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(54) Title: ELECTROLYTE MEMBRANE WITH SELECTIVE ION TRANSPORT PROPERTIES AND A REDOX FLOW BATTERY COMPRISING AN ELECTROLYTE MEMBRANE

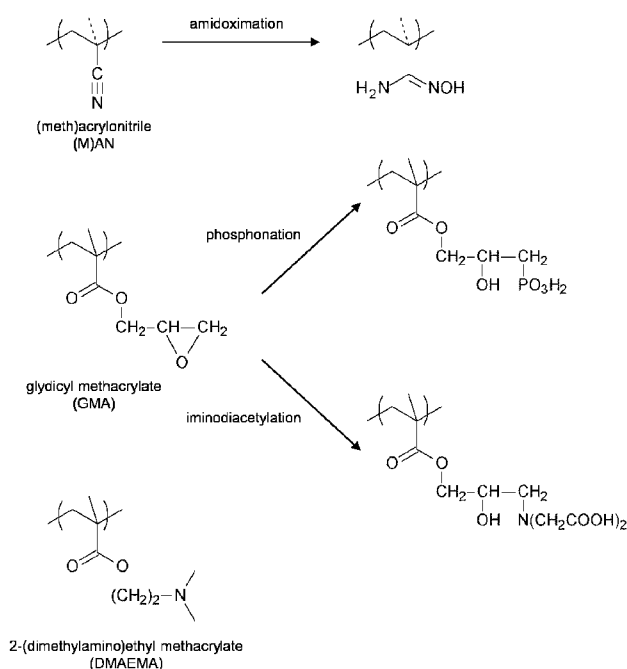


Fig. 5

(57) Abstract: It is the objective of the present invention to provide a membrane with high ion selectivity, high physico-chemical stability and low cost is of vital importance. This objective is achieved according to the present invention by an ion exchange membrane with selective ion transport properties, in particular for use in a redox flow battery, comprising: a) a mechanically robust and chemically resistant base polymer film (matrix); b) ion exchange groups covalently bound to the polymer matrix, being anion exchange groups or cation exchange groups or a mixture thereof; c) blocking groups covalently bound to the polymer matrix preventing the passage of redox-active species across the membrane; and d) optionally additional functional constituents, such as crosslinkers or antioxidants; Therefore, this membrane has a high ion selectivity, high physicochemical stability and low cost due to the selection of a base polymer film and the ion exchange groups as well as the blocking groups preventing the passage of redox-active species across the membrane. Preferably, the membrane is produced via radiation induced grafting, comprising the steps of: a) exposing the base polymer to ionizing radiation to introduce active sites; b) exposing the irradiated base polymer to a mixture of monomers comprising i) a monomer containing an ion exchange group or a precursor monomer yielding an ion exchange group in a subsequent step, ii) a monomer containing a functional group to block the passage of redox-active species through the membrane or a precursor monomer yielding the functional blocking group in a subsequent reaction step; iii) optional additional monomers, such as a crosslinker and

antioxidant; and c) in case of the use of precursor monomers for ion exchange sites and blocking groups, post-treatment of the grafted film to introduce ion exchange sites and/or blocking groups is performed.



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Electrolyte membrane with selective ion transport properties and a redox flow battery comprising an electrolyte membrane

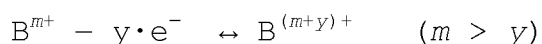
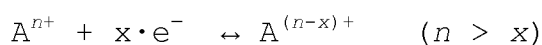
5 The present invention describes an improved electrolyte membrane, in particular for redox flow batteries (RFBs).

Redox flow batteries consist of two electrolyte solutions on the positive and negative electrode, separated by an ion exchange membrane. The electrolyte solutions contain redox couples,
10 typically charged species (ions), which allows the storage of electrical energy (during charging) and the generation of electrical energy (during discharge). The ion exchange membrane is required to allow the passage of desired ions and prevent the passage for ions involved in the energy storage as well as
15 solvent. Moreover, the membrane ought to be of low cost, mechanically robust, and stable in the respective chemical environment.

Redox flow batteries, originally developed in the 1970s, are being
20 considered as energy storage devices in the context of buffering supply and demand of electricity on various capacity levels, ranging from small units designed for single family homes up to units installed for grid-level electricity storage. The general assets of redox flow cells are high energy conversion efficiency,
25 flexible design, high energy storage capacity, flexible location, deep discharge capability, and low maintenance cost compared with other energy storage technologies.

A redox flow battery uses two soluble redox couples as
30 electroactive materials to store energy via oxidation and reduction reactions. In a typical set-up, the redox flow battery consists of 2 electrolyte reservoirs from which the electrolytes are circulated by pumps through an electrochemical reactor, consisting of a cell stack comprising a number of cells connected
35 in series or parallel to enable reaction taking place at inert electrodes (Figure 1). Figure 1 shows schematically a representation of a redox flow battery (RFB), comprising an ion-

exchange polymer as electrolyte membrane. Typically, each cell comprises of negative electrode, positive electrode and an ion exchange membrane separator to allow diffusion of ions across the membrane while preventing the cross-mixing of the electrolyte solutions from these 2 reservoirs. The electrolytes contain redox-active species which can change their oxidation state reversibly upon charge and discharge. These active species are commonly multivalent ionic species, such as transition metal ions. The type of redox couple used in the electrolyte and the concentration of the species in their different respective oxidation states determine the electrochemical potential on the particular electrode. The potential difference between the negative and positive electrode, which is achieved by choice of different redox couples on the two sides, determines the electromotive force or voltage of the cell. The voltage of the cell is therefore specific to the chemical species involved in the reactions. The general reactions can be written as



for the negative and positive electrode, respectively, where charge = $\rightarrow$ and discharge = $\leftarrow$. Examples of flow battery chemistries are the iron/chromium cell with Cr^{2+}/Cr^{3+} ($E^{\circ} = -0.41$ V vs. SHE) on the negative electrode and Fe^{2+}/Fe^{3+} on the positive electrode ($E^{\circ} = 0.77$ V vs. SHE), the bromine/polysulfide cell with S_2^{2-}/S_4^{2-} ($E^{\circ} = -0.27$ V vs. SHE) on the negative electrode and Br^{-}/Br_3^{-} on the positive electrode ($E^{\circ} = 1.09$ V vs. SHE), and the all-vanadium cell with V^{2+}/V^{3+} ($E^{\circ} = -0.26$ V vs. SHE) on the negative electrode and VO^{2+}/VO_2^{+} on the positive electrode ($E^{\circ} = 1.00$ V vs. SHE).

The energy capacity of the redox flow battery is fully independent of its power, because the energy available is related to the electrolyte volume (amount of liquid electrolyte) and the power to the surface area of the electrodes.

In addition, the flow battery unit includes balance-of-plant components, such as pumps, tubing, power electronics, etc., to constitute an independent system. The repetitive unit of the stack of cells is made up of a polymer electrolyte, typically a cation or anion exchange membrane, which is sandwiched between flow field plates, through which the electrolyte solutions are pumped. As electrodes, porous carbon fibre structures are used.

The primary function of the electrolyte membrane is to provide pathways for ion conduction to ensure charge balance between positive and negative electrode. However, the passage of redox-active species, such as the transition metal ions, is not desired, as this leads to a cross-contamination of the electrolytes and a decrease in faradaic efficiency of the cell. The positive and negative electrolytes contain a common ion, for instance through the presence of supporting electrolyte, whose transport through the electrolyte is desired to ensure charge balance. Typically, the electrolytes used are aqueous solutions of redox couples, for instance V^{3+}/V^{4+} and VO^{2+}/VO_2^{+} (see above), and a strong acid, such as sulfuric acid, hydrochloric acid, methanesulfonic acid, etc., or combinations thereof, is used as a background electrolyte. In this case, the membrane should allow the passage of H^{+} or (bi)sulfate anions (either cation or anion exchange membrane) and prevent the crossover of vanadium species.

As electrolyte membrane, typically dense ion exchange membranes are used, cation exchange membranes or anion exchange membranes. The resistance of the membrane should be as low as possible to minimize ohmic losses, concurrently the membrane should have a low permeability for the redox-active species. Moreover, the membrane should be mechanically robust, chemically stable in the respective electrolyte solution, and be of low cost. In case of the use of cation redox couples in the electrolytes, the use of an anion exchange membrane suggests itself. However, with the high concentration of electrolytes commonly used in redox flow batteries on the order of mol/L, the Donnan exclusion of co-ions breaks down, thus leading to significant cation transfer through

the membrane. Moreover, the chemical stability of anion exchange membranes is often insufficient. Cation exchange membranes are therefore more widely used. A typical and common cation exchange membrane is Nafion®, which is a perfluoroalkylsulfonic acid ionomer. Nafion® membranes are very widely used in RFBs, despite its high cost and high permeability for transition metal ions and water.

Therefore, it is the objective of the present invention to provide a membrane with high ion selectivity, high physicochemical stability and low cost which is of vital importance, too.

This objective is achieved according to the present invention by an ion exchange membrane with selective ion transport properties, in particular for use in a redox flow battery, comprising:

- a) a mechanically robust and chemically resistant base polymer film (matrix);
- b) ion exchange groups covalently bound to the polymer matrix, being anion exchange groups or cation exchange groups or a mixture thereof;
- c) blocking groups covalently bound to the polymer matrix preventing the passage of redox-active species across the membrane; and
- d) optionally additional functional constituents, such as crosslinkers or antioxidants;

Therefore, this membrane has a high ion selectivity, high physicochemical stability and low cost due to the selection of a base polymer film and the ion exchange groups as well as the blocking groups preventing the passage of redox-active species across the membrane.

Preferably, the membrane is produced via radiation induced grafting, comprising the steps of:

- a) exposing the base polymer to ionizing radiation to introduce active sites;

b) exposing the irradiated base polymer to a mixture of monomers comprising i) a monomer containing an ion exchange group or a precursor monomer yielding an ion exchange group in a subsequent step, ii) a monomer containing a functional group to block the passage of redox-active species through the membrane or a precursor monomer yielding the functional blocking group in a subsequent reaction step; iii) optional additional monomers, such as a crosslinker and antioxidant; and
c) in case of the use of precursor monomers for ion exchange sites and/or blocking groups, post-treatment of the grafted film to introduce ion exchange sites and/or blocking groups.

With respect to chemical stability, cost and ion conductivity, the base polymer can be a dense or porous fluoropolymer, such as ethylene-tetrafluoroethylene (ETFE), polyvinylidene fluoride (PVDF), ethylene-chlorotrifluoroethylene (ECTFE), or copolymers comprising the monomers vinylidene fluoride (VDF), hexafluoropropylene (HFP), chlorotrifluoroethylene (CTFE), trifluoroethylene (TrFE), or a polyolefin, such as polyethylene (PE) or polypropylene (PP).

For the pre-treatment prior to the grafting, the ionizing radiation can be an electron beam with energy above 100 keV.

Preferably, the monomer used as a precursor monomer to yield ion exchange sites is styrene, α -methylstyrene, α -fluorostyrene, α,β,β -trifluorostyrene, pentafluorostyrene, vinylbenzylchloride, 1-vinylimidazole, 2-vinylpyridine, 4-vinylpyridine, or glycidylmethacrylate.

Alternatively, the monomer already contains the ion exchange site, such as styrene sulfonate, vinylsulfonate, 2-Acrylamido-2-methylpropane sulfonate, or diallyldimethylammonium halide.

Further, the monomer used as a precursor monomer to yield blocking sites is acrylonitrile, methacrylonitrile, 2-vinylpyridine, 4-vinylpyridine, N-vinylformamide, or glycidylmethacrylate.

Alternatively, the blocking groups are introduced directly with a suitable comonomer, such as acrylamide, methacrylamide, glycidyl methacrylate, or 2-(dimethylamino)ethyl methacrylate.

- 5 Advantageously, the ion exchange site is a sulfonic acid group, introduced to the styrenic grafted monomer units via sulfonation followed by hydrolysis.

- 10 Alternatively, the ion exchange site is a cationic group, such as a quaternary ammonium group, introduced to the vinylbenzyl chloride grafted monomer units via quaternization, a pyridinium or imidazolium group, created by N-alkylation of the grafted pyridine or imidazole groups, respectively.

- 15 A further preferred embodiment of the present invention may provide blocking sites that are created by amidoximation of acrylonitrile or methacrylonitrile units in the grafted chains via the reaction with hydroxylamine. Another option may provide the blocking sites being created by amination of glycidyl methacrylate
20 units in the grafted chains. Alternatively, the blocking sites may be also created by the reaction of glycidyl methacrylate units in the grafted chains with iminodiacetate, phosphoric acid, L-amino acid, trialkylamine, or iminodipropionitrile followed by amidoximation using hydroxylamine. Yet another option to introduce
25 blocking sites may be to use 2-(dimethylamino)ethyl methacrylate as comonomer, which, after being incorporated into the grafted chain, already contains the blocking functionality and does not need to undergo further modification.

- 30 A superior redox flow battery is achieved according to the present invention by a redox flow battery comprising a membrane according to any of the claims 1 to 11 is used as a membrane electrolyte. Preferred redox flow batteries can be achieved when the negative electrolyte solution consists of an aqueous solution of sulfuric
35 acid as background electrolyte and V^{2+}/V^{3+} as redox-active species, and wherein the positive electrolyte solution consists of an aqueous solution of sulfuric acid as background electrolyte and

$\text{VO}^{2+}/\text{VO}_2^+$ as redox-active species. The membrane as claimed by the present invention therefore has the advantage over the prior art that the membrane shows less crossover of redox-active species than a comparable membrane without blocking groups.

5

Preferred examples of the present invention are discussed hereinafter in detail with reference to the attached drawings which depict in:

10 Figure 1 schematically a representation of a redox flow battery (RFB), comprising an ion-exchange polymer as electrolyte membrane;

15 Figure 2 a sketch of the primary target of the present invention in terms of conductivity and blocking of the redox active components to cross the membrane;

20 Figure 3 a schematic structure of the graft copolymer consisting of the inert base polymer and grafted functional units;

Figure 4 a schematic representation of the structure of the ionogenic group;

25 Figure 5 a schematic representation of the preferred structure of the blocking groups for redox-active transition-metal ion species;

Figure 6 polarization curves of the redox flow cell measured in discharge mode;

30 Figure 7 self-discharge curves in the all-vanadium redox flow cell; and

35 Table 1 an overview of the properties of the different membranes of Examples 1-2 and Comparative Examples 1-3.

In the present invention, a potential low cost electrolyte membrane with improved barrier properties for redox-active species and conductivity comparable to that of Nafion® is disclosed. The polymer membrane comprises separate functional constituents to a) provide ionic charge carriers in the membrane and b) block the passage of redox-active species (Figure 2).

Figure 2 shows a sketch of the primary target of this invention: the electrolyte membrane shows selective transport for supporting (non-redox-active) common anions or cations in the negative and positive electrolyte solution, respectively, and inhibits the passage of redox-active species.

This invention discloses a method to introduce these functionalities into a pre-existing inert polymer base film by means of radiation-induced grafting. Radiation grafting is a versatile and scalable technique to modify a polymer substrate by forming a graft copolymer to introduce desirable properties into the material. Irradiation of the base film by ionizing radiation (gamma, electrons) introduces active sites, from which in the subsequent grafting reactions polymer chains are grown from a monomer or mixture of monomers amenable to radical induced polymerization. The monomer mixture may be a liquid solution or gaseous mixture of monomers and diluent(s). Post treatment of the grafted film may be necessary to modify the grafted moieties to obtain the final desired functionalities.

One ionomer constituent embodies the ionogenic component, for instance a sulfonic acid group, which upon swelling of the ionomer in water yields mobile protons and a fixed sulfonate anion, or a quaternary ammonium group, which represents a fixed cation, while the counter-ion (HO^- , Cl^- , SO_4^{2-}) is mobile in the water-swollen polymer (Figure 3). The density of charged sites determines the ion exchange capacity, which itselfs determines the conductivity of the ionomer.

Another ionomer constituent embodies a moiety that develops a strong interaction with one or several of the redox-active species in the electrolytes, for instance via complex formation (Figure 3). It is conceivable that the membrane may contain several types of blocking units for the different redox active species in the two electrolytes.

Figure 3 shows a schematic structure of the graft copolymer consisting of the inert base polymer and grafted functional units. R and R', respectively, is an alkyl or aryl organic rest or a combination thereof. X^+ and Y^- are ionic groups fixed on the grafts (e.g., $-SO_3^-$), C^- and D^+ the corresponding mobile ions (e.g., H^+). Z is a functional group blocking the passage of redox-active species M^{n+} . n and m are molar fractions of respective monomer units in the grafts and vary between 10 and 90 %.

It is a key feature of the presented invention that the presence of the blocking units significantly increases the selectivity of ion transport in the membrane by reducing the crossover of redox-active species while the total conductivity is not or only insignificantly affected. In other words, the figure of merit of the membrane, defined as conductivity x selectivity, is enhanced in the presence of the blocking groups compared to the case where these are absent at an identical content of ionogenic units. The selectivity here describes the flux of non-redox-active species with respect to the total flux of ions through the membrane.

The electrolyte membrane may contain further constituents for specific purposes, such as crosslinker or antioxidants.

The present invention will now be described in detail with reference to a few preferred embodiments thereof. In the following description, numerous specific details are set forth in order to provide a thorough understanding of the present invention. It will be apparent, however, to one skilled in the art, that the present invention may be practiced without some or all of these specific details.

The electrolyte membrane described herein contains ion exchange groups, which upon swelling in water, will yield a mobile ion and a fixed counter-ion. This ionogenic group may be an acidic group, such as carboxylic acid, sulfonic acid (Figure 4), or phosphonic acid, which upon hydration yields mobile protons and fixed anions. In a preferred embodiment, the ionogenic group is a sulfonic acid group. Alternatively, the ionogenic group may be an acid salt, with the proton replaced by a metal ion, such as alkali metal ions. In another embodiment, the ionogenic group may be a cation exchange group, such as a quaternary ammonium, pyridinium, sulfonium, phosphonium, imidazolium, and guanidinium, with corresponding mobile anions, such as halide, (hydrogen)carbonate, (hydrogen)sulfate, and ((di)hydrogen)phosphate.

Figure 4 shows a schematic representation of the structure of the ionogenic group, which in the preferred embodiment is a sulfonic acid group.

The content of fixed ionic species in the membrane governs the water uptake of the membrane when immersed in water or an electrolyte solution and the resulting ionic conductivity of the material. As an essential ingredient, the polymer electrolyte membrane incorporates functionalities that block the passage of the redox-active species present in the positive and/or negative electrolyte solution. In the embodiment described here, the blocking sites are functional groups forming a complex with redox-active species (chelating agent) by coordination interaction or sometimes ionic interaction. The binding of the redox-active species by the polymer thus significantly reduces their crossover through the membrane. The most common coordinating atoms present in the chelating groups are nitrogen, oxygen, phosphorus and sulfur. In a preferred embodiment, the redox-active species are transition metal ions. Examples of chelating groups are amidoxime, which is selective towards Cu^{2+} , Ru^{6+} , Au^{3+} , Rh^{3+} , V^{4+} , Pd^{2+} , U^{6+} , Pt^{2+} , Fe^{3+} , Mo^{6+} , Ni^{2+} , Co^{2+} , Zn^{2+} and Mn^{2+} , iminodiacetate, which is selective towards Hg^{+} , Cu^{2+} , UO_2^{2+} , Pb^{2+} , Fe^{3+} , Cr^{3+} , Ni^{2+} , Zn^{2+} , Co^{2+} ,

Fe²⁺ and Mn²⁺, aminophosphonic acid, which is selective towards U⁴⁺, UO₂²⁺, Fe³⁺, Zn²⁺, Cu²⁺, Ni²⁺, Co²⁺ and Mn²⁺, thiol, which is selective towards Cu⁺, Pb²⁺, Zn²⁺, Ni²⁺ and Fe³⁺, N-bis-picolylamine, which is selective towards Ni²⁺ and Co²⁺. Examples of blocking groups are
5 given in Figure 5.

In the invention disclosed herein, these functional groups are introduced into a pre-existing yet inert polymer film by radiation induced graft copolymerization of suitable monomers amenable to
10 radical polymerization and, if necessary, suitable post-treatments to obtain the final functionalized and ion-conducting membrane. The radiation-grafted membrane may be prepared from a variety of base polymer films including fluoropolymers, such as PTFE, FEP, PFA, ETFE, PVDF, PVF, PCTFE, ECTFE, or polyolefins such as PE, PP
15 and their copolymers, or polyamides, or polyesters. In a preferred embodiment, the base polymer film is a partially fluorinated polymer, such as ETFE, PVDF, or ECTFE or copolymers derived from these.

Figure 5 shows a schematic representation of the preferred
20 structure of the blocking groups for redox-active transition-metal ion species, which are obtained either after post-functionalization of a suitable precursor monomer, such as in the case of (meth)acrylonitrile and glycidyl methacrylate, or directly
25 through grafting of a monomer that already carries the functional group, such as in the case of 2-(dimethylamino)ethyl methacrylate.

Activation of the film is performed using ionizing radiation, such as gamma, hard x-rays, or electron beam. The film may be pre-
30 irradiated or simultaneously radiated when the base polymer is exposed to the monomer mixture. In case of the pre-irradiation method, the irradiated substrate may be stored at reduced temperature and/or under inert atmosphere if the reactive sites are unstable. In a preferred embodiment, the base film is
35 irradiated in air with a high energy (>100 keV) electron beam in air.

The physical form of the monomer for grafting may be as a gas or a liquid, and the monomer may be either pure or diluted with a solvent or inert material and/or as a mixture with one or more additional monomers. Any radically active monomer may be used including vinyl, styrenic or acrylic monomers. Monomers can be selected according to the properties that are desired for the membranes. To introduce ion exchange groups, monomers having acidic, basic, salt or amphoteric functionality or their precursors may be selected. Non-limiting examples of monomers having acidic, basic, salt, or amphoteric functionality include vinyl phosphonic acid, vinyl sulfonic acid, 2-acrylamido-2-methylpropane sulfonic acid, sodium styrene sulfonate, N-vinyl-2-pyrrolidone, 4-vinyl pyridine. Monomers that can be used as precursors for the introduction of acidic, basic, and amphoteric groups may also be used. Non-limiting examples include styrenic monomers such as styrene, α -methylstyrene, α,β,β -trifluorostyrene, α -fluorostyrene, and vinylbenzyl chloride and their derivatives. The grafted polystyrenic chains derivatized in a subsequent step using methods known in the art to yield acidic, basic, or amphoteric functionalities in the membrane. For example, anion-exchange groups can be introduced by means of subsequent amination followed by ion exchange with aqueous hydroxide, and cation exchange groups can be introduced by treating with strong acids such as chlorosulfonic or sulfuric acids or sulfur trioxide dissolved in halogenated solvents or gaseous sulfur trioxide. In a preferred embodiment, the monomer is styrene or α -methylstyrene, which after grafting is sulfonated in chlorosulfonic acid solution and subsequently hydrolyzed in water to obtain (α -methyl)-styrene-sulfonic acid grafts.

The blocking groups, in the preferred embodiment chelating groups, are introduced via co-grafting of a suitable monomer with the primary ionomer yielding ionogenic groups. This monomer may yield the chelating group directly or after post-treatment. Examples of co-monomers are glycidyl methacrylate, (meth)acrylic acid, (meth)acrylamide, (meth)acrylonitrile, N-vinylpyrrolidone, 4-vinylpyridine, N-vinylformamide, and vinylbenzylchloride. Examples

of post-treatment are amination, amidoximation, treatment with disodium iminodiacetate, quaternization, phosphonation, alkaline hydrolysis, and phosphonation. In a preferred embodiment, the co-

5 amidoximation with hydroxylamine.

The ratio of the monomers, the ionogenic monomer and the blocking co-monomer, in the reaction mixture is adapted to adjust the ratio of the grafted monomer units in the graft copolymer according to

10 the specific copolymerization behavior or the two monomers, which is governed by the radical copolymerization kinetics of the two monomers chosen according to the theory of Mayo and Lewis. Therefore, the tuning of the fraction of ionogenic monomer units and blocking monomer units in the grafts is quite sensitive in

15 order to achieved both the desired ion conductivity and the desired blocking.

In a preferred embodiment, styrene is co-grafted with acrylonitrile at a molar ratio of 2:3, which yields a molar

20 fraction of styrene and acrylonitrile in the grafts of around 0.5, respectively. Through the choice of the ratio of ionogenic monomer units and blocking monomer units in the grafted chain, the transport properties of background (redox-inactive) species and redox-active species can be tuned. In one extreme case, only

25 ionogenic units are present in the grafts, thus the retention properties for redox-active species are not pronounced. In the other extreme case, the grafts contain only chelating monomer units. In this case, the ionic conductivity of the membrane is expected to be very low.

30 In addition to the monomers mentioned above, i.e. monomers that yield fixed ionic sites and monomers that provide binding sites for redox-active species, additional monomers may be included in the monomer mixture for specific purposes. For instance,

35 crosslinking monomers, such as divinyl benzene, bis(vinyl phenyl)ethane, diisopropenylbenzene, or diacrylates, can be used to modify the swelling or liquid crossover properties, or

stability and durability of such membranes. In addition, monomer units carrying antioxidants may be incorporated into the grafted chain to protect the polymer from oxidative attack.

5 Examples

The following Examples and Comparative Examples are provided for the purpose of further illustrating the present invention but are in no way to be taken as limiting.

10 Example 1

ETFE base film (DuPont Tefzel® 100LZ, 25 µm thickness) was irradiated in air using an MeV class electron beam facility with a dose of 5 kGy and subsequently stored at -80 °C. The grafting reaction was performed in glass reactors under nitrogen
15 atmosphere. The grafting reaction mixture was composed as follows: 20% (v/v) monomer solution (styrene/acrylonitrile at a volumetric ratio of 2/3) + 70% (v/v) iso-propanol + 10% (v/v) ultra-pure water. The ratio of styrene/acrylonitrile used corresponds to a molar fraction of styrene of 0.3 in the grafting solution, which
20 yields a molar fraction of styrene in the grafted film of around 0.4. Irradiated films of size 7 × 7 cm were introduced into the grafting solution. The glass reactor containing the grafting solution containing and the irradiated films was sparged with N₂ for 1 h. Then, the reactor was placed in a thermostatic water bath
25 held at 60°C for the duration of the grafting reaction. After removal of the films from the reactor, the grafted films were washed with acetone for 18 h and dried under vacuum at 80°C. The reaction time was adjusted such that a graft level, defined as the weight increase upon grafting with respect to the initial weight
30 of the base film, of around 40 % was obtained.

Amidoximation of the nitrile groups of the grafted acrylonitrile (AN) units was performed in a small glass reactor using 2 M solution of hydroxylamine hydrochloride in H₂O/EtOH (volumetric
35 ratio of H₂O/EtOH of 1:1). The pH value of the solution was adjusted to 7 by adding aqueous NaOH. Subsequently, the grafted films were introduced into the prepared solution and placed in a

thermostatic water bath at 70°C for 6 days. FTIR analysis of the samples indicated that, within the error of the measurement, the nitrile groups have completely reacted.

- 5 Sulfonation of the grafted and amidoximated films was carried out in a 2 L glass reactor using a 3 % solution of chlorosulfonic acid in dichloromethane. Grafted films were introduced into the solution and gas bubbles adhering to the film were removed with a glass rod. After stirring for 6 h at room temperature the
- 10 sulfonated films were removed from the reaction mixture, washed with ultra-pure water and hydrolyzed at 80°C in pure water for 16 h.

Example 2

- 15 Grafted films were prepared using styrene and acrylonitrile (AN) as monomers as described in Example 1. In this example, the grafted films were first sulfonated as described in Example 1, and then amidoximated. In contrast to Example 1, the amidoximation reaction was performed for 3 days, since the sulfonated membrane
- 20 swells in the presence of the amidoximation reagent, which facilitates the access of the hydroxylamine to the AN units. In this case, FTIR analysis of the obtained membranes indicated the presence of carbonyl groups, which is a result of partial hydrolysis of the nitrile units of AN to the respective carboxylic
- 25 acid during the sulfonation reaction. Therefore, the total amidoxime content of the membrane of Example 2 is lower than that of Example 1.

Comparative Example 1

- 30 The membrane of Comparative Example 1 is prepared according to the description of Example 2, except that the final amidoximation step is omitted. Therefore, the membrane does not contain any amidoxime groups, but carboxylic acid groups and residual nitrile groups.

35 Comparative Example 2

The membrane of Comparative Example 2 is prepared according to the procedure outlined above, yet without acrylonitrile in the

reaction mixture. Therefore, the membrane only contains grafted styrene, which is subsequently sulfonated to yield poly(styrenesulfonic acid) (PSSA) grafts. The graft level of the membrane is 40%.

5

Comparative Example 3

Nafion® 212 membrane is used as Comparative Example 3. The membrane was pretreated by immersion in water.

10 Membrane Characterization

The membranes were characterized for their key properties in the context of the application in redox flow batteries.

The ohmic resistance of a redox flow cell is largely influenced by the conductivity of the membrane in the respective electrolyte solution(s). Therefore, the ohmic resistance was measured in an assembled all-vanadium redox flow cell at room temperature comprising carbon felt electrodes and the respective membrane as polymer electrolyte. A redox flow test system (Model 857) by Scribner Associates was used to operate the cell. Both the negative and the positive electrolyte compartment were filled with an aqueous solution containing 1 M VOSO₄ and 2 M H₂SO₄. The cell was charged at a constant cell potential of 1.6 V until the current decreased below 4 mA/cm². The change of the state of charge in both electrolyte compartments was visible as a change in the color of the solutions. The ohmic area specific resistance R_{Ω} of the cell was then determined from the intercept of the impedance spectrum in Nyquist representation with the real axis at the high frequency end.

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The vanadium ion permeability at room temperature of prepared membranes was determined using self-made diffusion cells consisting of two round bottom flasks separated by the membrane. The left compartment was filled with a 1 M solution of VOSO₄ in 2 M H₂SO₄ while the right one was filled with 1 M solution of MgSO₄ in 2 M H₂SO₄. Solutions in both compartments were stirred in order to prevent concentration polarization at the membrane's surface. At

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regular time intervals the concentration of diffused VO^{2+} ions in the right compartment was measured using UV-Vis spectroscopy. The diffusivity of vanadium-ions $D(\text{V}^{4+})$ was then determined from the dimensions of the membrane and the concentration gradient of vanadium between the two compartments.

Based on the ohmic resistance R_{Ω} and the vanadium diffusivity $D(\text{V}^{4+})$, the figure of merit (FOM) from the membrane was calculated according to $1/(R_{\Omega} \cdot D)$, which indicates the suitability of a membrane material for application in a redox flow cell. The higher the number, the more suitable the membrane. An ideal membrane should have low ohmic resistance as well as low metal-ion diffusivity.

Table 1 shows key properties of membranes for redox flow applications, consisting of ohmic resistance R_{Ω} in the vanadium redox flow cell and the diffusivity of vanadium(IV) $D(\text{V}^{4+})$ across the membrane, which are combined to the figure of merit (FOM). The amidoxime content is the fraction of grafts with amidoxime groups, the balance is (sulfonated) styrene, in case of Example 2 a residual carboxylic acid groups are present as a result of partial hydrolysis of the nitrile groups during sulfonation. The FOM of membrane variations showing superior characteristics compared to Nafion 212 membrane (Comparative Example 3) are evident.

An overview of the properties of the different membranes of Examples 1-2 and Comparative Examples 1-3 are shown in Table 1. Comparative Example 3 (Nafion 212) serves as a benchmark. Examples 1 and 2 have the same graft level and composition of styrene / AN grafts. Example 1 has the higher content of amidoxime groups because the grafted film was first amidoximated and then sulfonated. In case of Example 2, the film was sulfonated first, which leads to hydrolysis of a fraction of the nitrile groups.

Therefore, after the subsequent amidoximation, the amidoxime content in the final membrane is lower than that of Example 1. The result shows that Example 1 with a higher amidoxime content has

better vanadium barrier properties. Comparative Example 1, which does not contain any amidoxime, shows an even higher vanadium crossover.

5 The polarization characteristics of the membranes of Examples 1 and 3, and Comparative Examples 1-3 were measured at room temperature in the redox flow single cell as described above (Figure 6). The current was increased stepwise and after 30 s the voltage of the cell was recorded. The initial state of charge of
10 the cell was 100%. Example 1, i.e., the membrane with the highest amidoxime content, showed a performance similar to that of Example 2, which had a lower amidoxime content, and superior to that of Comparative Example 3, which is Nafion 212. Comparative Example 1 and Comparative Example 2 showed significantly better performance
15 than the other tested membranes. Those membranes are styrene / acrylonitrile grafted and styrene-only grafted, respectively, and do not contain any amidoxime.

The vanadium crossover leads to slow self-discharge of the cell,
20 if the cell is initially fully charged and then set to open circuit voltage. The time to complete self-discharge is therefore a measure of the vanadium-ion permeability through the membrane. In Figure 7, the self-discharge experiment of Example 1 (grafted membrane with highest amidoxime content) and Comparative Example 3
25 (Nafion 212) is shown. The cell of Comparative Example 3 is discharge after around 19 h, whereas the cell of Example 1 is discharged after around 42.5 h. The ratio of these two values is almost identical to the ratio of the vanadium-ion diffusivities of these two samples.

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Claims

1. An ion exchange membrane with selective ion transport
5 properties, in particular for use in a redox flow battery,
comprising:
a) a mechanically robust and chemically resistant base polymer
film (matrix);
b) ion exchange groups covalently bound to the polymer matrix,
10 being anion exchange groups or cation exchange groups or a mixture
thereof;
c) blocking groups covalently bound to the polymer matrix
preventing the passage of redox-active species across the
membrane; and
15 d) optionally additional functional constituents, such as
crosslinkers or antioxidants;
2. The membrane according to claim 1, wherein the membrane is
produced via radiation induced grafting, comprising the steps of:
20 a) exposing the base polymer to ionizing radiation to introduce
active sites;
b) exposing the irradiated base polymer to a mixture of monomers
comprising i) a monomer containing an ion exchange group or a
precursor monomer yielding an ion exchange group in a subsequent
25 step, ii) a monomer containing a functional group to block the
passage of redox-active species through the membrane or a
precursor monomer yielding the functional blocking group in a
subsequent reaction step; iii) optional additional monomers, such
as a crosslinker and antioxidant; and
30 c) in case of the use of precursor monomers for ion exchange sites
and blocking groups, post-treatment of the grafted film to
introduce ion exchange sites and/or blocking groups is performed.
3. The membrane according to claim 1 or 2, wherein the base
35 polymer is a semi-crystalline fluoropolymer or polyolefin.

4. The membrane according to any of the preceding claims, wherein the ionizing radiation is an electron beam with energy >100 keV.

5. The membrane according to any of the preceding claims, wherein the monomer used as a precursor monomer to yield ion exchange sites is styrene, α -methylstyrene or vinylbenzylchloride.

6. The membrane according to any of the preceding claims, wherein the monomer used as a precursor monomer to yield blocking sites is acrylonitrile, methacrylonitrile, acrylamide, methacrylamide or glycidylmethacrylate.

7. The membrane according to any of the preceding claims, wherein the ion exchange site is a sulfonic acid group, introduced to the styrenic grafted monomer units via sulfonation followed by hydrolysis.

8. The membrane according to any of the preceding claims, wherein the ion exchange site is a quaternary ammonium group, introduced to the vinylbenzyl chloride grafted monomer units via quaternization.

9. The membrane according to any of the preceding claims, wherein the blocking sites are created by amidoximation of acrylonitrile or methacrylonitrile units in the grafted chains.

10. The membrane according to any of the preceding claims, wherein the blocking sites are created by amination of glycidyl methacrylate units in the grafted chains.

11. The membrane according to any of the preceding claims, wherein the blocking sites are created by the reaction of glycidyl methacrylate units in the grafted chains with iminodiacetate, phosphoric acid, L-amino acid, trialkylamine, or iminodipropionitrile followed by amidoximation.

12. A redox flow battery, wherein the membrane of any of the preceding claims is used as a membrane electrolyte.

13. The redox flow battery according to claim 11, wherein the negative electrolyte solution consists of an aqueous solution of sulfuric acid as background electrolyte and V^{2+}/V^{3+} as redox-active species, and wherein the positive electrolyte solution consists of an aqueous solution of sulfuric acid as background electrolyte and VO^{2+}/VO_2^+ as redox-active species.

14. The redox flow battery according to claim 11, wherein the membrane shows less crossover of redox-active species than a comparable membrane without blocking groups.

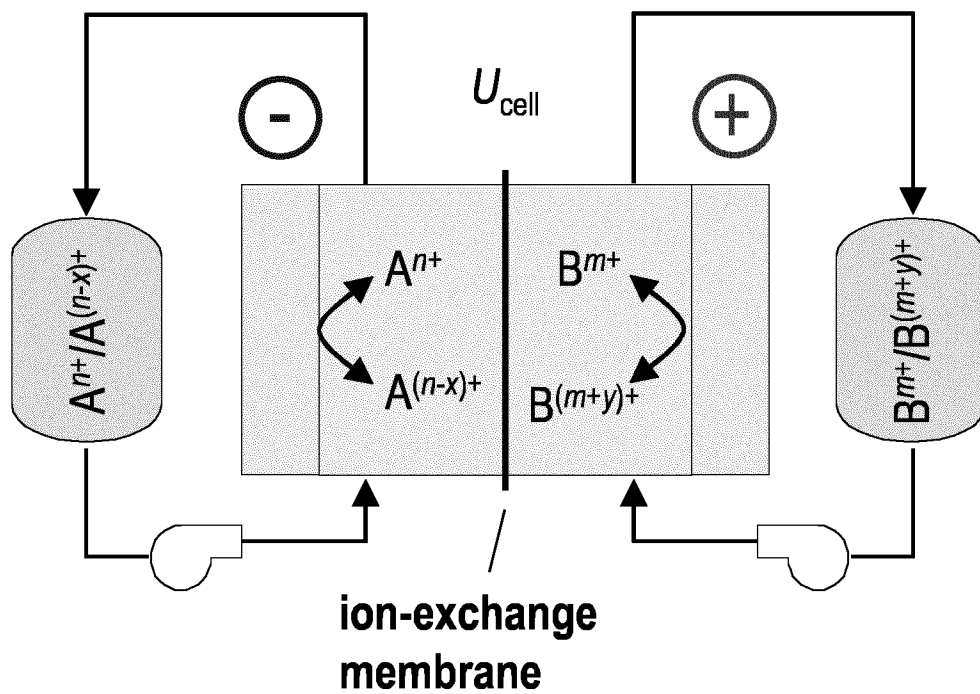


Fig. 1

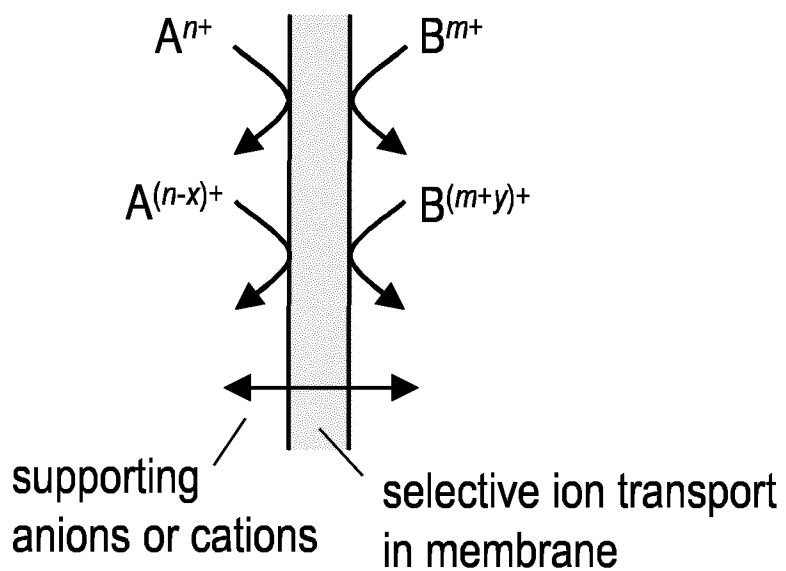


Fig. 2

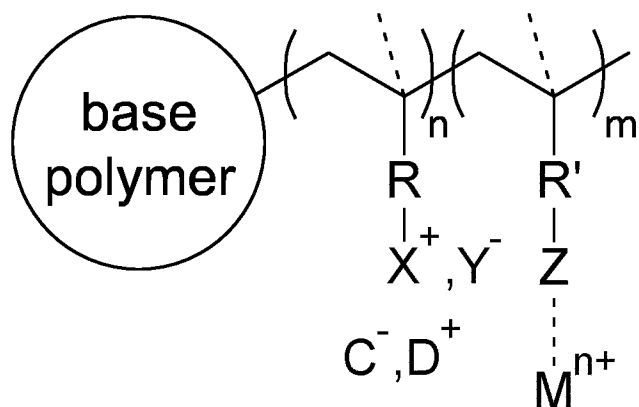


Fig. 3

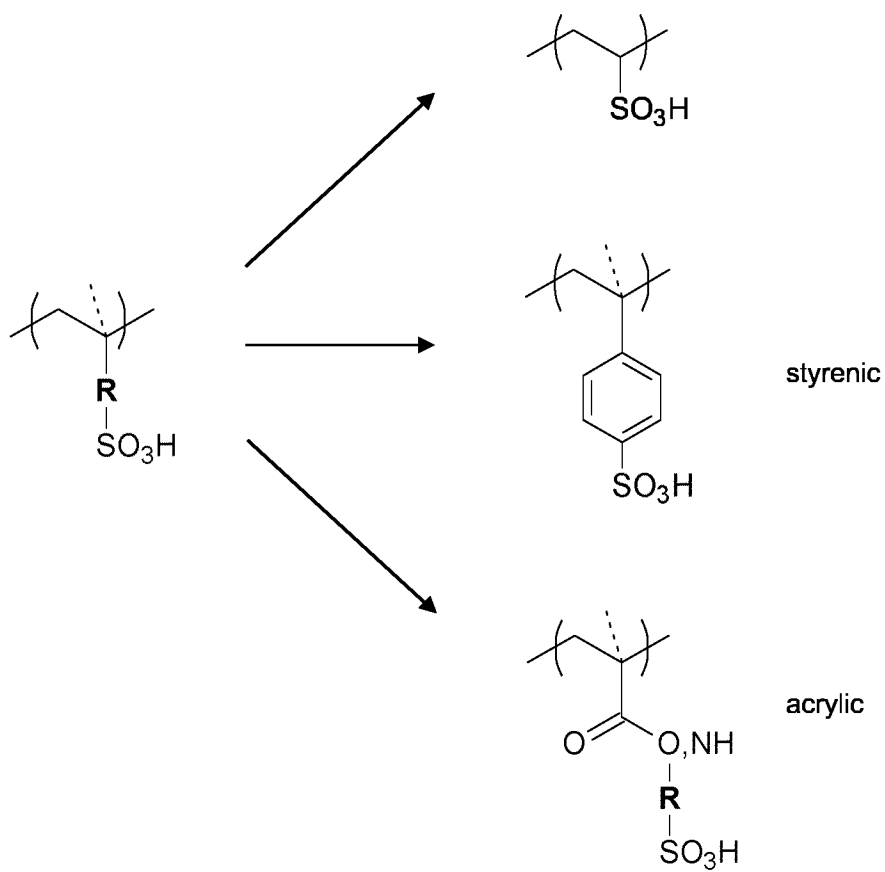


Fig. 4

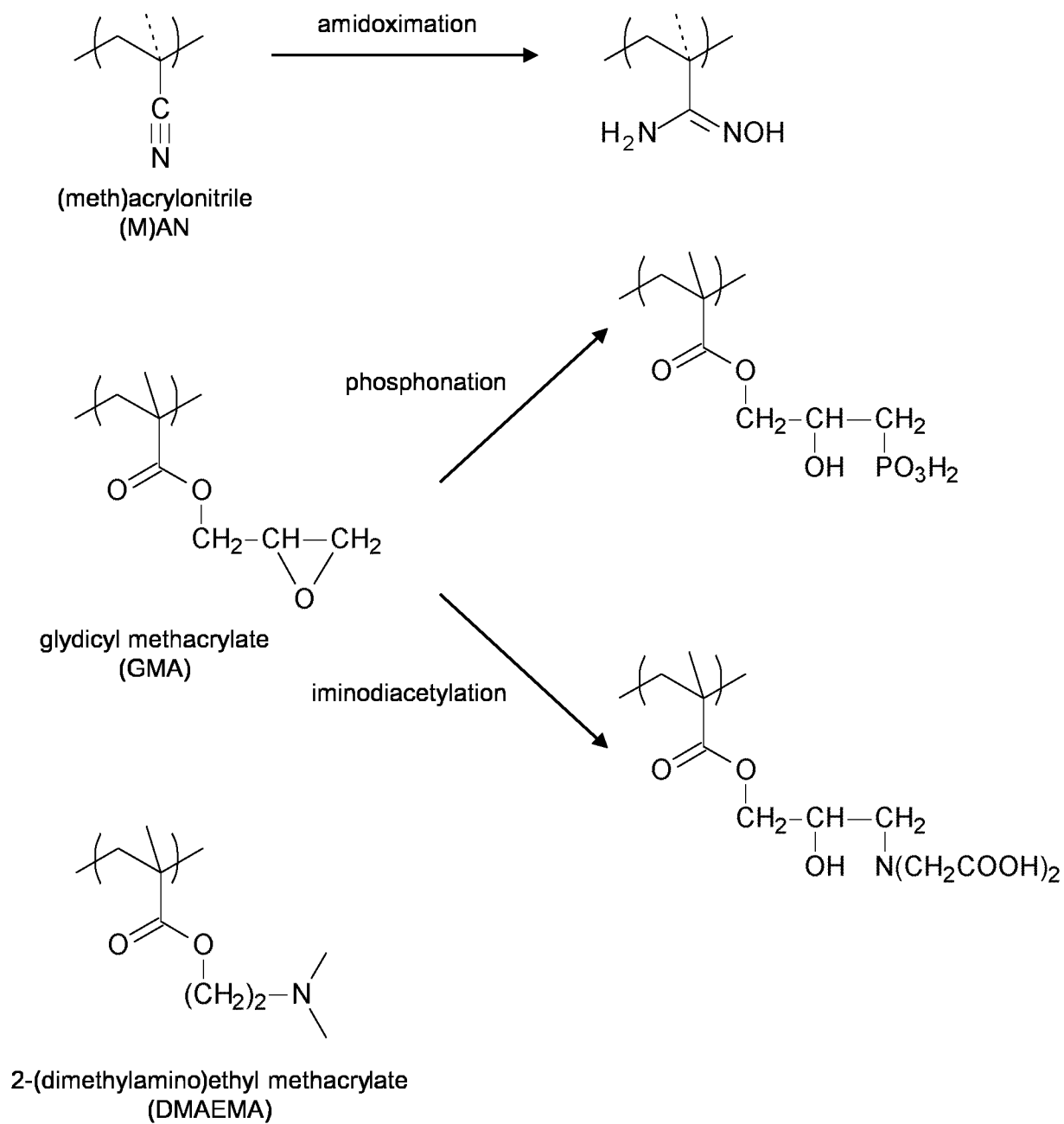


Fig. 5

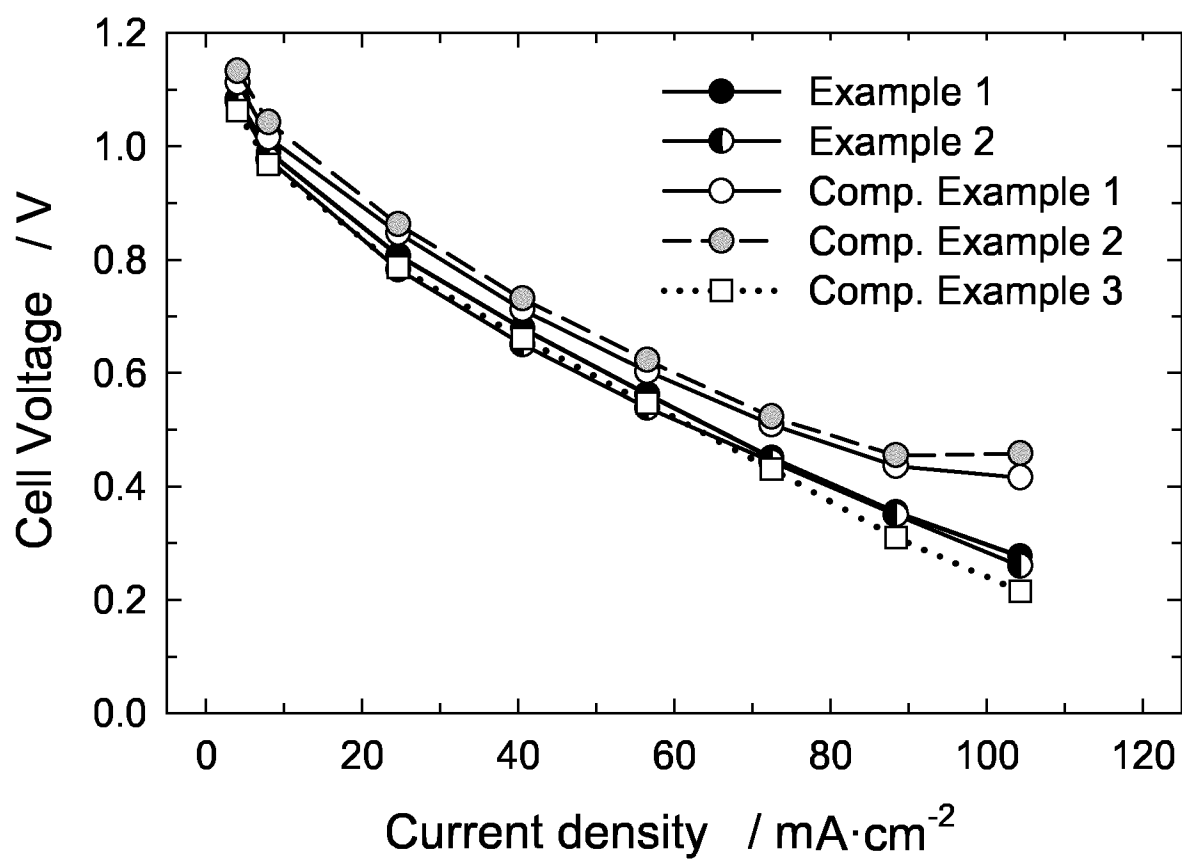


Fig. 6

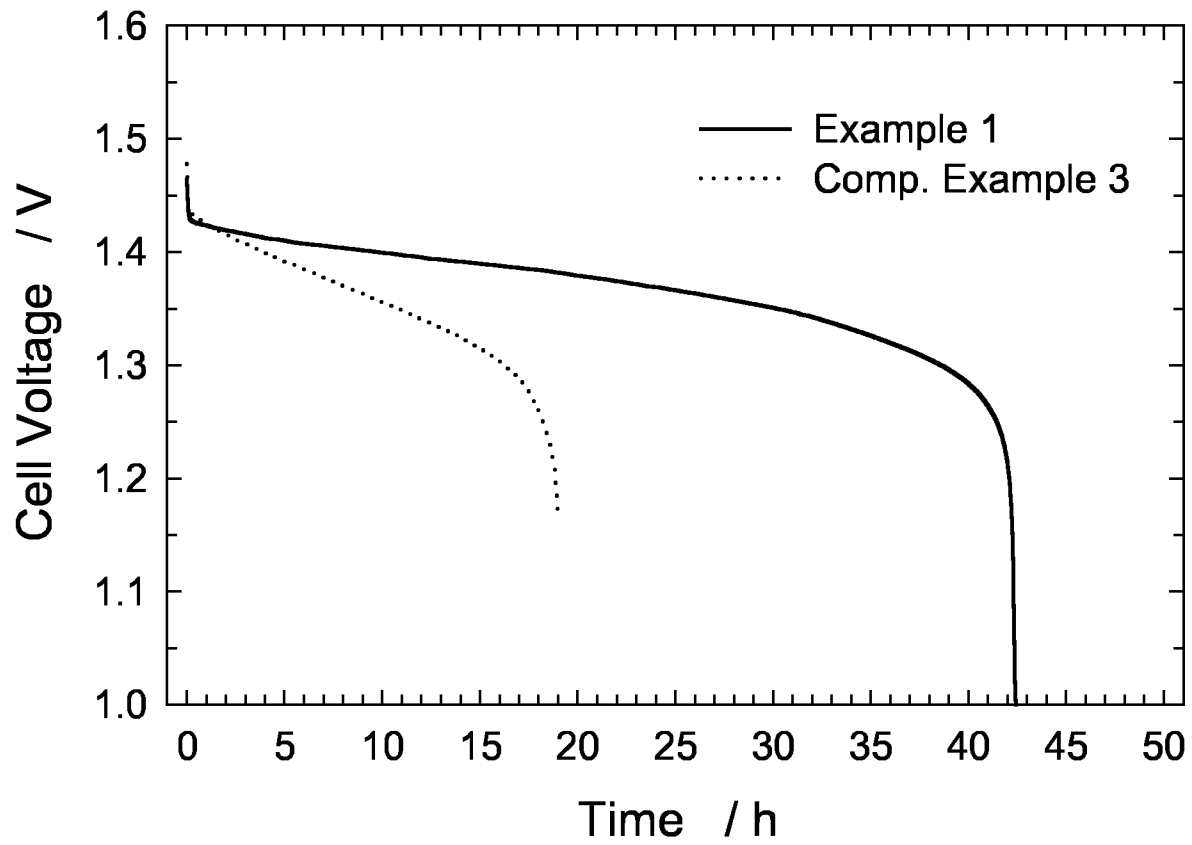


Fig. 7

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/051365

A. CLASSIFICATION OF SUBJECT MATTER

INV. H01M8/10 H01M8/106 H01M8/1088 H01M8/1023 H01M8/18
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EP0-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2013/115504 A1 (LEE MYUNG-JIN [KR] ET AL) 9 May 2013 (2013-05-09) paragraphs [0011] - [0028], [0052] - [0056], [0071] - [0073] -----	1-14
X	DE 10 2005 023897 A1 (VOLKSWAGEN AG [DE]) 30 November 2006 (2006-11-30) paragraphs [0001], [0002], [0026], [0029], [0030] - [0032] -----	1-11

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Further documents are listed in the continuation of Box C.

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See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

24 February 2016

Date of mailing of the international search report

03/03/2016

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2016/051365

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