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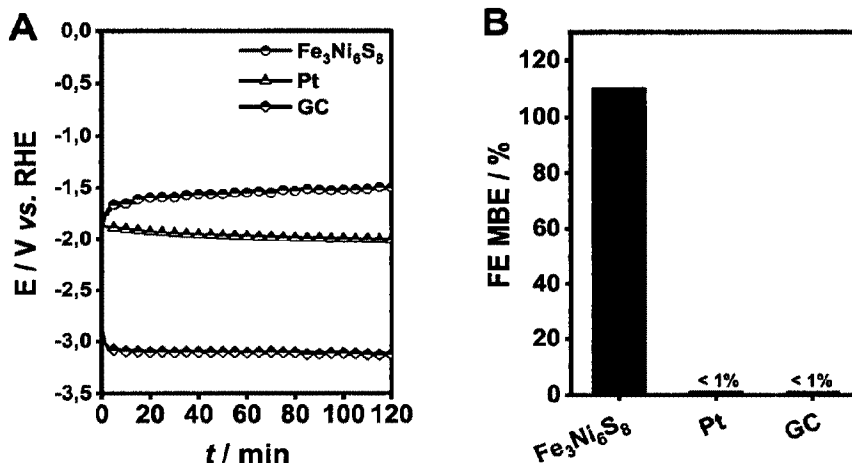
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(71) **Demandeurs/Applicants:**
FRAUNHOFER-GESELLSCHAFT ZUR FOERDERUNG
DER ANGEWANDTEN FORSCHUNG E.V., DE;
RUHR-UNIVERSITAT BOCHUM, DE
(72) **Inventeurs/Inventors:**
SIEGMUND, DANIEL, DE;
APFEL, ULF-PETER, DE;
JUNGE PURING, KAI, DE;
PELLUMBI, KEVINJEORJIOS, DE; ...

(54) **Titre : PROCÉDE D'HYDROGENATION CATALYTIQUE SELECTIVE DE COMPOSES ORGANIQUES, ELECTRODE ET CELLULE ELECTROCHIMIQUE POUR LA MISE EN OEUVRE DE CE PROCÉDE**
(54) **Title: METHOD FOR THE SELECTIVE CATALYTIC HYDROGENATION OF ORGANIC COMPOUNDS, AND ELECTRODE AND ELECTROCHEMICAL CELL FOR SAID METHOD**

Fig. 2



(57) **Abrégé/Abstract:**

The application relates to a method for the electrocatalytic hydrogenation of organic compounds in an electrochemical cell, in which the reducible organic compound is present in liquid form or at least partially in dissolved form, wherein the reducible organic compound is hydrogenated at the cathode. The cathode comprises, as a catalyst, a transition metal chalcogenide selected from sulfides, selenides and tellurides. The application also relates to an electrode, comprising a carrier material and a layer of the catalyst provided on the carrier material; to an electrochemical cell having an electrode of this type; and to the use of the transition metal chalcogenide catalyst for the electrochemical hydrogenation of organic compounds.

(72) **Inventeurs(suite)/Inventors(continued):** KLEINHAUS, JULIAN TOBIAS, DE

(74) **Agent:** RICHES, MCKENZIE & HERBERT LLP

Abstract

The present application relates to a process for electrocatalytic hydrogenation of organic compounds in an electrochemical cell in which the reducible organic compound is present in liquid form or at least partially in dissolved form and wherein the reducible organic compound may be hydrogenated at the cathode. The cathode comprises a transition metal chalcogenide selected from sulfides, selenides and tellurides as catalyst. The application further relates to an electrode comprising a carrier material and a layer of the catalyst arranged thereupon and to an electrochemical cell comprising such an electrode and to the use of the transition metal chalcogenide catalyst for electrochemical hydrogenation of organic compounds.

See figure 2

Method for the selective catalytic hydrogenation of organic compounds, and electrode and electrochemical cell for said method

The present application relates to a process for electrocatalytic hydrogenation of organic chemical compounds using an electrode comprising as a catalytically active layer a transition metal chalcogenide, substantially a sulfide, selenide and/or telluride. The application further relates to an electrode for electrocatalytic hydrogenation and to an electrochemical cell for performing the recited reaction. The composition of the employed catalysts may be varied and adjusted over wide ranges, so that the catalysts make it possible to establish elevated selectivity with respect to multiply-reducible compounds and different hydrogenable functional groups. The electrochemical hydrogenation according to the application may in principle be employed for any desired chemical synthesis, for example in the hydrogenation of unsaturated organic compounds. Examples include in particular the synthesis of fine chemicals, the hydrogenation of vegetable oils in fat hardening in the foodstuffs industry, the upgrading of biomass, the hydrogenolytic cleavage of relevant protecting groups and the storage of hydrogen in the form of liquid organic hydrogen carriers (LOHCs).

According to the prior art, hydrogenation of organic compounds may be performed by the following processes. Hydrogenation of organic compounds using stoichiometric hydride transfer agents, hydrogenation in thermal heterogeneously or homogeneously catalyzed processes and electrocatalytic hydrogenation reactions.

This type of hydrogenation using stoichiometric hydride transfer agents finds use especially in the reduction of C-O multiple bonds in small-scale batch processes or on a laboratory scale and requires separation of the stoichiometric waste products generated. These waste products may be subject to environmental concerns (for example cyanoboron compounds).

Thermocatalytic hydrogenations with elemental hydrogen in the presence of a suitable catalyst are associated with the inherent disadvantage of necessitating upstream hydrogen production. Furthermore, many hydrogenation reactions must be performed at elevated temperatures and pressures to ensure a sufficient conversion. This not only entails additional energy input but also makes elevated process safety demands. Often only costly transition metal complexes based on Pt, Pd, Ru, Ir or Rh may be contemplated as suitable catalysts of homogeneously catalyzed reactions. Nevertheless, selective hydrogenation of relatively complex systems, for example asymmetric hydrogenation, typically relies on thermocatalytic hydrogenations with noble metal catalysts. In heterogeneously catalyzed reactions too, noble metals are often employed. Noble metal-free catalysts are based on finely divided small particle size transition metals such as Ni. However, in contrast to the noble metals, elevated process pressures and in some cases elevated temperatures are necessary to achieve a sufficient degree of hydrogenation. A disadvantage of these systems is their severely limited selectivity in the hydrogenation of polyunsaturated compounds. In addition, the heterogeneous catalysts are often susceptible to catalyst poisons. This results in a limitation of the potentially hydrogenable substrates.

A relatively new type of hydrogenation is electrocatalysis. The electrocatalytic hydrogenation of unsaturated organic substrates through the use of electrodes based on Raney Ni on stainless steel is known (US2014110268 A). Electrocatalytic conversion with metal particles on substrates made of porous carbon has also been described (US2015008139 A). The use of (noble metal) catalysts which exhibit a low tolerance to catalyst poisons, are costly and whose extraction is associated with environmental concerns is in turn disadvantageous. US20190276941 A1 discloses the selective hydrogenation of alkynes to alkenes at copper electrodes. Catalyst-side adaptation to difficult substrates such as electron-poor alkynes is not possible here.

In addition to the focus on noble metal-based catalysts and Raney Ni, major disadvantages of electrocatalytic processes include the limitations on flexibility (especially

when two or more functional groups are present or upon hydrogenation of multiple bonds) at achievable degrees of hydrogenation and in turn susceptibility to catalyst poisons.

A noble metal-free electrocatalytic system is also known from electrocatalytic water splitting. WO 2020/169806 describes the use of pentlandites as electrocatalysts for the electrolytic production of H₂.

It is an object of the present invention to provide a process for electrocatalytic hydrogenation of organic compounds with which the disadvantages of the prior art may be overcome. The employed electrocatalyst shall in particular have a high selectivity and adaptability to complex organic substrates, operate as energy-efficiently as possible, achieve the highest possible yields and/or ideally also be noble metal-free; it is additionally sought to realize the greatest possible current densities with the electrodes producible therefrom.

At least one of these objects is achieved by the process, the electrode and the electrical cell according to the independent claims. The subclaims and the description and also the examples teach advantageous further developments.

The process for electrocatalytic hydrogenation of organic compounds according to the present application has the feature that the employed electrode comprises or consists of a transition metal chalcogenide as electrocatalyst, wherein the transition metal chalcogenide is a sulfide, a selenide or a telluride (or mixtures of two or more of the recited chalcogenides such as sulfoselenides for example). The electrode (in particular the cathode) used for the catalytic hydrogenation comprises or consists of this transition metal chalcogenide as catalyst. The hydrogenation is carried out such that an organic compound to be reduced (in particular to be hydrogenated) is reduced at the cathode in an electrochemical cell (which comprises not only a cathode and an anode but also a liquid and/or solid electrolyte). The hydrogenation may be carried out either continuously (in particular in a flow cell) or discontinuously (in a batch cell).

According to the the present application a reducible organic compound is in particular to be understood as meaning organic compounds comprising at least one aromatic or heteroaromatic structural unit but in particular at least one multiple bond. Included here in turn are in particular C-C multiple bonds, aromatics, heterocycles, C-O multiple bonds, C-N multiple bonds, NO₂ groups and N-N multiple bonds or combinations of compounds having two or more of the recited groups/bonds. Both double bonds and triple bonds are contemplated; and low molecular weight substances as well as polymers are suitable. The organic compound to be reduced may be liquid and may at least partially be in dissolved form in a solvent and in both cases may also partially be in the form of a solid (provided it is ensured that at least a portion has gone into solution/is liquid); the reduction of gaseous compounds, in particular when these are at least partially in dissolved form, is also conceivable in principle. The physical state at room temperature is the benchmark here. According to the present application the electrocatalytic reduction itself is typically carried out at temperatures between

-78°C and 100°C. Since - unlike hydrogenation reactions where H₂ is necessarily present - the hydrogenation reactions according to the invention are typically endothermic and according to current understanding atomic hydrogen present on the catalyst surface serves as the hydrogenating agent there is in principle no restriction in respect of the upper limit of temperature. The specified upper limit of temperature at 100°C is therefore based more on economic considerations. The temperature will usually be between 0°C and 100°C and often between 20°C and 80°C. Furthermore and irrespective thereof the reactions will typically be performed at standard pressure. The reduced organic compound is also typically in the abovementioned physical states, i.e. especially in the form of a dissolved substance or in the form of a liquid (the reduced compound may in principle also precipitate from the solvent as a solid which, through selection of the solvent/solvent mixture and in addition to catalyst selection, may in particular cases serve to steer the reduction towards a particular product. Irrespective of the abovementioned parameters the process according to the invention may achieve current densities of in particular at

least 10 mA cm⁻² and in particular above 100 mA cm⁻². It is also possible to realize current densities up to 1 A cm⁻² especially in the case of coated electrodes and current densities of up to 2 A cm⁻² are also possible when using appropriate electrodes. However, high current densities are highly relevant from an economic standpoint (and thus in particular for industrial processes).

It has now been found according to the invention that transition metal sulfides, selenides and tellurides employed as catalysts have the property of selectively reducing/hydrogenating organic compounds. The catalytic activity is based on the presence of the chalcogenide in particular and on the metal (cation) only to a lesser extent. It was especially found that there is a great range of variation in respect of the catalysts and their selectivity and it is possible to influence according to the employed transition metal chalcogenide which functional group of a molecule having a plurality of reducible groups is reduced in the catalytic hydrogenation and which configurational isomers are obtained in the hydrogenation of a triple bond. It goes without saying that the chalcogenides of the invention are salt-like compounds where the chalcogen is the anion and the transition metal is the cation. A route of production for these chalcogenides typically proceeds either from mixtures of powders of the elements or from powders of the elements and from metal chalcogenides (the latter for example to establish a particular stoichiometry); in this process and alternative processes chalcogenides are typically present with a substantially uninterrupted chalcogenide structure; in other words the chalcogenides are substantially in the form of a stoichiometric chalcogenide, wherein substantially is to be understood as meaning that a certain non-stoichiometry may also be present in the context of what follows two paragraphs below. However, in exceptional cases it is also possible to carry out a production process where only the surface of the catalyst particles involved in the catalytic process bears a sulfide, selenide and/or telluride layer obtained for example by reaction of the elementary metal particles with the chalcogen. The chalcogenides according to the present application thus make it possible to effect a process optimization to form a desired product. It was further found that the recited catalysts can achieve high Faraday

efficiencies. In contrast to the hydrogenation processes that have long been known it is not necessary to employ a stoichiometric reduction reagent and waste products are avoided. The supply of gaseous hydrogen can likewise be eschewed; an active reduction is effected directly at the catalyst surface without the intermediate step of forming H_2 . The protons required therefor may in particular be provided by a protic solvent or supplied to the cathodic half-cell by the anodic half-cell and the oxidation process to form protons occurring there via a membrane arranged between the half-cells and/or a solid-state electrolyte. Compared to the thermal and electrocatalytic hydrogenations according to the prior art, in particular with the noble metal catalysts palladium, platinum or ruthenium (which have hitherto been among the most active catalysts for hydrogenation reactions), the catalysts according to the present application are markedly more cost effective and sustainable and (in electrocatalytic reactions) likewise exhibit a high activity. The systems according to the invention likewise make it possible to hydrogenate organic compounds of low purity or to perform hydrogenations of organic compounds containing sulfur. This is because the known catalyst poisons for noble metal catalysts or for other typical hydrogenation catalysts (for example H_2S) do not pose a problem for the catalysts employed according to the invention.

In one embodiment of the invention the transition metal chalcogenide for the electrocatalytic hydrogenation is selected from compounds substantially conforming to empirical formula MX , MX_2 , M_2X_3 , M_2X_4 , M_3X_4 , M_9X_8 or $M''_6M_kX_lX'_m$. M is selected from a transition metal of the 4th, 5th or 6th period wherein – for the reasons elucidated above – preference is given to the metals of the 4th period, in particular the metals of the 4th period of groups 4 to 10, and to a lesser extent also the metals of the 5th or 6th period which are not noble metals. If in doubt preference should be given to the metals of 4th period, if only for reasons of cost. M may also be a mixture of two or more of the recited metals. The metal M will often be Fe, Co and/or Ni or comprise at least one or more of these metals.

The metal M'' is a main group metal, in particular an alkali metal or alkaline earth metal, and M'' may also represent a mixture of two or more main group metals.

X represents S, Se or Te and mixtures of the recited chalcogenides and X' represents a halide, wherein in the case of the compound class $M''_6M_kX_mX'_n$ k, m and n represent decimal numbers, wherein $24 \leq k \leq 25$, $26 \leq m \leq 28$ and $0 \leq n \leq 1$.

It will often also be the case that the sulfides and the sulfoselenides are preferred among the recited chalcogenides for reasons of toxicity alone. Without wishing to limit the generality of the foregoing and the following it appears particularly advantageous to the applicant at the present time to employ in particular transition metal chalcogenides where either the transition metal in the crystal structure can assume two different oxidation stages and/or the chalcogenide X cannot be assigned exclusively one charge in the form of X^{2-} , as is the case for example in the presence of X_2^{2-} . This applies in particular to pentlandites, chalcogenides having a spinel structure or spinel-like structure as well as, to a slightly lesser extent, to chalcogenides whose structure comprises X_2^{2-} ions, for example chalcogenides having a pyrite structure or a pyrite-like structure. Such structures appear to favor the coordination of atomic hydrogen to the catalyst surface. By contrast, compounds of empirical formula MX or MX_2 will be selected only with lesser priority since these generally have a slightly lower stability under electrochemical conditions.

It is thus in principle the case that chalcogenides of formulae M_2X_4 , M_9X_8 or $M''_6M_kX_mX'_n$ are particularly suitable, in particular when M is a metal of the 4th period of groups 4 to 10, and here in turn especially is Fe, Co and/or Ni or comprises at least one or more of these metals.

According to the invention "substantially conforming to empirical formula" is to be understood as meaning that the transition metal chalcogenides need not be pure compounds but may also be nonstoichiometric compounds or that a doping may be present. In the nonstoichiometric compounds the molar ratio X/M may be altered

(upwards or downwards) for example by up to 2%, in some cases also up to 5% or in extreme cases also up to 10% relative to the integer ratio. Dopings that may be present include in particular a doping with a nonmetal, for example with one or more of the elements B, O, N, P, As, F, Cl, Br, I, in a content of up to 5 at% based on the metal M. A doping may for example be carried out by means of the thermal production, possible for all stoichiometries, of the compounds MX, MX₂, M₂X₃, M₂X₄, M₃X₄, M₉X₈ or M''₆M_kX_lX'_m from the elements M (wherein – as mentioned – M may also represent different transition metals) and X by admixing of the corresponding nonmetal with which doping is effected. An oxygen doping may be carried out for example by partially oxidizing the transition metal chalcogenide, for example the pentlandite. This comprises carrying out a partial surface modification with the result that a backbone of the transition metal chalcogenide X has a surface which also comprises oxygen in addition to the chalcogen X. It is also possible to carry out a doping - for example with nitrogen or a halogen - by additionally adding a chemical compound of the nonmetal with which doping is to be effected, for example a transition metal nitride or a transition metal halide, during production from the elements.

Transition metal chalcogenides which substantially conform to the formula M₉X₈ and are at least partially present crystallized in the pentlandite structure (according to the present application the relevant measurement is carried out by powder x-ray diffraction) have proven particularly suitable. The compounds of formula Fe_{9-a-b-c}Ni_aCo_bM'_cS_{8-d}Se_d are in turn of particular importance here. M' is selected from the same transition metals with the same preference variants as specified above for M and is especially selected from one or more metals from the group consisting of Ag, Cu, Zn, Cr and Nb. a, b, c and d are decimal numbers, but often integer or half-integer (wherein here too a stoichiometric compound and a nonstoichiometric compound as defined above may be present), wherein a is a number from 0 to 7, in particular from 1 to 6, b is a number from 0 to 9, in particular from 0 to 8, c is a number from 0 to 2, in particular from 0 to 1 and d is a number from 0 to 6, in particular from 0 to 4. The sum of a+b+c is typically a number from 0 to 9, especially from 3 to 7. It is often the case that, simultaneously, a is a number from 1 to 6, b is a number from

0 to 8, c is a number from 0 to 1, d is a number from 0 to 4 and the sum of a+b+c is a number from 3 to 7.

The proportion of the transition metal chalcogenide M_9X_8 present in the pentlandite structure is typically at least 80%, usually even at least 90%. Such contents are readily achievable with customary synthesis processes, in particular with the abovementioned thermal production from the elements.

In a further embodiment the compound $Fe_{9-a-b-c}Ni_aCo_bM'_cS_8-dSe_d$ contains only two of the three metals or substantially only two of the three metals iron, cobalt and nickel and no metal M' or substantially no metal M'. "Substantially" is to be understood as meaning that the proportion of the metal not present, i.e. of the metal M', based on the metal is less than 5 mol%.

In a further embodiment the electrocatalytic reduction may be performed in both liquid electrolyte cells and solid electrolyte cells and in particular also polymer electrolyte cells. In the case of liquid electrolyte cells the organic compound to be hydrogenated is typically in aqueous/organic solution. In addition, polymer electrolyte cells also allow hydrogenation of the organic compound in pure form or as a solution. In addition the solvent may also contain a conductivity salt - for example when water or an alcohol are used as solvent; in the case of polymer electrolyte cells conductivity salts will often be eschewed. The hydrogenation may be carried out in any of the recited cells both in a discontinuous batch mode and in a continuous flow mode. The Faraday yields may additionally be optimized for the desired hydrogenation through the choice of the cell and the electrolyte. The selectivity for different hydrogenation products may additionally be influenced.

The process according to the invention may further be advantageously developed when an electrode configured as more particularly described below is employed and in

particular comprises one or more of the advantageous embodiments of the electrode described below.

An electrode for electrocatalytic hydrogenation of organic compounds in an electrochemical cell comprises, in addition to an optionally present electrical contact of the electrode belonging to the electrode, a carrier material and a catalyst layer arranged at least on a portion of the surface area of the carrier material. It goes without saying that according to the present application the contact (which may be effected for example via a metal and is often attached by bonding or pressing) is thus not considered part of the carrier material. The catalyst layer contains or consists of a transition metal chalcogenide as catalyst, wherein the transition metal chalcogenide is selected from sulfides, selenides and/or tellurides.

That the catalyst layer is arranged "on" the carrier material may be understood to mean here and in the following that the catalyst layer is arranged or applied on the carrier material directly in direct mechanical and/or electrical contact. Indirect contact may also be described where further layers or regions are arranged between the catalyst layer and the carrier material.

An electrode according to the the present application for the electrocatalytic process especially has one or more of the following features:

- In addition to the transition metal chalcogenide the catalyst layer comprises a polymeric binder, in particular a polymeric non-ion-conducting binder, or consists of the two components.
- In addition to the transition metal chalcogenide and an optionally present binder the catalyst layer also comprises an additive or consists of the two or (in the presence of a binder) three components.

- The electrode at least partially comprises porous regions.
- The electrode has a catalytically active surface area of at least 0.2 cm².

As more particularly elucidated above in respect of the process, hereby incorporated by reference in its entirety, particularly good results are typically achieved when the catalyst employed is selected from transition metal chalcogenides which substantially conform to the formula M_9X_8 and are at least partially present crystallized in the pentlandite structure.

In an advantageous embodiment the catalyst layer comprises a polymeric binder, in particular a polymeric binder which is not considered as belonging to the ionic polymers. This binder results in improved adhesion of the individual catalyst particles to one another and usually results in improved mechanical stability and/or also in simpler processing of the catalyst material. Depending on the carrier material it may also make it possible to realize better adhesion to the carrier material. A binder may advantageously be employed when the catalyst layer may be applied, in particular spray-applied, to the carrier material in the form of inks or when the catalyst material is employed in the form of a heat-pressable composition.

Contemplated binders especially include hydrophobic binders. These may especially be selected from polyolefins, fluorinated polyolefins, copolymers with polyolefins and/or fluorinated polyolefins and polymer blends containing polyolefins and/or fluorinated polyolefins, wherein non-ion-conducting polymers are preferred throughout. It is optionally also possible to employ or to co-employ chlorinated polymers or copolymers (for example PVC or PVC-containing copolymers). The polyolefins and fluorinated polyolefins are especially selected from the group consisting of PE, PP, PVDF, FEP and PTFE. The proportion of the binder in the catalyst layer is typically 1% to 90% by weight, in particular 5% to 80% by weight, for example 10% to 25% by weight. At levels above 25% by weight the efficiency of the reaction often decreases in respect of the yields achieved. A

sufficient adhesion of the catalyst particles to one another and on an optionally present carrier material may typically be realized above 1% by weight and in particular above 5% by weight.

In a further embodiment the catalyst layer comprises an additive in addition to the transition metal chalcogenide and an optionally present binder. The additive may especially be selected from substances for increasing electrical conductivity (for example carbon black, graphite or carbon nanotubes), substances for increasing ionic conductivity (for example ionomers such as Nafion, Sustainion, Piperion, Aemion, Durion, Orion), substances for increasing thermal conductivity, substances for increasing corrosion resistance, substances for modifying hydrophobicity and substances for improving adsorption of the organic compound to be hydrogenated (for example carbon blacks and activated carbons). It is also possible for a plurality of the recited additives to be present. Additives for improving mechanical properties and/or additives for improving adsorption properties may also be present in addition or simultaneously. Alternatively or in addition (at least) one intermediate layer may also be present between the catalyst layer and the carrier material. Conceivable here are for example layers for improving the adhesion of the catalyst layer on the carrier material or layers for improving electrical conductivity. An electrically conductive additive in the catalyst layer can also result in better distribution of the active centers. Finally, the side of the catalyst layer facing away from the carrier material may for example have a further layer applied to it for improving corrosion resistance or for altering hydrophilic/lipophilic properties of the surface.

The catalyst layer may be arranged on the carrier material in various ways. The catalyst layer may be spray-applied (in particular using an ink) but may also be applied by immersing, knife coating, printing processes, decal processes or heat pressing to form functional electrode laminates. Electrical contacting may be effected both via the front side and via the back side, i.e. the contacting may be effected either at the carrier material or at the catalyst layer itself.

The catalyst particles used for the catalyst layer may in principle have any particle size. However, particles having a d_{90} smaller than 10 μm determined by sieving methods have proven advantageous because larger particles are often more difficult to process, in particular when employed in inks to be spray-applied.

In a further embodiment the carrier material employed may be a porous material. Using a porous material allows the active surface area of the catalyst layer (which in the internal surface area, i.e. pores, cavities, interspaces and the like, does not form an actual layer but rather a coating) to be markedly enlarged. A surface area enlarged in this way may be obtained in particular when the porous carrier material is infiltrated with the catalyst ink, for example by immersion processes or else by spray-application. According to the present application a porous carrier material is to be understood as meaning not only a carrier material having pores (in particular having a significant proportion of macropores), wherein the porous carrier material may also have an open-pored structure, but also a carrier material in the form of a felt, in the form of a woven fabric or in the form of a braided fabric, for example a nickel mesh. Mesh-like structures are also conceivable.

Irrespective of whether the carrier material is porous it will typically be a sheetlike structure and it is especially possible to employ a carrier material which is a metal, a metal oxide, a polymer, a ceramic, a carbon-based material, a composite material or a mixture of such substances. The carrier material is generally not catalytically active itself. However, the carrier material will often exhibit electrical conductivity. The sheetlike carrier material may be in the form of a fabric, expanded mesh, felts or films for example. It may also be a membrane (in particular in the case of electrodes of a polymer electrolyte cell) or else a filter film (composed of a polymer or metal for example), for example a PTFE membrane or an Ag filter.

In a further embodiment the catalyst layer has a surface area of at least least 0.2 cm^2 , in particular at least 1 cm^2 , preferably 1 cm^2 to 4 m^2 . This may be an uninterrupted

surface area but the layer/the coating may also be interrupted or divided into a plurality of mutually separate regions of the carrier material. The reported values are the external surface area and in fact only the surface area that is not facing the carrier material (this is thus substantially the side facing away from the carrier material); the internal surface area of a porous carrier material is not included in the calculation, i.e. the mathematical calculation is carried out only on the basis of the external dimensions, in the simplest case from height, length and width. According to the present application it is thus possible to produce electrodes of any desired size, wherein for a large industrial-scale application it is also possible to realize surface areas in the square meter range while for smaller amounts areas of 1 cm^2 or less may be advantageous.

In a further embodiment the catalyst layer of the electrode is configured such that the catalyst loading is $0.1\text{-}500 \text{ mg cm}^{-2}$, in particular $1\text{-}250 \text{ mg cm}^{-2}$, for example $2\text{-}10 \text{ mg cm}^{-2}$. The catalyst loading may be measured by weight measurement before and after application of the catalyst layer to the carrier material. A distribution of the active centers allowing significant conversion to be realized may typically be effected above surface areas of 0.5 to 1 mg cm^{-2} . Only a small additional effect is achieved at catalyst loadings above 250 mg cm^{-2} .

Also essential to the amount of active centers is the layer thickness, wherein thicker layers, however, also achieve good results upon addition of a conductivity additive. However, it is also possible to provide very thin layers (in the range of just a few nanometers, for example up to 10 nm) while thicker layers of up to $500 \text{ }\mu\text{m}$ are also possible, with upper limits being very difficult to specify due to their very strong dependence on the catalyst material. Often employed for economic reasons are layer thicknesses of 5 to $50 \text{ }\mu\text{m}$ (the layer thickness may be measured by scanning electron microscopy).

The object of the invention is further also achieved by an electrochemical cell for electrochemical hydrogenation which contains as an electrode, in particular as the cathode, the electrode more particularly described hereinabove. The electrochemical cell for electrocatalytic hydrogenation especially comprises a reactor containing a cathode, an anode and an electrolyte, wherein the reactor contains a reducible organic compound in liquid form or at least partially in dissolved form and wherein the reducible organic compound may be hydrogenated at the cathode. The electrode comprises a catalyst layer and a carrier layer such as are more particularly described hereinabove.

The electrochemical cell according to the present application is in particular not configured to produce a gas. The apparatus thereof is thus configured such that, while it is ensured that a gas is formed as a byproduct, the hydrogenated organic compound may be formed as the main product. This is especially to be understood as meaning that the hydrogen often formed in the electrocatalytic hydrogenation is at most 50% (based on the total current yield) provided that reasonably advantageous reaction conditions are realized. In most cases the proportion of hydrogen formed is actually less than 20%. The formation of hydrogen is ideally very largely avoided so that only values in the single-figure percent range occur.

The object of the invention is finally also achieved by the use of a transition metal chalcogenide, in particular a transition metal chalcogenide selected from compounds substantially conforming to empirical formulae MX , MX_2 , M_2X_3 , M_2X_4 , M_3X_4 , M_9X_8 or $M''_6M_kX_lX'_m$, for example a pentlandite, as catalyst for the electrocatalytic hydrogenation of organic compounds. The use of the compounds more particularly specified hereinabove is particularly advantageous, wherein the foregoing applies equally here too.

Without any intention to limit generality the invention is more particularly described below with reference to figures and working examples.

I. Electrocatalysis in batch mode

The process according to the invention was initially performed with an electrochemical cell in batch mode. Figure 1 shows a schematic view of an electrochemical batch cell 1 comprising two half-cells 2, 3. In addition to the catholyte chamber 37, the cathode half-cell 3 contains the cathode comprising the actual electrode 32, the end plate 31 and the electrode holder 33 and also reference electrode 36. In addition to the anolyte chamber 24, the anode half-cell 2 contains the anode comprising the actual electrode 22 and the end plate 21. An ion exchange membrane 4 is provided between the two chambers 2 and 3. A plurality of seals 23, 25, 5, 34, 35 are arranged therebetween.

Example 1 - Electrocatalytic hydrogenation of MBY with pentlandite catalysis

The cell according to Fig. 1 is used for the electrocatalytic hydrogenation of 2-methyl-3-butyne-2-ol (MBY) to afford 2-methyl-3-buten-2-ol (MBE) or 2-methyl-butan-2-ol (MBA) at room temperature. Here and hereinbelow the reaction is terminated approximately at the stage of the alkene but under appropriate reaction conditions may also be performed until substantially only the alkane is present. Pentlandite-based non-porous catalysts composed entirely of metal chalcogenide were employed as the cathode. Ni wire was used as the anode. A Nafion cation exchanger membrane was used as the membrane. A 1 M solution of MBY in a solvent/conductivity salt combination of 0.3 M KOH in methanol was employed. The cathode had a surface area of 0.071 cm² and was contacted via a brass rod in a PTFE housing. The electrocatalytic reduction was carried out for 2 hours.

For different pentlandite-based catalysts (the pentlandite catalysts were obtained by thermal synthesis from the respective elements according to B. Konkena et al., Nat. Commun. 7: 12269 doi: 10.1038/ncomms12269 (2016), wherein more than 90% by weight - measured with PXRD - were always present in the pentlandite structure) table 1 shows the Faraday efficiencies achieved based on the desired reduction to MBE in the reaction according to example 1 and the potentials (relative to a reversible hydrogen

electrode E_{RHE} as reference electrode) required for the hydrogenation at a current density of

-100 mA cm⁻². It is apparent that Faraday efficiencies up to 100% are achievable and that lower potentials than for the use of platinum electrodes were required throughout. According to the present application the potentials were always determined using a Gamry 1010B potentiostat. According to the invention yields were always determined by NMR spectrometry using potassium hydrogenphthalate as internal standard.

Table 1

Catalyst	FE-MBE / %	E / V vs. RHE
Fe _{4.5} Ni _{4.5} S ₇ Se	100	-1.72
Fe _{4.5} Ni _{4.5} S ₄ Se ₄	59	-1.430
Fe _{4.5} Ni _{4.5} S ₃ Se ₅	72	-1.98
Fe ₆ Ni ₃ S ₈	55	-1.78
Fe ₃ Ni ₆ S ₈	100	-1.51
Fe ₂ Co ₄ Ni ₃ S ₈	69	-1.75
Fe ₄ Co ₂ Ni ₃ S ₈	101	-1.67
Fe ₄ Co ₂ Ni ₃ S ₈	102	-1.50
Co ₈ NiS ₈	95	-1.60
Co ₇ Ni ₂ S ₈	61	-1.97

Fig. 2 shows for example 1 with Fe₃Ni₆S₈ as catalyst the required potentials (E/V) for a current density of -100 mA cm⁻² and the achieved Faraday efficiencies (FE) compared

to experiments using a platinum electrode or a glassy carbon electrode. It is apparent that a significant efficiency is observed only in the case of $\text{Fe}_3\text{Ni}_6\text{S}_8$ as catalyst and simultaneously a lower/markedly lower potential is required than in the case of the electrodes investigated for comparison.

Example 2 - Electrocatalytic hydrogenation of butynediol with pentlandite catalysis

In an electrochemical cell according to example 1 the selectivity of the hydrogenation of 2-butyne-1,4-diol with two pentlandites already used in example 1 and different conductivity salt/solvent combinations was investigated (MeOH = methanol):

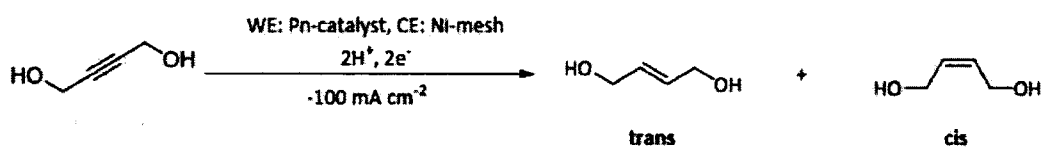


Table 2 shows that in this reaction with $\text{Fe}_3\text{Ni}_6\text{S}_8$ it is substantially the cis product that is formed while $\text{Fe}_3\text{Co}_3\text{Ni}_3\text{S}_8$ leads to elevated formation of the trans product. The use of water as the solvent and KOH as the conductivity salt shows the best selectivity and the most advantageous potential values.

Table 2:

Catalyst	Conditions	Faraday efficiency cis / %	Faraday efficiency trans / %	E / V vs. RHE
$\text{Fe}_3\text{Ni}_6\text{S}_8$	0.3 M KOH / MeOH	16 ± 1	3	-1.38
$\text{Fe}_3\text{Ni}_6\text{S}_8$	0.3 M LiCl / MeOH	18	4 ± 1	-1.70

Fe ₃ Ni ₆ S ₈	0.3 M KOH / H ₂ O	22	<1	-1.00
Fe ₃ Co ₃ Ni ₃ S ₈	0.3 M KOH / MeOH	5 ± 3	9 ± 1	-1.33

Example 3 - Electrocatalytic hydrogenation of MBY using M''₆M_kX_mX'_n catalysis

The M''₆M_kX_mX'_n catalysts were produced in evacuated ampoules by high-temperature synthesis. Stoichiometric amounts of the respective elements in a quartz glass ampoule were treated in a furnace at a temperature typically between 650°C and 800°C for 96 h. The temperature to be selected depends on the employed stoichiometry. Ba₆Ni₂₅: 675°C, Ba₆Fe_{12.5}Co₂₅: 675°C, Ba₆Fe_{8.33}Co_{8.33}Ni_{8.33}: 700°C. Ba₆Fe_{12.5}Co₂₅ subsequently heat treated for a further 96 h at 775°C and Ba₆Fe_{8.33}Co_{8.33}Ni_{8.33} for a further 96 h at 800°C. The successful synthesis of the catalysts is confirmable by PXRD analysis.

In an electrochemical cell according to example 1 the selectivity of the hydrogenation of 2-butyne-1,4-diol was investigated. In contrast to examples 1 and 2, non-porous M''₆M_kX_mX'_n-based catalysts composed entirely of metal chalcogenide were used as the cathode. The reaction was carried out with a 1 M MBY solution in 0.3 M KOH/H₂O or 0.3 M KOH/MeOH as conductivity salt/solvent to afford butenediol.

Table 3 shows that all materials are suitable for an electrocatalytic hydrogenation.

Table 3

Catalyst	Conditions	FE / %
Ba ₆ Ni ₂₅ S ₂₇	0.3 M KOH/H ₂ O	24.2
Ba ₆ Ni ₂₅ S ₂₇	0.3 M KOH/MeOH	17.6

Ba ₆ Fe _{12.5} Co ₂₅ S ₂₇	0.3 M KOH/MeOH	19.4
Ba ₆ Fe _{8.33} Ni _{8.33} Co _{8.33} S ₂₇	0.3 M KOH/MeOH	25.1

Example 4 - Electrocatalytic hydrogenation of MBY with MX and MX₂ catalysis

The reaction according to example 1 was carried out with transition metal sulfides of empirical formulae MS and MS₂ as catalyst with a 1 M MBY solution in 0.3 M KOH/H₂O as conductivity salt/solvent to afford MBE. For comparison, the last row gives an example of a catalyst with pentlandite structure (Fe₃Ni₆S₈ from example 1). Table 4 shows the required potentials (E/V) for a current density of -100 mA cm⁻² and the achieved Faraday efficiencies (FE).

Table 4:

Catalyst	FE / %	E / V vs. RHE
NiS	44	-0.925
FeS	37	-1.27
CuFeS ₂	78	-1.16
MnS	18	-1.42
Fe ₃ Ni ₆ S ₈	23	-1.04

Example 5 - Electrocatalytic hydrogenation of nitrocompounds, aldehydes and terminal alkynes with pentlandite catalysis

The hydrogenation according to the invention can also be used to reduce functional groups other than disubstituted alkynes. The reaction was performed under the same

conditions as in example 1. In addition, table 5 specifies the employed conductivity salts, solvents, concentrations and pentlandite catalysts (also used in example 1).

Table 5:

Catalyst	Conditions	Reactant	Product	FE / %	E/V
Fe ₃ Ni ₆ S ₈	0.3 M KOH/ethanol	0.5 M nitrobenzene	Aniline	7	-1.27
Fe ₃ Ni ₆ S ₈	0.3 M LiCl/ethanol	0.5 M p-anisaldehyde	p-hydroxymethylanisole	25	-1.69
Fe _{4.5} Ni _{4.5} S ₄ Se ₄	0.3 M KOH/methanol	1 M phenylacetylene	Styrene	75	-2.05

Example 6 - Electrocatalytic hydrogenation of MBY with pentlandite catalysis in a solid electrolyte cell using different electrode concepts

The reaction according to example 1 was also performed with other electrode concepts instead of electrodes composed entirely of metal chalcogenide, namely electrodes comprising a pentlandite coating, comprising pressed catalyst composition or comprising catalyst composition pressed onto a metal mesh.

For the coated electrode a SIGRACELL GFD 2.5 carbon felt was immersed several times in an ink composed of 90% by weight of Fe₃Ni₆S₈ and 10% by weight of PTFE and dried at 80°C until the desired catalyst loading (5 mg*cm⁻²) was achieved. In a departure from example 1 a 1 M MBY solution in 0.3 M KOH/H₂O was employed as conductivity salt/solvent and the electrocatalytic hydrogenation performed at 80 mA cm⁻² and in a solid electrolyte cell. The produced electrodes achieved a Faraday efficiency of 25% based on MBE and 5% based on MBA at a cell voltage of 2.5 V.

For an electrode comprising a pressed catalyst composition a mixture of Kynar Superflex 2501 PVDF and $\text{Fe}_{4.5}\text{Ni}_{4.5}\text{S}_7\text{Se}$ was commixed using an IKA M20 knife mill. The composition produced was subjected to heat pressing at 170°C and a contact pressure of 1 kN cm^{-2} . It is alternatively possible to employ other thermoplastics instead of PVDF. Conductive additives may optionally be added to increase the conductivity between the active centers. In a departure from example 1 a 1 M MBY solution in 0.3 M KOH/ H_2O was again employed as conductivity salt/solvent and the electrocatalytic hydrogenation performed in a solid electrolyte cell. Table 6 shows the required cell voltages (U/V) for a current density of 80 mA cm^{-2} in the solid electrolyte cell.

Table 6

<u>Electrode composition / % by weight</u>	<u>Membrane</u>	<u>FE-MBE</u> <u>/ %</u>	<u>Cell voltage /</u> <u>V</u>
<u>30% PVDF / 70% $\text{Fe}_{4.5}\text{Ni}_{4.5}\text{S}_7\text{Se}$</u>	<u>Nafion</u> <u>115</u>	<u>58</u>	<u>2.5</u>
<u>30% PVDF / 1% super P carbon / 69% $\text{Fe}_{4.5}\text{Ni}_{4.5}\text{S}_7\text{Se}$</u>	<u>Nafion</u> <u>115</u>	<u>48</u>	<u>2.4</u>
<u>30% PVDF / 70% $\text{Fe}_{4.5}\text{Ni}_{4.5}\text{S}_7\text{Se}$</u>	<u>FM-FAA-</u> <u>3-PK-130</u>	<u>74</u>	<u>2.5</u>

For an electrode comprising a catalyst composition pressed onto a metal mesh a mixture of Kynar Superflex 2501 PVDF and $\text{Fe}_3\text{Co}_3\text{Ni}_3\text{S}_8$ was commixed using an IKA M20 knife mill. The produced composition was pressed onto a stainless steel mesh (Haver & Boecker, $0.2 \text{ mm} \times 0.16 \text{ mm}$) at 170°C and a contact pressure of 2 kN cm^{-2} . The produced electrode has an elevated mechanical stability. In a departure from example 1 a 1 M MBY solution in 0.3 M KOH/ H_2O was again employed as conductivity salt/solvent and the

electrocatalytic hydrogenation performed in a solid electrolyte cell. Table 7 shows the required cell voltages (U/V) for a current density of 80 mA cm⁻² in a solid electrolyte cell.

Table 7

<u>Electrode composition / % by weight</u>	<u>FE-MBE</u>	<u>Cell voltage / V</u>
<u>30% PVDF / 70% Fe₃Co₃Ni₃S₈</u>	<u>21</u>	<u>2.2</u>

II. Electrocatalysis with a flow cell

The process according to the invention was initially performed with an electrochemical cell in batch mode. Figure 3 shows a schematic view of an electrochemical flow cell 101 comprising two half-cells 102, 103. In addition to the catholyte chamber 135, the cathode half-cell 103 contains the cathode comprising the actual electrode 133 and the end plate 131 and also the reference electrode 136. The catholyte chamber 135 is supplied with catholyte from the reservoir 138 via a pump 137. In addition to the anolyte chamber 125, the anode half-cell 102 contains the anode comprising the actual electrode 123 and the end plate 121. The anolyte chamber 125 is supplied with anolyte from the reservoir 127 via a pump 126. An ion exchange membrane 104 (in the following examples an FS-10120-PK cation exchange membrane was used for example) is provided between the two chambers 102, 103. A plurality of seals 122, 124, 132, 134 and the membrane-retaining seals 105, 106 are arranged therebetween.

The transition metal chalcogenide-containing electrodes were produced by spray-application of a mixture of the transition metal chalcogenide with a binder, for example PTFE, onto a porous carbon-containing carrier material, for example onto a carbon fiber fabric, or by application thereof onto the carrier material in the form of a heat-pressable

composition. Spray-application may be effected for example using 15 ml of an ink composed of 5% by weight of PTFE and 85% by weight of $\text{Fe}_3\text{Ni}_6\text{S}_8$ on a 10 cm x 10 cm W1S1010 CeTech Carbon Cloth to obtain a catalyst loading of 2 mg cm^{-2} . Heat pressing is carried out using a mixture of ground PTFE powder with the transition metal chalcogenide catalyst and a 10 cm x 10 cm carbon substrate which has an active area of 9 cm x 7 cm.

This makes it much easier to create larger electrode surface areas. Compared to the cells described at I, these higher surface area electrodes also make it possible to realize markedly higher current densities, for example current densities of up to 1 A cm^{-2} .

Example 7 - Electrocatalytic hydrogenation of MBY with pentlandite-coated electrodes with different binders and current densities

In a flow cell according to figure 3 a 1 M solution of MBY in 0.3 M KOH in H_2O is hydrogenated at room temperature using an electrode with a catalyst loading of the pentlandite $\text{Fe}_3\text{Ni}_6\text{S}_8$ (production as in example 1) of 2 mg cm^{-2} . The electrolyte chamber has a volume of 15 ml and the flow rate is 8 ml min^{-1} . The electrocatalytic reduction was carried out for 2 hours. The cathode was produced by spray-application of the catalyst onto the carrier material using an ink, wherein the size of the electrode as described above with a one-sided coating obtained by spray application is 7.1 cm^2 . The ink contains (A) 258 μL of a 60% by weight PTFE dispersion as a binder, 15 g of a 1% by weight methyl cellulose (MC) solution in water as an inert additive, 5 g of water as solvent and 1 g of the catalyst or (B) 258 μL of a 60% by weight PTFE dispersion as binder and 15 g isopropanol (IPA) and 5 g of water as solvent and 1 g of the catalyst.

Figure 4A shows for a current density of -100 mA cm^{-2} that the composition of the ink has only a small effect on the required potential. However, Figure 4B shows that the use of IPA inks results in somewhat better yields (Y) and Faraday efficiencies (FE) and a somewhat better selectivity with respect to stopping the reduction at the alkane (MBE)

while forming only relatively little alkane (MBA). The slightly better yields for the IPA ink are likely due to better exposed active centers.

Figures 5A and 5B show for the IPA-based ink the effect of the current density on the required potential (E/V) and on the yield (Y) and Faraday efficiency (FE). It is apparent (figure 5A) that the current density has no significant effect on the required potential. While Faraday efficiency decreases at higher current densities (CD); yield and selectivity (MBE/MBA) remain fairly constant (figure 5B).

Example 8 - Electrocatalytic hydrogenation of MBY with pentlandite-coated electrodes with different binder contents

The procedure of example 8 corresponds to that of example 7 / IPA ink with the exception that the employed ink contains a varying content of the binder PTFE. Experiments were carried out with 10%, 15% and 25% by weight of PTFE based on the total weight of the catalyst layer.

Figures 6A and 6B show the effect of the binder content on the required potential (E/V) and on the yield (Y) and Faraday efficiency (FE). It is apparent (figure 6A) that an elevated binder content has only a very small effect on the required potential. However, Faraday efficiency and yield decrease slightly; selectivity (MBE/MBA) remains reasonably constant. It may be deduced therefrom that while a markedly elevated binder proportion has a positive effect on mechanical stability, excessive binder contents usually result in lower yields.

Example 9 - Electrocatalytic hydrogenation of MBY with pentlandite-coated electrodes with different catalyst loadings

The procedure of example 9 corresponds to that of example 7 / IPA ink having a PTFE content of 10% by weight with the difference that more ink was spray-applied onto

the carrier material. The spraying process was performed until a loading of 0.6, 1, 2 or 5 mg cm⁻² was able to be detected.

Figures 7A and 7B show the effect of catalyst loading (CL) on the required potential (E/V) and on the yield (Y) and Faraday efficiency (FE). It is apparent (Fig. 7A) that very low catalyst loadings result in a worsening in respect of the potential to be applied. However an increase in loading above a value of 1 mg cm⁻² does not result in significant changes. It has only a very small effect on the required potential. However, higher loadings result in greater yields; selectivity (MBE/MBA) remains reasonably constant.

Example 10 - Electrocatalytic hydrogenation of MBY with pentlandite-coated electrodes with different catalysts and different membranes

In contrast to example 7, the polymer electrolyte membranes of the flow cell were varied. Employed on the one hand was a proton exchange membrane (PEM) (Fumatech BWT GmbH (FS-10120-PK)); and on the other hand an anion exchange membrane (AEM) (Fumatech BWT GmbH (FM-FAA-3-PK-130)). Different catalysts were also employed in contrast to example 7. The inks used for this purpose correspond to those of example 7 / IPA-based but wherein 15% by weight of PTFE were employed as binder. The catalyst loading was in each case 2 mg cm⁻².

Figures 8A and 8B show the effect of the membrane (PEM or AEM) on the required potential (E/V) and on the yield (Y) and Faraday efficiency (FE). It is apparent (Fig. 8A) that the proton exchange membranes consistently lead to better results in respect of the required potential. However, when the employed catalyst is also taken into account different catalysts/membrane combinations that are particularly advantageous become apparent. In terms of potential the selenium-containing catalyst Fe_{4.5}Ni_{4.5}S₄Se₄ is best for PEM and about equal with Fe₂Co₄Ni₃S₈; by contrast for AEM Fe₂Co₄Ni₃S₈ is slightly poorer than the other two catalysts. A different picture emerges for yields and Faraday efficiencies. Here, Fe₃Ni₆S₈ provides the best results for both membranes, wherein these are markedly

better for the anion exchange membrane than for the proton exchange membrane. However, $\text{Fe}_{4.5}\text{Ni}_{4.5}\text{S}_4\text{Se}_4$ shows slightly poorer selectivity in respect of the MBE/MBA ratio. In summary it must be noted that, while the proton exchange membranes are slightly more energy efficient since the required potential is lower, they also provide lower yields.

Example 11 - Electrocatalytic hydrogenation of MBY with pentlandite-coated electrodes at different temperatures

In contrast to example 7 the hydrogenation reactions were performed at different temperatures.

Figures 9A and 9B show the required potential (E/V) and the yield (Y) and Faraday efficiency (FE) for various reaction temperatures. While higher temperatures result in a slightly lower required potential, yield and Faraday efficiency are slightly higher at room temperature. A significant effect on selectivity is not observable.

Example 12 - Electrocatalytic hydrogenation of MBY with pentlandite-coated electrodes in a solid electrolyte cell

Figure 10 shows a schematic view of a solid electrolyte cell 201 comprising two half-cells 202, 203. In addition to the cathode flow field 234, the cathode half-cell 203 contains the cathode comprising the actual electrode 235, the collector plate 233 and the end plate 231 as well as the plastic spacer 232. The cathode flow field 234 is supplied with catholyte from the reservoir 237 via a pump 236. In addition to the anode flow field 224, the anode half-cell 202 contains the anode comprising the actual electrode 225, the collector plate 223 and the end plate 221 as well as the plastic spacer 222. The anode flow field 224 is supplied with anolyte from the reservoir 227 via a pump 226. An ion exchange membrane 204 is provided between the two chambers 202 and 203. A plurality of seals 205, 206 are arranged therebetween.

In contrast to example 7 a polymer electrolyte system was used instead of a liquid electrolyte system. Instead of the FS-10120-PK cation exchange membrane an FM-FAA-3-PK-130 anion exchange membrane was used. Furthermore, as in example 7, the IPA ink was employed but with a PTFE content of 10% by weight. The current density was not -100 but only -80 mA cm⁻². A Faraday efficiency of 67% (for MBE) was achieved at a cell voltage of -2.5 V.

Example 13 - Electrocatalytic hydrogenation of MBY in a solid electrolyte cell with pentlandite electrodes at different current densities

The reaction according to example 12 (Fe₃Ni₆S₈-coated electrodes) was initially repeated at different currents with 1 M MBY in 0.3 M KOH/H₂O. Table 8 shows that while at constant reaction times (2 hours) and higher current densities the Faraday efficiency decreases, the yield increases. Further increases in selectivity and conversion for the target hydrogenation products at higher current densities are achievable by adapting the employed electrolyte.

Table 8

Current density / mA cm ⁻²	FE-MBE / %	Conversion MBE / %	FE-MBA / %	Conversion MBA / %	Cell voltage / V
40	62.4	23.3	9.1	1.7	2.4
80	71.8	56.9	7.9	3.1	2.3
160	44.4	66.3	12	8.6	2.7
240	30.2	67.7	8.2	9.1	2.9

Example 14 - Electrocatalytic hydrogenation of MBY in a solid electrolyte cell with pentlandite electrodes with different binders

For the reaction according to example 12 the binders of the pentlandite coating were also varied. Different ion exchange membranes were also used: the Piperion A80 (Versogen) and FM-FAA-3-PK-130 (Fumatech) anion exchange membranes and the Nafion 115 (IonPower) cation exchange membrane. Binders employed included both fluorine-containing polymers and the ionomers Piperion (Versogen), Aemion (Ionomr) and Nafion (IonPower). The abovementioned ionomers not only have the function of a binder but also the function of a conductivity-increasing additive.

The electrodes examined were produced on W1S1010 Carbon Cloth (CeTech) using an IPA ink at a binder loading of 10% by weight and a catalyst loading of 2.5 mg cm⁻². The reaction according to example 10 is performed at 80 mA cm⁻² with the recited membranes and the coated electrodes.

Table 9 shows the effect of different binders on the hydrogenation reaction.

Table 9

Binder	Membrane	FE-MBE / %	FE-MBA / %
Nafion	Nafion 115	23.2	2.2
PVDF	Nafion 115	9.1	2.3
Aemion	Nafion 115	12.4	4.1
PTFE	Nafion 115	20.8	6.5
Piperion	Piperion A80	9.1	2.3

PTFE	Piperion A80	12.4	7.4
PTFE	FM-FAA-3- PK-130	22.4	8.5
Aemion	FM-FAA-3- PK-130	24.7	1.8

The Faraday efficiency for the hydrogenation changes according to the employed combination. Hydrophobic binders such as the recited fluorine-containing polymers generally show a higher Faraday efficiency for the electrochemical hydrogenation (as is demonstrable with PTFE, Nafion and PVDF).

Example 15 - Electrocatalytic hydrogenation of MBY in a solid electrolyte cell with different catalysts (comparative example)

For comparison with the present application the reaction according to example 12 was also performed with electrocatalysts of the prior art. For comparison, Pd-based electrodes (current industrial state-of-the-art) were generated with Pd particles (Alfa Aesar, 0.35-0.8 μm) analogously to example 12. Furthermore, Ni foam (1.6 mm, Goodfellow) was employed directly as electrode material.

Table 10 shows the effect of the electrocatalyst on the hydrogenation of MBY. The reaction was performed according to example 12 again with a 1 M MBY solution in 0.3 M KOH/H₂O as conductivity salt/solvent at 80 mA cm⁻². The Fe₃Ni₆S₈ catalyst shows slightly better Faraday efficiencies and cell voltages than the industrial Pd standard. Compared to the Ni foam the Fe₃Ni₆S₈ shows a markedly higher activity and selectivity for the hydrogenation.

Tab. 10

Catalyst	FE-MBE / %	FE-MBA / %	Cell voltage / V
Fe ₃ Ni ₆ S ₈	71.8	7.9	2.3
Pd	63.6	28.2	2.1
Ni foam	10.2	4.1	2.6

Example 16 - Electrocatalytic hydrogenation of aromatic alkynes and aldehydes with pentlandite catalysis

To produce the electrode the IPA ink having a PTFE content of 10% by weight was spray-applied to a carbon felt (Sigracell GFD 2.5). An Fe₃Ni₆S₈ coating was applied with a loading of 5 mg cm⁻². Analogously to example 7 the reaction of a 1 M phenylacetylene solution in 0.3 M KOH/MeOH as conductivity salt/solvent was performed at a current density of 80 mA cm⁻². A cation exchange membrane (Nafion 115) was employed in the solid electrolyte cell. The hydrogenation achieved a Faraday efficiency of 30% (for phenylethylene) at a cell voltage of 2.2 V.

The same electrode under the same conditions was used to perform the hydrogenation of a 1 M benzaldehyde solution in 0.3 M sodium acetate/MeOH as conductivity salt/solvent. A Faraday efficiency of 10% (for benzyl alcohol) was achieved at a cell voltage of 4.0 V.

Claims

1. A process for electrocatalytic hydrogenation of organic compounds in an electrochemical cell comprising a cathode, an anode and an electrolyte, wherein the reducible organic compound is in liquid form or at least partially in dissolved form and wherein the reducible organic compound is hydrogenated at the cathode,

wherein

the cathode comprises or consists of a transition metal chalcogenide as catalyst, wherein the transition metal chalcogenide is selected from sulfides, selenides and tellurides.

2. The process as claimed in the preceding claim, wherein

the reducible organic compound comprises at least one multiple bond and in particular at least one C-C multiple bond, C-O double bond, C-N multiple bond, NO₂ group or N-N multiple bond and/or is an aromatic or heteroaromatic compound.

3. The process as claimed in either of the preceding claims, wherein

the reducible organic compound comprises at least two different reducible functional groups.

4. The process as claimed in either of the preceding claims, wherein

the transition metal chalcogenide substantially conforms to the empirical formula MX, MX₂, M₂X₃, M₂X₄, M₃X₄, M₉X₈ or M''₆M_kX_mX'_n,

wherein M represents one or more metals selected from the transition metals of the 4th, 5th or 6th period and

M'' is selected from alkali and alkaline earth metals,

wherein X represents S, Se and Te and

X' represents a halide and

k, m and n represent decimal numbers, wherein $24 \leq k \leq 25$ and $26 \leq m \leq 28$ and $0 \leq n \leq 1$.

5. The process as claimed in the preceding claim, wherein

the transition metal chalcogenide substantially conforms to the empirical formula M_2X_4 , M_9X_8 or $M''_6M_kX_mX'_n$ and M is selected from a transition metal of the 4th period of groups 4 to 10, and in particular represents one, two or three of the metals Fe, Co and Ni or comprises at least one or more of these metals.

6. The process as claimed in one of the two preceding claims, wherein

the transition metal chalcogenide conforms to formula M_9X_8 and is at least partially present crystallized in the pentlandite structure and is in particular a compound of formula $Fe_{9-a-b-c}Ni_aCo_bM'_cS_{8-d}Se_d$, wherein

- M' is a transition metal of the 4th, 5th or 6th period and is in particular selected from one or more metals of the group consisting of Ag, Cu, Zn, Cr, Nb,

- a is a number from 0 to 7, in particular from 1 to 6

- b is a number from 0 to 9, in particular from 0 to 8

- c is a number from 0 to 2, in particular from 0 to 1

- d is a number from 0 to 6, in particular from 0 to 4

- wherein the sum of $a+b+c$ is a number from 0 to 9, in particular from 3 to 7.

7. The process as claimed in the preceding claim, wherein

the transition metal chalcogenide conforms to $\text{Fe}_{9-a-b-c}\text{Ni}_a\text{Co}_b\text{M}'_c\text{S}_{8-d}\text{Se}_d$ and

the compound contains substantially only two of the three elements Fe, Ni and Co and also substantially no metal M' .

8. The process as claimed in either of the preceding claims, wherein

the electrocatalytic hydrogenation is performed in batch mode or in continuous flow mode.

9. The process as claimed in either of the preceding claims, wherein

the applied current density is greater than 10 mA cm^{-2} , in particular greater than 100 mA cm^{-2} .

10. An electrode for electrocatalytic hydrogenation of organic compounds in an electrochemical cell, in particular by the process as claimed in any of the preceding claims,

comprising a carrier material and a catalyst layer arranged at least on a portion of the surface area of the carrier material, wherein

the catalyst layer contains or consists of a polymeric binder and a transition metal chalcogenide as catalyst, wherein the transition metal chalcogenide is selected from sulfides, selenides and tellurides.

11. The electrode as claimed in the preceding claim, wherein

the catalyst layer is porous or the carrier material is at least partially formed from a porous material and the catalyst layer is arranged as a coating at least partially also on the internal surface area of the porous carrier material.

12. The electrode as claimed in any of the preceding claims, wherein

the polymeric binder is selected from polyolefins, fluorinated polyolefins, copolymers with polyolefins and/or fluorinated polyolefins and polymer blends containing polyolefins and/or fluorinated polyolefins, wherein the polyolefins and fluorinated polyolefins are especially selected from the group consisting of PE, PP, PVDF, FEP and PTFE.

13. The electrode as claimed in any of the preceding claims,

wherein the proportion of the binder in the catalyst layer is 1% to 90% by weight, in particular 5% to 80% by weight, for example 10% to 25% by weight.

14. The electrode as claimed in any of the preceding claims, wherein

the catalyst layer contains or consists of the transition metal chalcogenide, optionally a binder and at least one additive,

wherein the at least one additive is selected from substances for increasing electrical conductivity, substances for increasing ion conductivity, substances for increasing thermal conductivity, substances for increasing corrosion resistance, substances for increasing hydrophobicity and substances for improving adsorption of the organic compound to be hydrogenated.

15. The electrode as claimed in any of the preceding claims, wherein

the catalyst layer has a catalyst loading of $0.1 - 500 \text{ mg cm}^{-2}$, in particular $1 - 250 \text{ mg cm}^{-2}$, for example $2 - 10 \text{ mg cm}^{-2}$.

16. The electrode as claimed in any of the preceding claims, wherein

the transition metal chalcogenide substantially conforms to the empirical formula $\text{MX}, \text{MX}_2, \text{M}_2\text{X}_3, \text{M}_2\text{X}_4, \text{M}_3\text{X}_4, \text{M}_9\text{X}_8, \text{M}''_6\text{M}_k\text{X}_m\text{X}'_n$,

wherein M represents one or more metals selected from the transition metals of the 4th, 5th or 6th period and

M'' is selected from alkali and alkaline earth metals,

wherein X represents S, Se and Te and

X' represents a halide and

k, m and n represent decimal numbers, wherein $24 \leq k \leq 25$ and $26 \leq m \leq 28$ and $0 \leq n \leq 1$.

17. The electrode as claimed in the preceding claim, wherein

the transition metal chalcogenide substantially conforms to the empirical formula $\text{M}_2\text{X}_4, \text{M}_9\text{X}_8$ or $\text{M}''_6\text{M}_k\text{X}_m\text{X}'_n$ and M is selected from a transition metal of the 4th period of groups 4 to 10, and in particular represents one, two or three of the metals Fe, Co and Ni or comprises at least one or more of these metals.

18. The electrode as claimed in either of the two preceding claims, wherein

the transition metal chalcogenide conforms to formula M_9X_8 and is at least partially present crystallized in the pentlandite structure and is in particular a compound of formula $\text{Fe}_{9-a-b-c}\text{Ni}_a\text{Co}_b\text{M}'_c\text{S}_{8-d}\text{Se}_d$, wherein

- M' is a transition metal of the 4th, 5th or 6th period and is in particular selected from one or more metals of the group consisting of Ag, Cu, Zn, Cr, Nb,
- a is a number from 0 to 7, in particular from 1 to 6
- b is a number from 0 to 9, in particular from 0 to 8
- c is a number from 0 to 2, in particular from 0 to 1
- d is a number from 0 to 6, in particular from 0 to 4
- wherein the sum of $a+b+c$ is a number from 0 to 9, in particular from 3 to 7.

19. The electrode as claimed in any of the preceding claims, wherein

the carrier material is selected from metals, carbon, ceramic materials, polymers and composite materials.

20. The electrode as claimed in any of the preceding claims, wherein

the carrier material is sheetlike and selected from fabric layers, felts, meshes, membranes and films.

21. The electrode as claimed in any of the preceding claims, wherein

the catalyst layer has an external surface area of at least 0.2 cm^2 , in particular at least 1 cm^2 , preferably 1 cm^2 to 4 m^2 .

22. An electrochemical cell for electrocatalytic hydrogenation of organic compounds comprising a reactor containing a cathode, an anode and an electrolyte, wherein the reactor contains a reducible organic compound in liquid form or at least

partially in dissolved form and wherein the reducible organic compound is hydrogenated at the cathode,

wherein

the cathode comprises or consists of a transition metal chalcogenide as catalyst, wherein the transition metal chalcogenide is selected from sulfides, selenides and tellurides, and in particular is an electrode as claimed in any of claims 9 to 19 and wherein

the electrochemical cell is not configured to produce a gas.

23. The use of a transition metal chalcogenide as catalyst for the electrocatalytic hydrogenation of organic compounds, in particular a transition metal chalcogenide selected from compounds substantially conforming to empirical formula MX , MX_2 , M_2X_3 , M_2X_4 , M_3X_4 , M_9X_8 or $M''_6M_kX_lX'_m$, for example a pentlandite,

wherein M represents one or more metals selected from the transition metals of the 4th, 5th or 6th period and

M'' is selected from alkali and alkaline earth metals,

wherein X represents S, Se and Te and

X' represents a halide and

k, m and n represent decimal numbers, wherein $24 \leq k \leq 25$, $26 \leq m \leq 28$ and $0 \leq n \leq 1$.

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Fig. 1

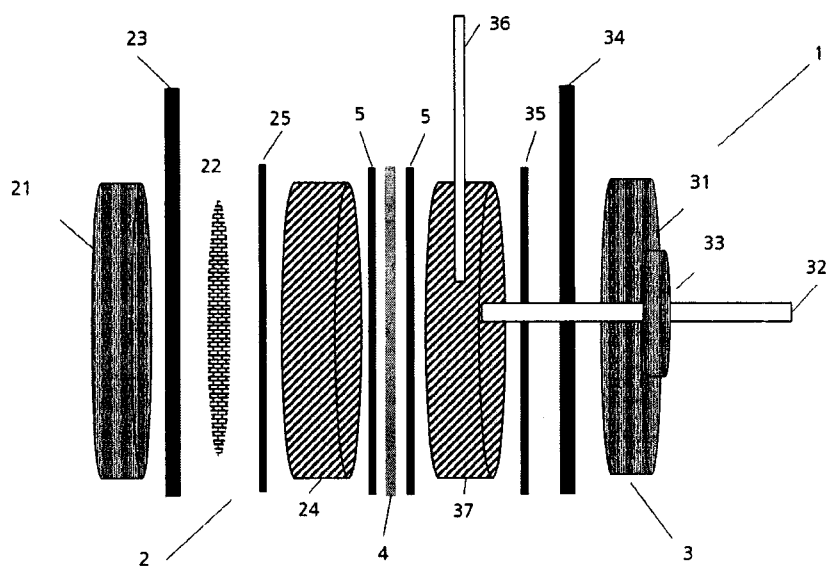
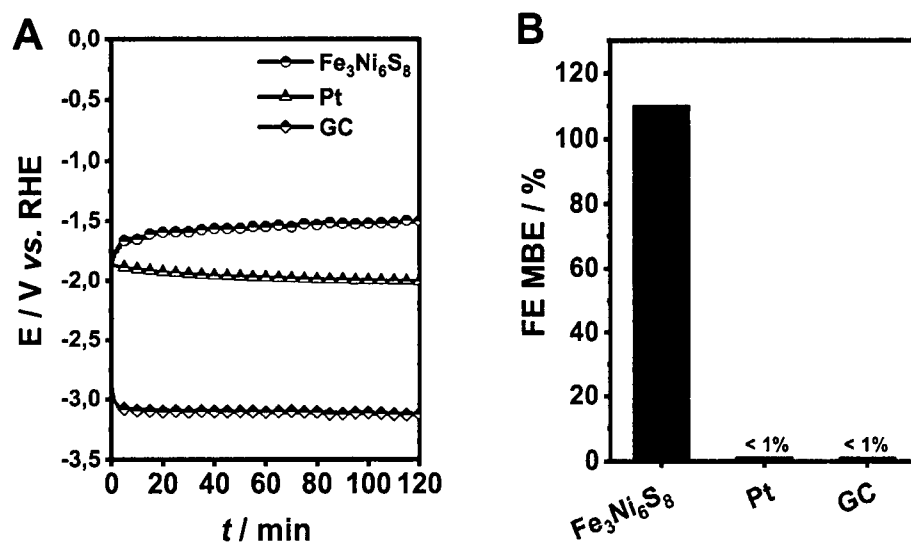


Fig. 2



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Fig. 3

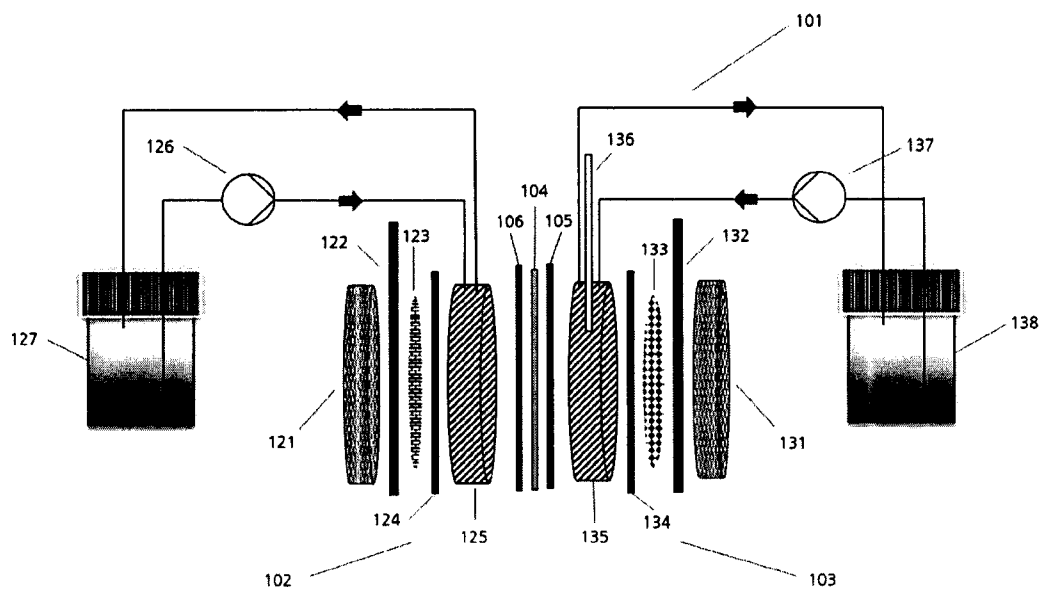
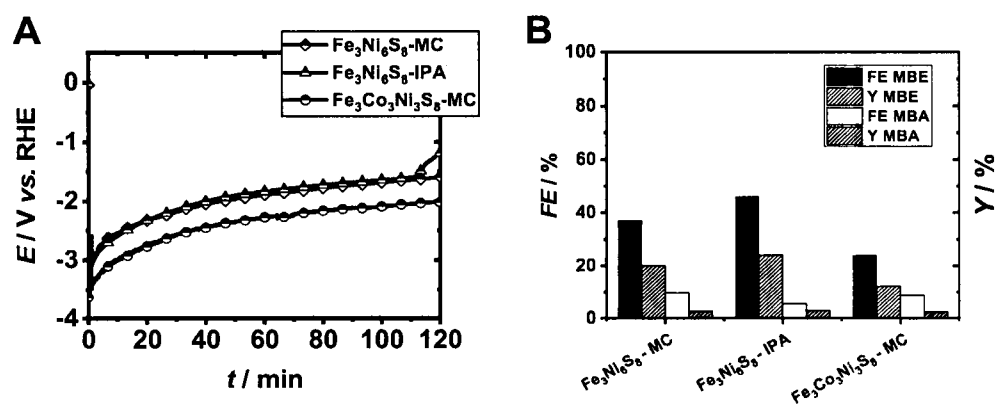


Fig. 4



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Fig. 5

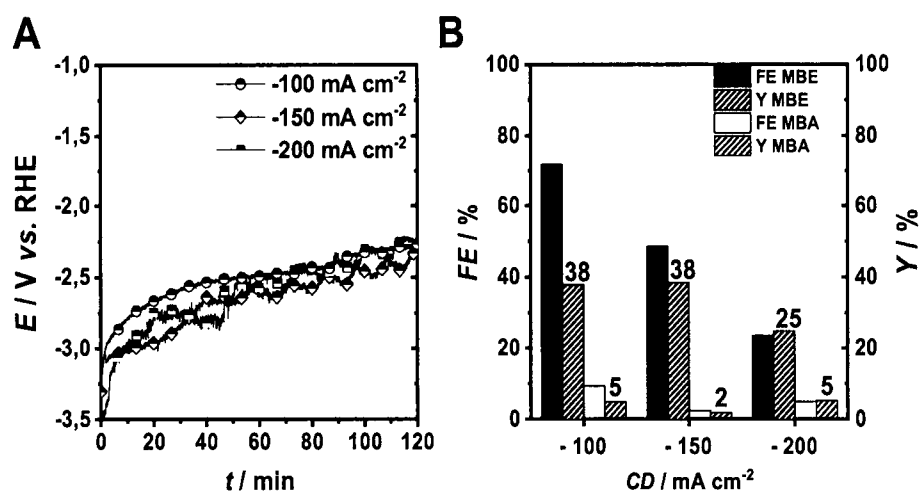
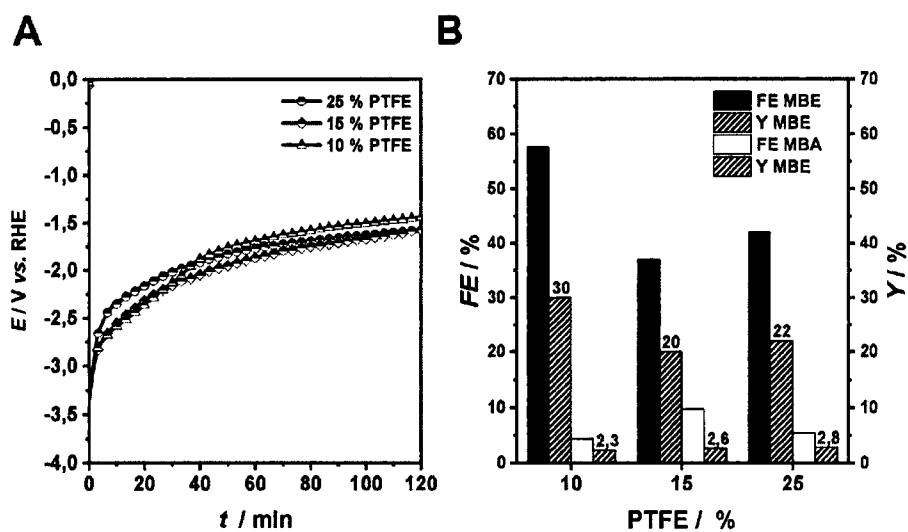


Fig. 6



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Fig. 7

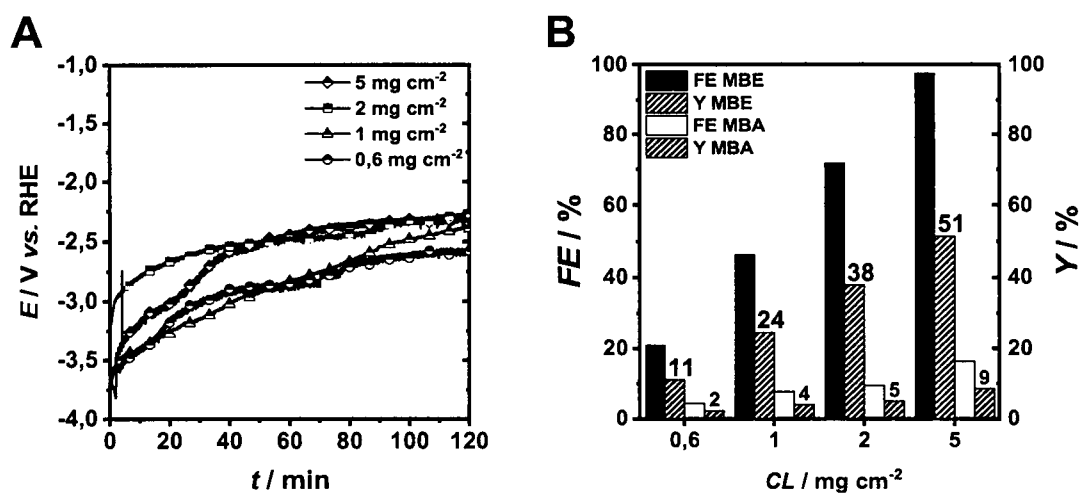
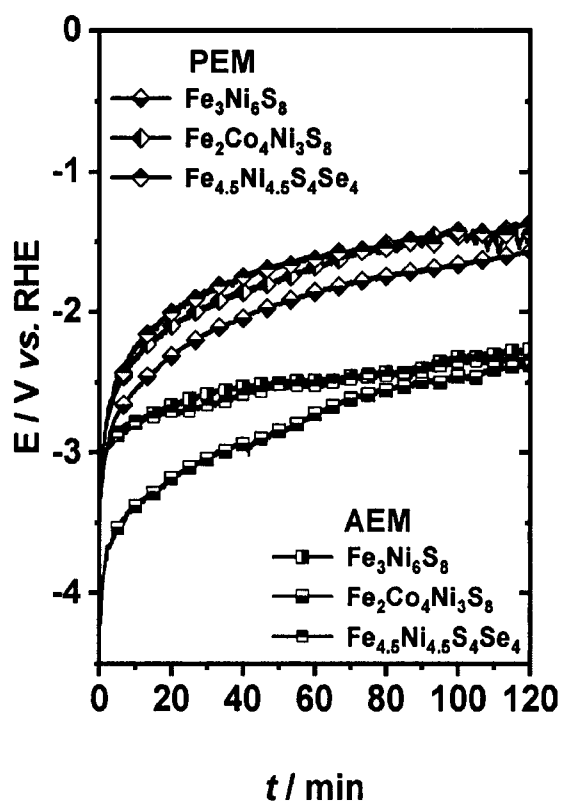


Fig. 8A



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Fig. 8B

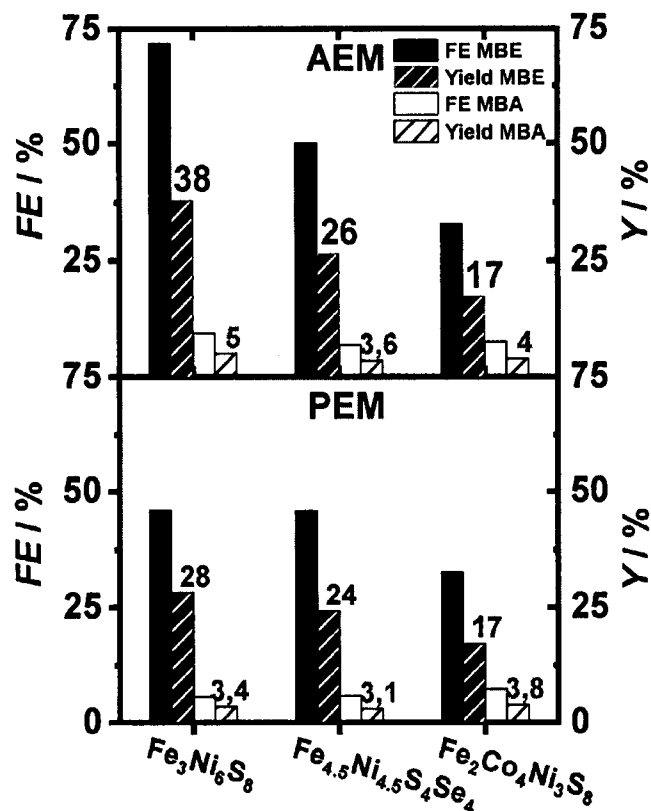
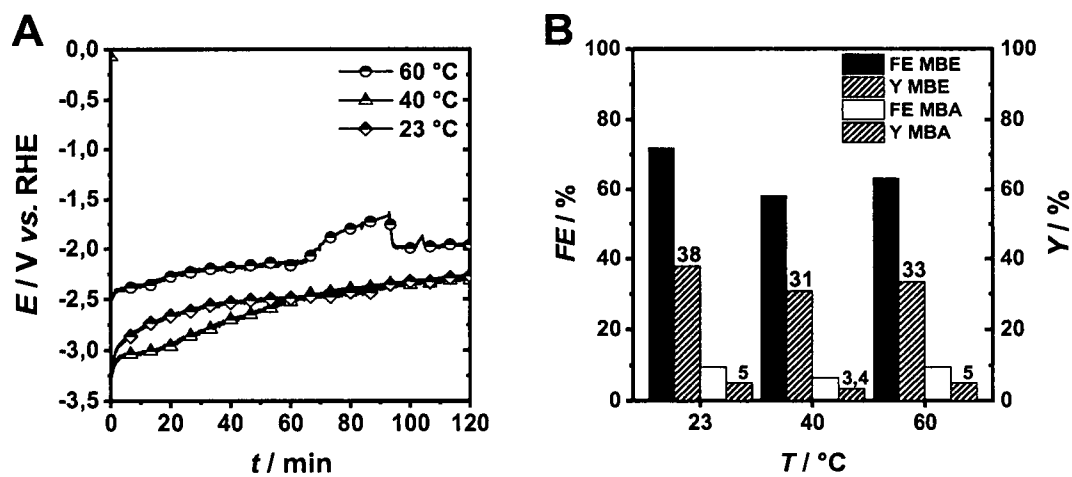


Fig. 9



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Fig. 10

