

COMPOSITE MATERIALS AND THEIR USE IN ELECTROCHEMICAL
APPLICATIONS AND ELECTRODE COATINGS MADE THEREFROM

FIELD OF THE INVENTION

[01] The present invention relates to composite materials and their uses in electrochemical applications.

BACKGROUND OF THE INVENTION

[02] Electrochemical processes and devices are constantly gaining in popularity and commercial relevance. Electrochemical energy storage systems are in high demand, for example as batteries for cars, bicycles and hand-held devices, and as capacitors or supercapacitors for electronic memories or short-term energy storage applications. Electrochemical energy conversion systems are expected to become a cornerstone of the green economy, for example as fuel cells, electrolyzers, or for the production of e-fuels.

[03] All these processes have in common the requirement for suitable surfaces on which electrochemical reactions can occur, in particular on electrodes of rechargeable batteries, electrolyzers and fuel cells. These are referred to as electrocatalysts.

[04] It is known that the suitability of electrodes and electrocatalysts is greatly dependent, besides their chemical composition and surface structure, on the electrical impedance and electrical conductivity of the surfaces on which electrochemical reactions occur. There is a constant need for improving the surface properties of functional electrodes and electrocatalysts, contingent on the requirements of specific applications.

[05] The skilled person in the art is aware that catalytic activity on functional electrode surfaces is limited by (i) surface activation resistance and (ii) electrical resistance (ohmic resistance).

[06] Low catalytic activity on functional electrode surfaces leads to high over-potential needing to be applied to the electrode in order to reasonably proceed a chemical reaction on the electrode surface. On the other hand, reducing surface activation resistance leads to improved catalytic activity, thereby resulting in a reduced voltage applied to the functional electrode to proceed the chemical reaction.

[07] Low electrical conductivity on the surface of functional electrodes leads to reduced efficiency of surface reactions due to reduced mass transfer and increased bulking of inactive species on the functional electrode surfaces. Electrodes are often

produced using a polymeric binder, which holds the catalyst particles together. The presence of such a binder lowers the conductivity of the electrodes, and therefore of the whole system.

SHORT DESCRIPTION OF THE INVENTION

[08] The present invention is defined in the appended claims.

[09] In particular, the present invention is embodied by a composite material having an elemental composition consisting of 30 to 70 wt.-% nickel, 5 to 20 wt.-% iron, 2 to 10 wt.-% chromium, 2 to 10 wt.-% X, wherein X represents one or more elements selected from the group cerium, cobalt, copper, gadolinium, lanthanum, lithium, magnesium, niobium, praseodymium, samarium, scandium, strontium, tantalum, titanium, tungsten, ytterbium, yttrium and mixtures thereof, and optionally up to 30 wt.-% oxygen, wherein the balance of the composite material is made up of aluminium or zinc or mixtures thereof and inevitable impurities. All the weight-percentage indications are with respect to the total weight of the composite material. It has been found that improved performance may be achieved with functional electrodes coated with composite materials according to the present invention. As used herein, in case X is a mixture of two or more elements selected from the group cerium, cobalt, copper, gadolinium, lanthanum, lithium, magnesium, niobium, praseodymium, samarium, scandium, strontium, tantalum, titanium, tungsten, ytterbium, and yttrium, then the total amount of X in the composite material of the invention is 2 to 10 wt.-%.

[10] According to a preferred embodiment of the invention, the nickel content of the composite material may be from 33 to 65 wt.-% nickel, for example from 39 to 52 wt.-% nickel.

[11] According to a preferred embodiment of the invention, the iron content of the composite material may be from 7 to 17 wt.-% iron, for example from 12 to 14 wt.-% iron.

[12] According to a preferred embodiment of the invention, the chromium content of the composite material may be from 3 to 6 wt.-% chromium, for example from 4 to 5 wt.-% chromium.

[13] According to a preferred embodiment of the invention, the content of element X of the composite material may be from 3 to 7 wt.-% X, for example from 4 to 6 wt.-% X.

[14] According to a preferred embodiment of the invention, the oxygen content of the composite material may be from 0.2 to 30 wt.-% oxygen, for example from 2 to 30 wt.-% oxygen, for example from 4 to 13 wt.-% oxygen.

[15] According to a preferred embodiment of the invention, the content of aluminium or zinc or mixtures thereof of the composite material may be from 4 to 38 wt.-% aluminium or zinc or mixtures thereof, for example from 8 to 33 wt.-% aluminium or zinc or mixtures thereof.

[16] According to one separate embodiment of the present invention, the composite material may have an elemental composition consisting of 52 to 63 wt.-% nickel, 8 to 14 wt.-% iron, 3 to 6 wt.-% chromium, 3 to 7 wt.-% X, and 13 to 29 wt.-% oxygen, wherein the balance of the composite material is made up of aluminium or zinc or mixtures thereof and inevitable impurities. According to this embodiment, the weight of metal oxide phase in the composite material may represent from 18 to 48 wt.-%. According to this embodiment, the composite material may be present as a coating having a thickness of 10 to 1000 μm , preferably of 70 to 400 μm and a surface area from 1.2 to 30,000 m^2/m^2 , such as for example from 2 to 25,000 m^2/m^2 , for example from 200 to 20,000 m^2/m^2 .

[17] According to one embodiment of the present invention, the composite material may have an elemental composition consisting of 34 to 39 wt.-% nickel, 13 to 17 wt.-% iron, 3 to 5 wt.-% chromium, 4 to 6 wt.-% X, and optionally up to 4 wt.-% oxygen, wherein the balance of the composite material is made up of aluminium or zinc or mixtures thereof and inevitable impurities. According to this embodiment, the weight of metal oxide phases may represent from 6 to 15 wt. %, based on the total weight of the metal-alloy matrix composite. Also according to this embodiment, the composite material may be present as a coating having a thickness of 10 to 1000 μm , preferably of 70 to 400 μm and a surface area from 1.0 to 200 m^2/m^2 , such as for example from 1.2 to 30,000 m^2/m^2 , for example from 2 to 25,000 m^2/m^2 , for example from 200 to 20,000 m^2/m^2 .

[18] According to an alternative embodiment of the present invention, the elements aluminium and zinc in the content of aluminium or zinc or mixtures thereof may be partially or fully exchanged for each other.

[19] Also part of the present invention is the use of the composite material of any of the previous claims in the production of electrochemical catalyst systems, or electrodes for energy storage or energy conversion applications.

[20] Also part of the present invention are thin layer electrodes comprising a coated substrate consisting of a composite material according to the present invention in the shape of a coating having a thickness from 10 to 1000 μm , preferably of 70 to 400 μm and a surface area from 1.0 to 30,000 m^2/m^2 .

SHORT DESCRIPTION OF THE FIGURES

[21] The invention will be further illustrated by reference to the following figures:

Fig. 1 shows a schematic representation of a metal alloy matrix composite with interspersed metal oxide phases according to one aspect of the present invention;

Fig. 2 shows a micrograph of a metal alloy matrix composite with interspersed metal oxide phases according to one aspect of the present invention, prepared using scanning electron microscopy using an electron backscattered diffraction detector (EBSD);

Fig. 3 shows a schematic representation of a cell configuration for the measurement of iV curves and impedance spectroscopy data of Example 2;

Fig. 4 shows current-voltage curves of an electrode of the state of the art and the electrode prepared in accordance with Example 2;

Fig. 5 shows a Nyquist plot from electrochemical impedance spectroscopy (EIS) measurements for cells with an electrode of the state of the art and the electrode prepared in accordance with Example 2, at 0.05 A/cm²;

Fig. 6 shows a Nyquist plot from electrochemical impedance spectroscopy (EIS) measurements for cells with an electrode of the state of the art and the electrode prepared in accordance with Example 2, at 2 A/cm².

[22] It is understood that the following description and references to the figures concern exemplary embodiments of the present invention and shall not be limiting the scope of the claims.

DETAILED DESCRIPTION OF THE INVENTION

[23] The present invention according to the appended claims provides composite materials allowing the provision of coatings for functional electrodes to achieve improved electrical properties.

[24] According to the present invention, composite materials are provided having the elemental compositions as shown above. The composite materials according to the present invention are suitable for coatings of functional electrode surfaces and electrocatalysts, improving their chemical and physical surface properties for more efficient and active use in electrochemical applications.

[25] In particular, since low catalytic activity is the challenge leading to high over-potential needing to be applied, according to the present invention catalytic activity is improved through (a) a synergy between different elements of alloy (for example Ni

- Fe - Cr - X - (Al or Zn)) that increase the intrinsic surface activity and lowers the Tafel slope of the reaction, and (b) an improved active surface area, reducing the over-potential.

[26] In addition, the problem of low electrical conductivity on the functional electrode surface has been alleviated by the fact that no binder is required to apply the composite material according to the present invention to a functional electrode surface. Furthermore, the addition chromium and element X along with iron reduces insulating passive phase formation and the magnetic properties of Ni, thereby improving surface conductivity. This effect is particularly potent in the case where element X is copper.

[27] It should be noted that the present invention may comprise any combination of the features and/or limitations referred to herein, except for combinations of such features which are mutually exclusive. The foregoing description is directed to particular embodiments of the present invention for the purpose of illustrating it. It will be apparent, however, to one skilled in the art, that many modifications and variations to the embodiments described herein are possible. All such modifications and variations are intended to be within the scope of the present invention, as defined in the appended claims.

EXAMPLE 1 – PRODUCTION OF AN INITIAL COATING

[28] In the following, an initial coating is formed by conversion of a feedstock powder into a functional electrode on top of a substrate. In order to achieve this, a feedstock powder is provided by vacuum melting and inert gas atomisation. This allows high level of control and the oxygen content may be kept low. It is preferable that at this stage, the oxygen content is 5 ppm by weight or less. The elemental composition of the feedstock powder corresponds to the desired elemental composition of the initial coating. The particle size distribution of the feedstock powder obtained after gas atomisation may be such that it is suitable for use in thermal spraying applications. The particle sizes may range from 0.5 μm to 220 μm . In a preferred embodiment, the particle size distribution is such that $d_{10} = 5 \mu\text{m}$ and $d_{90} = 45 \mu\text{m}$, as determined using a laser diffraction particle size distribution analyser. If necessary, the powder obtained after gas atomisation may be classified into a desired particle size range.

[29] The obtained feedstock powder is then converted into a functional electrode on top of a substrate. This is done by using thermal spraying with a build-up customised gun on a multi-mesh structured substrate. Ar may be used as the primary forming gas whereas N_2 or H_2 or a mixture thereof may be used as the secondary gas.

The feedstock powder is injected through external injection nozzles into a thermal spray flame with an enthalpy in the range of 20 to 40 MJ/kg. The heated and accelerated particles are impacted on the multi-mesh substrate to form an electrode.

[30] The obtained initial coating may have a thickness in the range of 10 to 1000 μm , as measured by micro-gauge. The elemental composition of the initial coating was about 34 to 39 wt.-% Ni, about 13 to 17 wt.-% Fe, about 33 to 38 wt.-% Al, about 3 to 5 wt.-% Cr, about 4 to 6 wt.-% X and about 2 to 4 wt.-% O.

EXAMPLE 2 – ACTIVATION OF THE INITIAL COATING

[31] While the initial coating displays good properties as an electrode in electrochemical applications, it may be further activated to improve properties. In order to do this, the initial coating may be submerged in an activation solution for 24 hours at 80° to 90°C. The activation solution may be a mixture of water and 10 to 40 wt.-% KOH and 1 to 10 wt.-% K-Na-tartrate-tetrahydrate solution.

[32] The activation treatment serves to increase the surface area of the coating. While the thickness of the electrode material remains broadly unchanged at 70 to 400 μm , the surface area is dramatically increased. Gas adsorption method based on Brunauer–Emmett–Teller (BET) analysis was utilized to measure the surface area of electrodes using a BELSORP-max X device. Dry solid samples of 3 times 3.5 grams were utilised and nitrogen was used as adsorption gas. The average of the surface area of these three samples is reported. The elemental composition of the activated coating was about 52 to 63 wt.-% Ni, about 8 to 14 wt.-% Fe, about 4 to 8 wt.-% Al, about 3 to 6 wt.-% Cr, about 3 to 7 wt.-% X and about 13 to 29 wt.-% O.

EXAMPLE 3 – STUDY OF ELECTROCHEMICAL PROPERTIES

[33] In the following, the current-voltage characteristics and electrochemical impedance spectroscopy (EIS) measurements were carried out on a state of the art nickel cathode, and a cathode coated with the composite material obtained in Example 2 above.

Electrode preparation

[34] Comparative nickel electrode is a simple punched nickel plate. This was compared to a cathode coated with the composite material obtained in Example 2 above.

Electrode testing

[35] The electrodes were tested in a zero-gap electrolyzer cell as schematically represented in Fig. 3. The cell consisted of four main parts: nickel bipolar plates, nickel wire mesh as the current collector, test electrodes and Zirfon PERL UTP 500 as a diaphragm.

[36] The tests were carried out under atmospheric pressure in 30 wt.-% KOH at 70°C, by recording polarization curves at a scan rate of 10 mA s⁻¹, after 30 min activation at constant current of 0.2 A, and using a biologic potentiostat.

[37] EIS was performed at low and high current densities and plotted from 50 kHz to 100 MHz to identify the ohmic and activation losses. The operating conditions and cell hardware were kept the same for all the tests. The fitting of Nyquist plots was done by RelaxIS software.

Results

[38] The current-voltage curves in Fig. 4 show a clear improvement of the intrinsic surface activity of the electrode having a surface coated with the composite according to the present invention over the nickel electrode.

[39] As can be seen in Fig. 5 and 6, the electrode according to the present invention provides lower activation resistance (Impedance spectroscopy measurements at low current density as per Fig. 5) as well as lower ohmic resistance (Impedance spectroscopy measurements at high current density as per Fig. 6), leading to the improved current-voltage measurement behaviour identified in Fig. 4.

CLAIMS

1. Composite material having an elemental composition consisting of:
 - 30 to 70 wt.-% nickel;
 - 5 to 20 wt.-% iron;
 - 2 to 10 wt.-% chromium;
 - 2 to 10 wt.-% X, wherein X represents one or more elements selected from the group cerium, cobalt, copper, gadolinium, lanthanum, lithium, magnesium, niobium, praseodymium, samarium, scandium, strontium, tantalum, titanium, tungsten, ytterbium, yttrium and mixtures thereof, and
 - optionally up to 30 wt.-% oxygen,wherein the balance of the composite metal and metal oxide material is made up of aluminium or zinc or mixtures thereof and inevitable impurities, and wherein the wt.-% indications are with respect to the total weight of the composite material.
2. Composite material according to claim 1, wherein the amount of nickel in the elemental composition is from 33 to 65 wt.-% nickel, for example from 39 to 52 wt.-% nickel.
3. Composite material according to any one of the previous claims, wherein the amount of iron in the elemental composition is from 7 to 17 wt.-% iron, for example from 12 to 14 wt.-% iron.
4. Composite material according to any one of the previous claims, wherein the amount of chromium in the elemental composition is from 3 to 6 wt.-% chromium, for example from 4 to 5 wt.-% chromium.
5. Composite material according to any one of the previous claims, wherein the amount of element X in the elemental composition is from 3 to 7 wt.-% X, for example from 4 to 6 wt.-% X.
6. Composite material according to any one of the previous claims, wherein the amount of oxygen in the elemental composition is from 0.2 to 30 wt.-% oxygen, for example from 4 to 13 wt.-% oxygen.

7. Composite material according to any one of the previous claims, wherein the amount of aluminium or zinc or mixtures thereof in the elemental composition is from 4 to 38 wt.-% aluminium or zinc or mixtures thereof, for example from 8 to 33 wt.-% aluminium or zinc or mixtures thereof.
8. Composite material according to any one of the previous claims which is a metal-alloy matrix composite with interspersed metal oxide phases.
9. Composite material as defined in any one of the previous claims, wherein the elements aluminium and zinc in the content of aluminium or zinc or mixtures thereof are partially or fully exchanged for each other.
10. Composite material according to any one of claims 1 to 9, wherein the composite material has an elemental composition consisting of 52 to 63 wt.-% nickel, 8 to 14 wt.-% iron, 3 to 6 wt.-% chromium, 3 to 7 wt.-% X, and 13 to 29 wt.-% oxygen, wherein the balance of the composite material is made up of aluminium or zinc or mixtures thereof and inevitable impurities.
11. Composite material according to any one of claims 1 to 9, wherein the composite material has an elemental composition consisting of 34 to 39 wt.-% nickel, 13 to 17 wt.-% iron, 3 to 5 wt.-% chromium, 4 to 6 wt.-% X, and optionally up to 4 wt.-% oxygen, wherein the balance of the composite material is made up of aluminium or zinc or mixtures thereof and inevitable impurities.
12. Composite material according to claim 11 having a metallic oxide content of 6 to 15 wt.-%.
13. Use of the composite material of any of the previous claims in the production of electrochemical catalyst systems, or electrodes for energy storage or energy conversion applications.
14. Thin layer electrode comprising a coated substrate, wherein the coating consists of a composite material of any one of claims 1 to 12 and has a thickness from 70 to 400 μm and a surface area from 1.0 to 30,000 m^2/m^2 .

15. Thin layer electrode according to claim 14, wherein the coating consists of a composite material of claims 1 to 9 or 11 or 12 and has a surface area from 1.0 to 200 m²/m², or from 1.1 to 20 m²/m², or from 1.2 to 2 m²/m².
16. Thin layer electrode according to claim 14, wherein the coating consists of a composite material of claims 1 to 10 and has a surface area from 200 to 30,000 m²/m², or from 2,000 to 25,000 m²/m², or from 5,000 to 20,000 m²/m².

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