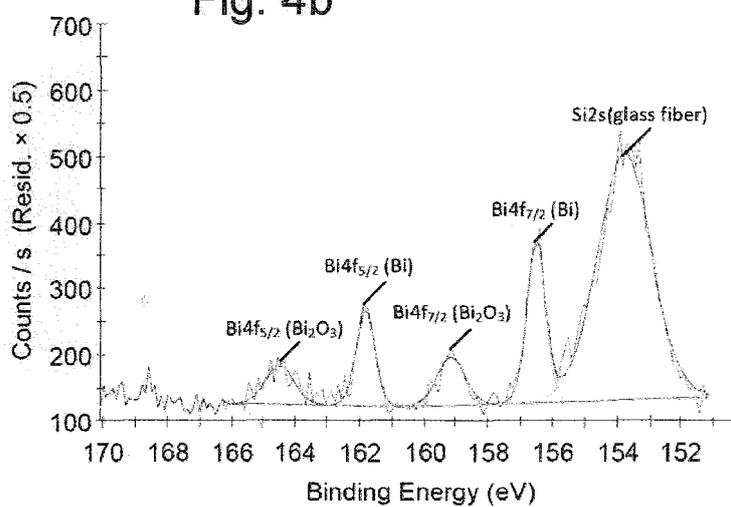
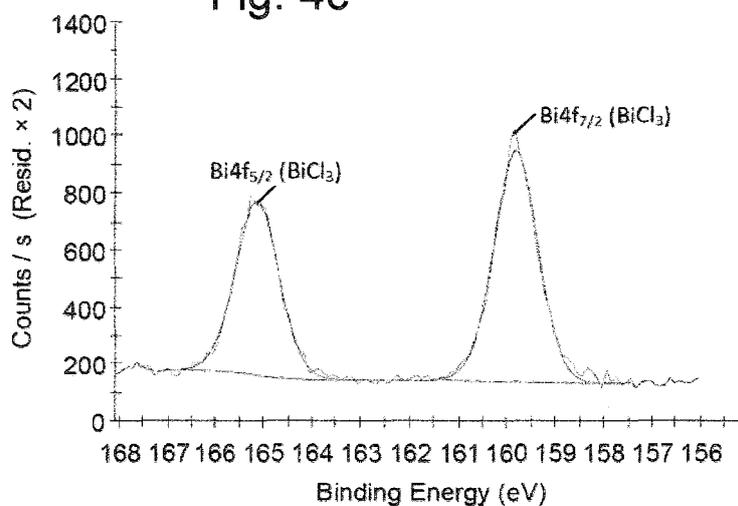


Fig. 4c





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Application Number
EP 12 40 1224

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Place of search The Hague		Date of completion of the search 15 April 2013	Examiner Kelly, Michael
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