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Current progress in membranes for fuel cells and reverse electrodialysis

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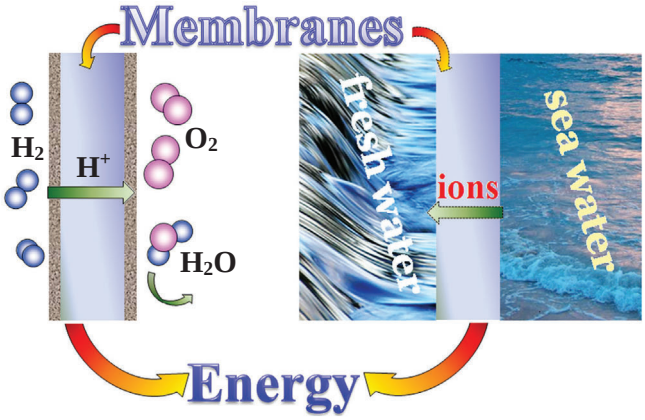
The deterioration of the environmental situation has led to the need to restructure the world's power industry, and clean renewable power sources are coming to the forefront. This review deals with recent advances in the development of promising ion-exchange membrane materials for two types of application that have been intensely developing recently, namely, hydrogen energy and reverse electrodialysis. Special attention is paid to the comparison of two properties of membranes, conductivity and selectivity, that are competing but fundamentally important in both areas. Perfluorinated sulfonic acid membranes now play a dominant role in hydrogen power engineering, as they provide not only high proton conductivity but also chemical stability and low gas permeability. The review also covers other types of membrane materials, including anion exchange membranes, polybenzimidazoles and hybrid membranes containing inorganic nanoparticles that have been actively developed in recent years. The milder operating conditions of membranes in reverse electrodialysis units allow one to use less expensive non-perfluorinated membranes, including grafted ones. It is of note that in devices of this type, the selectivity of membranes to the transfer of oppositely charged ions is a more important parameter.



Keywords: membranes, hydrogen energy, fuel cells, reverse electrodialysis, proton conductivity, selectivity.

Introduction

For a long time, the mankind has been consuming an increasing amount of energy every year. The energy sources included firewood at first, then fossil fuels. Along with the growth in industrial production, this resulted in a significant deterioration of the environmental situation. In view of this, it becomes of utmost importance to switch to renewable energy sources that reduce the environmental load. Among these, solar panels and wind generators should be noted in the first place.[1,2] To dampen the seasonal power fluctuations, long-term energy storage devices are required, the hydrogen cycle being among the promising approaches.[3,4] In addition, fuel cells (FC) that generate

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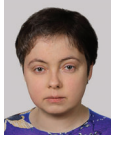

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energy by oxidation of hydrogen or hydrogen-containing fuel can be considered as a renewable energy source that utilize fuels obtained upon conversion of biomass or bio-alcohols.[5–8] As a result, many leading world countries have adopted programs for the development of hydrogen energy.[9]

At the same time, other possible energy sources exist. Among them reverse electrodialysis that makes it possible to obtain energy by mixing salt water with fresh water attracts considerable attention.[10–12] At first glance, it appears to be an unexpected approach since great attention is being paid to the opposite process, *i.e.* the production of drinking water from sea water.[13,14] However, rivers inevitably flow into seas, so the mixing process occurs spontaneously. Therefore, the utilization of this process can provide another efficient 'green' source of energy.[4]

A key role in both devices belongs to membrane materials whose parameters determine their efficiency. As a result, much attention in the literature is paid to the synthesis of new membranes that differ in the optimal parameters of transfer processes.[15–19]

The purpose of this brief review is to describe the recent progress in ion exchange membranes used in low temperature fuel cells and in devices for reverse electrodialysis.

1. Ionic conductivity and selectivity of membranes

Ion exchange membranes have numerous practical applications, including water purification, food processing, concentrating, electrochemical synthesis, sensorics, *etc*.[20–24] Their utilization in modern power engineering has been growing in recent years. Along with fuel cells and reverse electrodialysis considered in this review, membranes can be in demand in metal-ion batteries[25–28] and redox cells.[29–32]

Analysis of the ion-exchange membranes operation in all these devices shows that the efficiency of their use is determined by two key factors, namely, ionic conductivity and selectivity of transport processes.[33] The transfer of ionic fluxes in membranes is always accompanied by an undesirable transfer of oppositely charged ions or molecules. In low-temperature fuel cells, proton conductivity is important, while the main adverse process that reduces their performance is the crossover, *i.e.* transfer of the feeding reagents (oxygen and hydrogen or methanol) in molecular form that is not accompanied by power generation.[34–36] The key role in reverse electrodialysis usually belongs to the transfer of cations and anions with small charges, whereas the interfering processes include the nonspecific transfer of anions and cations through the cation and anion exchange membranes and the osmotic water transfer that causes the equalization of salt concentrations in the system without generating current.[37–40]

To describe the transport processes in ion-exchange membranes, it is necessary to have an idea of the structure of their pores and channels formed due to self-organization processes.[41–43] The most popular Gierke model describes the structure of ion-exchange membranes and was developed on the example of perfluorinated sulfonic acid Nafion membranes. Hydrophilic SO_3H groups assemble into clusters and absorb water that fills the pores and channels in the hydrophobic matrix formed by perfluorinated or hydrocarbon chains (Figure 1).

The pore size in hydrated state amounts to 4–5 nm. The pores are filled with an aqueous solution that contains cations formed upon dissociation of functional groups.[45–47] Dissociation also gives fixed SO_3^- ions located on the pore walls. Due to the interaction with negatively charged walls, the majority of the cations are located in the Debye layer along the pore walls with a characteristic thickness of about 1 nm, while an electrically neutral solution is localized in their center. The composition of this solution is believed to be close to that of the solution contacting the membrane.[18,45,47,48] Moreover, this solution may

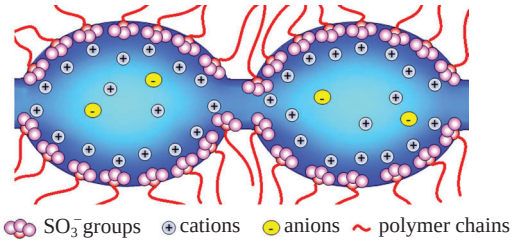

Figure 1 Scheme of the structure of pores and channels in ion-exchange membranes.

contain non-polar molecules of the feed gases. In view of this, nonselective transfer (anions, nonpolar molecules) is primarily determined by this electrically neutral solution. In contrast, the Debye layer largely determines the ionic conductivity of membranes. A significant contribution to the conductivity of an electrically neutral solution can be achieved only upon contact with concentrated solutions of electrolytes.[33]

It may be assumed that the conductivity of membranes is largely determined by the size of channels connecting the pores. In view of this, the degree of membrane hydration should be increased to enhance conductivity. On the other hand, an increase in water uptake occurs mainly due to an increase in the specific volume of the electrically neutral solution. This determines the inverse relationship between conductivity and selectivity noted in a number of publications.[49,50] This relationship is of statistical nature, since the properties of membranes depend considerably on the nature of the polymer matrix, the concentration of functional groups, the degree of crosslinking, and some other factors.[33] It should be noted that in practice, other electrochemical applications often employ heterogeneous membranes which, in addition to an ion-exchange polymer, also contain a binder and a reinforcing mesh.[51–53] Due to the specific methods of their production, these membranes possess secondary porosity between the particles of the materials they contain, with a characteristic size of the order of micrometers. This determines the lower selectivity of heterogeneous membranes.[41,54,55]

2. Membranes for fuel cells

Fuel cells make it possible to oxidize hydrogen or hydrogen-containing fuel for energy generation with high performance. Among the various types of such devices, we will focus on low-temperature FC with a proton-conducting polymer membrane (Figure 2) that are most popular on the market and constitute about 90% of the total production. A fuel (hydrogen or alcohols) is fed to the catalyst through a porous gas diffusion layer. In the case of hydrogen, it is sorbed in dissociatively [reaction (1)], and the protons migrate to the cathodic catalyst where the electroreduction of oxygen occurs to give water [reaction (2)]:[9]

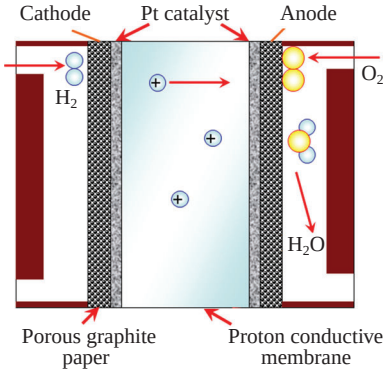

Figure 2 Operation scheme of a hydrogen–oxygen fuel cell based on proton-conductive membranes.

$$H_2 = 2H^+ + 2e^-, \quad (1)$$

$$O_2 + 4H^+ + 4e^- = 2H_2O. \quad (2)$$

The efficiency of FC usually does not exceed 50% at conventional current loads, although it can approach 90% at lower loads. The current density in low-temperature fuel cells abruptly decreases with an increase in the CO concentration in hydrogen, since at low temperatures carbon monoxide is irreversibly sorbed on a platinum catalyst and does not undergo oxidation at a typical anodic potential of about 1 V.[56] It should be noted that methanol is also used as a fuel in low-temperature FC. It is oxidized in direct methanol fuel cells according to reaction (3):

$$MeOH + H_2O - 6e^- = CO_2 + 6H^+. \quad (3)$$

The membranes used in FC should have high protonic conductivity (10^{-2}–10^{-1} S cm^{-1}) along with low gas permeability (methanol permeability) and electronic conductivity.[9] Important parameters also include high chemical stability (primarily to peroxy radicals), dimensional stability, mechanical strength, and ability to maintain conductivity at elevated temperatures. These requirements are currently best satisfied by Nafion membranes whose perfluorinated polymer chain contains side branches, usually $–OCF_2CF(CF_3)C_2F_4SO_3H$, with SO_3H functional groups. Despite their high cost, they are now most popular in low-temperature fuel cells since, in addition to high proton conductivity and selectivity, they also feature excellent chemical stability.[57,58] The considerable length of the side chains usually containing five carbon atoms complicates the crystallization of the polymer[59,60] and determines the high fragmental mobility of the side chains.[57] This favors a good organization of the pore and channel system.[58,59] Materials of this kind are usually prepared by polymerization in solutions or in emulsions.[63,64] Meantime, new approaches are being developed, in particular those using synthesis at high pressures.[65]

In view of the data on the importance of the volume and mobility of side chains, it is not entirely clear why much interest has recently been given to membranes with a short side chain containing only two carbon atoms ($–OC_2F_4SO_3H$). The high conductivity at elevated temperatures is often considered as one of their advantages.[61,66–68] At the same time, it seems that the variation in the ion-exchange capacity whose relationship with the conductivity of ion-exchange membranes of various types has been noted repeatedly is an important factor.[69–73] The properties of a representative series of perfluorinated sulfonic acid membranes with both short and long side chains and ion-exchange capacities from 0.66 to 1.35 mg-equiv. g^{-1} were reported.[74] One can see from the data presented in Figure 3 that the proton conductivity of membranes increases significantly with an increase in the ion-exchange capacity (by 2–3 orders of magnitude, depending on humidity), and this relationship is the same both for membranes with short and long side chains.

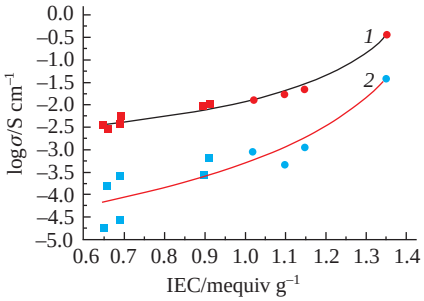

Figure 3 Plot of the proton conductivity of perfluorinated sulfocationite membranes in contact with water (*1*) and at 32% relative humidity (*2*) *vs.* their ion-exchange capacity at 25 °C. The squares indicate the membranes with a long side chain (Nafion) and the circles – with a short side chain (Aquivion) based on the data reported in ref. 74.

It should be noted that the proton conductivity of Aquivion membranes with a maximum ion-exchange capacity of 1.35 mequiv g^{-1} depends on humidity much more weakly than that of Nafion membranes in which the concentration of functional groups is usually noticeably smaller. In accordance with the general regularities, an increase in the water uptake with an increase in the ion-exchange capacity also results in a decrease in the selectivity of transport processes in perfluorinated membranes. In fact, the diffusion permeability of membranes in an HCl solution determined by anion transfer increases in this series by the same two orders of magnitude. As a result, the transport numbers of cations change insignificantly in this series. However, the oxygen permeability of these membranes changes by only half an order upon variation in the ion-exchange capacity.[74] This determines the significant advantage of membranes of this type in fuel cells. The significantly smaller decrease in the gas permeability is most likely due to the fact that gas molecules are transferred not only through a system of pores and channels but also due to diffusion through the perfluorinated matrix, as also noted for other gases.[75]

Obviously, there are few opportunities for improving the properties of perfluorinated membranes by changing their chemical structure. At the same time, their properties can also be changed in another way, namely, by changing the structure of the pore and channel system or by modifying the surface. One of the promising approaches involves the production of hybrid membranes by incorporation of nanoparticles of various inorganic materials.[59,76–78] There are two principal ways to incorporate them into a membrane structure. The first one involves the synthesis of nanoparticles followed by their use when membranes are cast from polymer solutions. Advantages of this approach include the relative simplicity and facility of integration into the membrane production chain.[30,79,80] The main problem in this synthesis is that agglomeration of nanoparticles occurs, which prevents their uniform distribution and reduces the modification efficiency. Ultrasonic treatment of a membrane solution with a dopant is a common method for breaking agglomerates.[81–83] However, to take the effect of the dopant on the properties of membranes correctly into account, one should also consider the effect of ultrasonic treatment of membrane solutions that results in changes in the microstructure, water uptake, mechanical and transport properties of the resulting materials.[84–86] We believe that another method is more attractive, namely, the synthesis of inorganic particles directly (*in situ*) in the membrane matrix where the membrane pores are used as nanoreactors.[87,88]

The most commonly used dopants include hydrated oxides of polyvalent elements (silicon, zirconium, *etc.*)[89–92] and materials based on them.[93–95] The hydrophilic surface of dopants can increase the water content of membranes and enhance the proton conductivity, even at low humidity. A decrease in gas permeability and methanol permeability was noted in certain materials.[21,78] Presumably, the main reason for the increase in conductivity is that the sizes of pores and channels connecting them increase when nanoparticles are embedded in them.[96,97]

The conductivity can additionally be increased by incorporating nanoparticles with surfaces containing proton-donor groups into the membrane matrix, by adding inorganic acids or their acid salts.[98–101] A number of authors noted a decrease in the permeability of gases and methanol upon incorporation of dopants with surfaces having acid properties.[9,102] Due to an increase in the concentration of protons in the membrane matrix, these materials have an enhanced water uptake and proton conductivity, which is especially important at

low humidity. This allows them to be used for the production of fuel cells with performance exceeding that of fuel cells based on Nafion membranes operating at high humidity.[103] On the other hand, it should be noted that the properties of FC can be improved by using membranes incorporated some other polymers, in particular, poly(3,4-ethylenedioxythiophene).[104–107] It is rather difficult to compare the performance of fuel cells achieved in various studies since membranes with different thicknesses prepared by different methods (extrusion, casting), different methods for producing the FC, water uptake and composition of feed gases, catalyst loading and catalytic layer composition are often used. Therefore, many authors compare investigated membranes with a reference sample, most commonly with Nafion in the case of cation-exchange membranes (Table 1).

It should be noted that the high cost of perfluorinated membranes results in their extremely small usage in the majority of electro-membrane technologies where cheaper heterogeneous membranes are mainly used.[22,23,52] The main obstacle to the use of heterogeneous membranes in hydrogen power engineering is their much lower selectivity due to additional formation of larger pores of micrometer size.[54,55] Graft polymerization may be among the most fruitful approaches for overcoming this problem.[142] For this purpose, radical polymerization of styrene in polyethylene films activated by γ-radiation can be used. The formation of the polystyrene 'phase' occurs by separating the polymer chains of the base film without the generation of additional porosity. Sulfonation of a copolymer makes it possible to obtain membranes with various ion-exchange capacities and water uptake.[143,144] To prevent the loss of membrane strength and selectivity due to excessive swelling, they are crosslinked with divinylbenzene. Ion-exchange membranes based on other copolymers were produced using similar approaches.[145–147]

Table 1 Examples of ion-exchange membranes and their FC performance.

Sample	Conditions	Peak power density/ mW cm^{-2}	Reference
Cation-exchange membranes			
Nafion-117	H_2/O_2 PEMFC,[a] 70 °C, 100% RH[b]	310	108
Nafion-117	H_2/O_2 PEMFC, 65 °C, 100% RH	510	107
Nafion-117/poly(3,4-ethylenedioxythiophene)	H_2/O_2 PEMFC, 65 °C, 100% RH	810	107
Nafion-212	H_2/air PEMFC, 65 °C, 100% RH	563	109
Recast Nafion	H_2/air PEMFC, 65 °C, 100% RH	417	109
Nafion/0.05 wt% GO[c]	H_2/air PEMFC, 65 °C, 100% RH	586	109
Recast Nafion	H_2/O_2 PEMFC, 80 °C, 100% RH	160	110
Nafion/2.5 wt% TiO_2	H_2/O_2 PEMFC, 80 °C, 100% RH	343	110
Recast Nafion	H_2/air PEMFC, 80 °C, 20% RH	210	111
Nafion/PW-mGO	H_2/air PEMFC, 80 °C, 20% RH	841	111
Recast Nafion	H_2/O_2 PEMFC, 70 °C, 20% RH	220	112
Nafion/sulfonated graphene	H_2/O_2 PEMFC, 70 °C, 20% RH	300	112
Recast Nafion	H_2/O_2 PEMFC, 70 °C, 20% RH	150	113
Nafion/sulfonated mesoporous carbon	H_2/O_2 PEMFC, 70 °C, 20% RH	660	113
Recast Nafion	H_2/O_2 PEMFC, 60°C, 80% RH	630	114
Nafion-sMWCNT[d] (0.25 wt%)	H_2/O_2 PEMFC, 60°C, 80% RH	867	114
Nafion-115/[1,4-phenylenebis(hydroxymethanetriyl)]tetrakis(phosphonic acid)	H_2/O_2 PEMFC, 70 °C, 100% RH	383	115
Aquivion® R79-01SX+	H_2/air PEMFC, 80 °C, 100% RH	890	116
Nafion® XL	H_2/air PEMFC, 80 °C, 100% RH	610	116
Aquivion® R79-03S	H_2/O_2 PEMFC, 130 °C, 100% RH	870	117
Nafion® 112	H_2/O_2 PEMFC, 130 °C, 100% RH	620	117
Recast Aquivion®	H_2/air PEMFC, 80 °C, 100% RH	442	118
1-wt%Co-tri MOF[e]/Aquivion® blend membrane	H_2/air PEMFC, 80 °C, 100% RH	451	118
Polybenzimidazoles (PBI)			
Celtecs MEA[f] (commercial PBI)	H_2/air PBIFC,[g] 180 °C	200	119
PA[h]/PBI	H_2/air PBIFC, 200 °C	409	120
PA/PBI/5 wt% PWA-meso-silica	H_2/air PBIFC, 200 °C	376	120
PA/PBI/15 wt% PWA-meso-silica	H_2/air PBIFC, 200 °C	386	120
Poly(2,5-benzimidazole) membrane	H_2/air PBIFC, 160 °C	120	121
PBI	H_2/O_2 PBIFC, 160 °C	556	122
PBI containing heterocyclic benzo[*c*]cinnoline structure	H_2/O_2 PBIFC, 160 °C	1253	122
PBI	H_2/air PBIFC, 160 °C	185	123
PBI/SiO_2	H_2/air PBIFC, 160 °C	240	123
PBI/SiO_2	H_2/O_2 PBIFC, 250 °C	283	124
PBI	H_2/O_2 PBIFC, 150 °C	530	125
PBI/*N*-(*p*-carboxyphenyl)maleimide functionalized SiO_2	H_2/O_2 PBIFC, 150 °C	650	125
Hexafluoroisopropylidene-containing PBI/functionalized Carbon nanofibers	H_2/O_2 PBIFC, 160 °C	461	126
Grafted cation-exchange membranes			
A membrane based on sulfonated RX-PTFE[i] with grafted styrene	H_2/O_2 PEMFC, 25 °C, 16% RH	469	127
Nafion-212	H_2/air PEMFC, 30 °C, 100% RH	180	128
A membrane based on polymethylpentene with grafted sulfonated polystyrene	H_2/air PEMFC, 30 °C, 100% RH	180	128

Table 1 (continued).

Sample	Conditions	Peak power density/ mW cm^{-2}	Reference
Anion-exchange membranes			
An AEM with ethylene oxide spacers incorporated into imidazolium-containing cationic side-chains	H_2/O_2 AEMFC,[j] 65 °C, 100% RH	437	129
A double crosslinked AEM based on PBI and poly(vinylbenzyl chloride) with *N*,*N*,*N*′,*N*′-tetramethyl-1,6-hexanediamine	H_2/O_2 AEMFC, 60 °C, 100% RH	245	130
An ethylene-tetrafluoromethylene-based AEM containing saturated-heterocyclic benzyl-quaternary ammonium groups	H_2/O_2 AEMFC, 60 °C, 100% RH	630	131
A poly(ethylene-*co*-tetrafluoroethylene) AEM grafted with 2-methyl-*N*-vinylimidazole and styrene	direct $N_2H_4 \cdot H_2O$/air FC, 80 °C	230	132
An *N*-spirocyclic functionalized AEM achieved through rod-coil grafts with polysulfone backbone	H_2/O_2 AEMFC, 80 °C, 100% RH	850	133
An AEM based on cross-linked quaternized poly(vinylbenzyl chloride) and cross-linked poly(vinyl alcohol)	H_2/air AEMFC, 60 °C, 100% RH	640	134
An imidazolium-based graft-type AEM consisting of an ethylene-tetrafluoromethylene copolymer as a base film	H_2/O_2 AEMFC, 60 °C, 100% RH	710	135
A polystyrene-based AEM grafted with bromoalkyl chains	H_2/O_2 AEMFC, 60 °C, 100% RH	407	136
A quaternized aryl ether-free poly(fluorene)-based AEM	H_2/O_2 AEMFC, 80 °C, 100% RH	1460	137
A quaternary ammonia poly(*N*-methylpiperidine-*co*-*p*-terphenyl)-based AEM	H_2/O_2 AEMFC, 80 °C, 100% RH	1500	138
A poly(aryl piperidinium)-based AEM	H_2/air AEMFC, 95 °C, 100% RH	920	139
A low-density polyethylene-based radiation grafted AEM with benzyltrimethylammonium head-groups	H_2/O_2 AEMFC, 110 °C, 100% RH	2100	140, 141

[a] PEMFC – FC based on proton exchange membranes. [b] RH – relative humidity. [c] GO – graphene oxide. [d] sMWCNT – sulfonic acid functionalized multiwalled carbon nanotube. [e] MOF – metal-organic framework. [f] MEA – membrane electrode assembly. [g] PBIFC – FC based on polybenzimidazole membranes. [h] PA – phosphoric acid. [i] RX-PTFE – radiation-cross-linked polytetrafluoroethylene. [j] AEMFC – FC based on anion exchange membranes.

Polymerization of styrene in pores formed by mechanical deformation of polyethylene, Teflon and other polymers is also used.[148–150]

Activation by ultraviolet radiation can be used to create ion-exchange membranes based on polymers containing tertiary carbon atoms. In fact, a wide range of both cation and anion exchange membranes with a wide range of capacity and conductivity have been obtained by grafting polystyrene on polymethylpentene films.[151,152] Comparison of the ionic conductivity and selectivity (transport numbers) of the membranes obtained shows that in terms of the ratio of selectivity and ion-exchange capacity, they are not inferior to the best commercial membranes, including perfluorinated samples.[50,152] Testing such membranes in fuel cells shows that they are not inferior in terms of performance to Nafion® 212 based membrane-electrode assemblies, though the latter were made using catalytic and gas-diffusion layers optimized for Nafion® 212 membranes[128] (see Table 1). Although the use of pores created by stretching of films for grafting does not prevent the preservation of large pores inside the polymer, membranes that showed rather a high efficiency in fuel cells were also prepared *via* this approach.[153–155]

A decade and a half ago, while analyzing the prospects of anion-exchange membranes in fuel cells,[156] some separate advantages of these devices were noted and the main emphasis was made on methanol fuel cells. However, the slow oxidation of hydrogen and the low conductivity of such membranes and its additional decrease due to the sorption of carbon dioxide made it doubtful that commercialization of fuel cells based on them would be feasible.[157,158] The relative novelty of this approach was considered to be its main advantage. However, the situation changed significantly in recent years.[140,159,160] One of the main advantages of such membranes lies in their significantly reduced corrosivity compared to sulfonic acid cation-exchange membranes in H^+ form, which makes it possible to use non-perfluorinated membranes and non-platinum catalysts based on silver, nickel, cobalt and some other metals.[161–163] Replacement of these two most expensive components can significantly reduce the cost of fuel cells and hence the cost of electricity they produce. In recent years, new anion-exchange membranes featuring high conductivity and stability of operation in FC were developed.[164–168] The operating temperature of such membranes is being increased.[169] New design concepts and catalysts allow the problems associated with the absorption of carbon dioxide, water balance violation and instability to be handled.[170–172] As a result, the performance of fuel cells based on anion-exchange membranes increases rapidly, so that their peak power density can now exceed 2 W cm^{-2} (see Table 1).[140,141,158,169] The majority of researchers develop fuel cells using hydrogen as a fuel, however the use of alcohols and other types of fuel based on hydrogen compounds with carbon and nitrogen is attracting more and more attention.[159]

There is a severe problem that dehydration of ion-exchange membranes accompanied by a sharp decrease in conductivity occurs as temperatures above 90 °C. This is a very serious problem, since the operation of fuel cells at elevated temperatures makes it possible to reduce the adverse effect of the sorption of CO molecules on platinum catalysts that results in a decrease in their performance.[173,174] This determines the high interest of researchers in membranes based on polybenzimidazole.[175–177] Materials of this type exhibit weak anion exchange properties and low proton conductivity by themselves. However, the situation changes drastically once polybenzimidazoles are doped with phosphoric acid that is intensely absorbed by their nitrogen-containing groups. At temperatures of 160–200 °C, such membranes have low methanol permeability and high proton conductivity along the chain of hydrogen bonds between H_3PO_4 molecules.[4,178] In view of this, FC based on polybenzimidazole can operate at low humidity and in the presence of CO impurity in the feed gases or if CO is formed upon oxidation of alcohols[179,180] (see Table 1). In contrast, a decrease in strength at high temperatures and phosphoric acid washout by water vapor become an important problem for polybenzimidazole. Cross-linking of the base polymer chains is used to stabilize the mechanical properties. It invloves the incorporation of polymers that can form salt bridges with basic nitrogen atoms of the imidazole ring,[181,182] the use of silanes,[183–185] halogenated

Table 2 Some characteristics of fuel cells based on various types of polymer membranes.

Membrane	Fuel cell parameters				
	Fuel	Oxidant	*T*/°C	Current carrier/medium	Drawbacks
Proton-exchange membrane	H_2/methanol	oxygen/air	20–100	H^+/H_2O	High cost, gas humidification is needed, the CO concentration should be low
PBI	H_2/methanol	oxygen/air	140–200	H^+/H_3PO_4	H_3PO_4 washout, high requirements for corrosion resistance of materials
Anion-exchange membrane	H_2	oxygen	20–100	OH^-/H_2O	Gas humidification is needed, the CO concentration should be low

methylbenzene derivatives[186] and other compounds capable of nucleophilic replacement of the NH group proton in polybenzimidazoles.[187,188]

The modification of polybenzimidazole with nanoparticles of inorganic compounds favors an increase in conductivity and better retention of phosphoric acid.[124,189–192] The modification is often performed using nanoparticles with functionalized surface[193–197] and organic polymers of various nature.[198] The use of hybrid membranes based on polybenzimidazoles in fuel cells results in an increase in their performance.[124,176] Studies are also in progress where polybenzimidazole itself is grafted with new functional groups capable of generating current carriers or increasing the sorption of phosphoric acid.[199–201]

A brief comparison of the characteristics of fuel cells based on various polymer membranes is provided in Table 2.

3. Membranes for reverse electrodialysis

Rather a new approach that has been rapidly gaining the interest of researchers in recent years involves power generation by mixing salt water with fresh water.[10,11,202] The very existence of this technology seems paradoxical, since the mankind is seriously concerned about the problem of the shortage of pure fresh water. In view of this, much power is spent annually for water purification and desalination.[203,204] However, rivers inevitably flow into seas and all we can do is use this process to produce power. It is also suggested to obtain power from the concentrates produced at desalination plants.[205] For example, it is suggested to employ the osmosis phenomenon (pressure retarded osmosis) for this purpose.[206–208] However, it turns out that reverse electrodialysis (RED) is a more attractive approach where the membrane potential that appears upon diffusion of cations and anions from compartments with salt water into fresh water serves as the driving force (Figure 4).[15,29] It is assumed that the application of this approach can significantly reduce CO_2 emissions to the atmosphere.[209]

Like in fuel cells, membranes are among the main components that determine the overall operation of a unit. In this case, priority is usually given to membranes with high selectivity, conductivity and small thickness that are necessary to minimize the ohmic losses, and high stability.[29,210] On the other hand, since the operating conditions of these devices are significantly milder

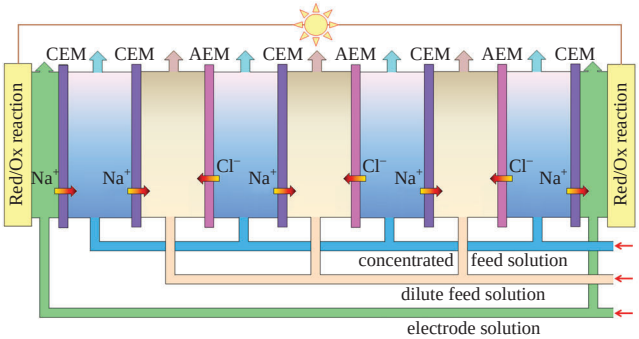

Figure 4 Scheme of a membrane-electrode stack in a reverse electrodialysis unit.

than those of FC, the requirements concerning the chemical stability of membranes are much less critical. Since the early stages of the development of RED processes, the majority of researchers used cheaper, mostly pseudo-homogeneous membranes such as FujiFilm, Fumatech, Tokuyama and Neosepta.[12,211–218] The maximum power density (2.2 W m^{-2}) was obtained for a pair of Fumatech cation- and anion-exchange membranes.[29,214] Optimization of the unit parameters[219] made it possible to achieve a significantly higher power density of 12 W m^{-2} using 0.1 and 5 M NaCl solutions at 40 °C. At the same time, the power density of such units was invariably found to be lower in later studies. In fact, a recent study reports that the power density achieved with such membranes is 0.43 W m^{-2}.[218] Some gain in power density can be obtained by profiling the surface of membranes used in RED units.[220]

Nafion 117 and Nafion 115 membranes were compared with the CMX (Neosepta) and Fuji-CEM 80050 (Fujifilm) membranes that are widely used in RED units.[205] A relatively high power density of 1.4 W m^{-2} of the unit with the Nafion 117 membrane using 4.0 and 0.5 M NaCl solutions was noted. Moreover, it was shown that their power density, like that of Fuji-CEM-80050 membranes, decreased by more than 20% in the presence of magnesium chloride. Meantime, the effect of $MgCl_2$ addition on other membranes was found to be significantly smaller.[205]

It is worthy of note that though the theoretical power density should increase with a decrease in the concentration of the more dilute solution, it is actually maintained no lower than 0.1 M in most cases. The reason is that the conductivity of membranes in contact with dilute solutions decreases considerably.[45]

Some successful attempts to use nanoporous membranes with high selectivity and permeability for the RED process can also be noted. They provide selective transfer of ions with the same charge sign, and their power density, according to some publications, reaches 7–10 W cm^{-2} for nanotubes of silicon oxide[221] and anodic aluminum oxide.[222]

Grafted ion-exchange membranes may also be considered one of the most promising membrane types.[223] The prospects of their application in RED units has been shown in a number of works, for example, in refs. 50 and 224. As noted above, this method allows one to obtain membranes with both high conductivity and selectivity.[225] At the same time, these parameters are usually opposite to each other.[33] Their balance can be controlled by varying the extent of grafting and crosslinking of a functional polymer and by choosing an appropriate crosslinking agent.[224] However, the choice between selectivity and conductivity remains in force in this case.

A significant effect of membrane fouling in RED units that can reduce the performance of a unit more than twofold even in the first hours of operation was reported.[226,227] The effects of biofouling, contamination with organic compounds and deposition of salts of multicharged ions were mentioned. Various strategies have been suggested to produce membranes preventing this adverse effect.[228] Among the promising solutions to this problem, one can note the use of membranes that are selective to the transfer of single-charged ions[229] and coating of a membrane

with polydopamine.[230] An alternative solution is to use bipolar shielding membranes to suppress the formation of inorganic deposits on a cathode.[231]

On the other hand, the use of bipolar membranes makes it possible to implement another approach based on the neutralization reaction between solutions of acids and alkalis.[232,233] This approach allows a higher performance to be attained but has much more limited applicability due to the specifics of the raw materials used. For example, it can be used for neutralization of effluents from chemical or electrochemical plants.

Conclusions

The processes of hydrogen oxidation and mixing of salt and fresh water for highly efficient power generation are becoming significant approaches in the modern power industry. The hydrogen energy programs adopted by the majority of developed countries in recent years give a new impetus to the development of membrane science and membrane technologies. Ion-exchange membranes based on perfluorosulfonic acids characterized by high conductivity, chemical stability, and low gas permeability for application in the hydrogen power industry attract the greatest attention. At the same time, the high cost of these membranes prompts researchers to search for new materials, including a wide range of grafted membranes, that can efficiently work in fuel cells. A significant improvement in the transport properties of membranes can often be achieved by modification of membranes with inorganic nanoparticles. The fast development of fuel cells based on anion-exchange membranes should also be noted. Their main advantages include the feasibility of using non-platinum catalysts and less stringent requirements for chemical stability. Moreover, the fact that it is impossible to obtain relatively cheap high-purity hydrogen makes the synthesis of membranes capable of operating at elevated temperatures, among which polybenzimidazoles should be noted, an urgent task. They provide operation at temperatures up to 200 °C, which allows one to partially solve the problem of increasing the tolerance of FC catalysts to carbon monoxide, an unavoidable contaminant in cheap hydrogen obtained by steam reforming of hydrocarbons and alcohols.

Compared to the hydrogen energy, reverse electrodialysis is a relatively new approach, but this fact does not weaken the advantages of this efficient and environmentally friendly method of power generation. Due to lower requirements for chemical stability, this method allows cheaper pseudo-homogeneous, porous, grafted, and other types of membranes to be widely used. Membrane fouling is an important problem in the development of this method. A number of approaches have been suggested for overcoming this problem, including the use of new membrane types. Moreover, new methods and membrane materials are being developed for this method.

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References

1 J. Widén, N. Carpman, V. Castellucci, D. Lingfors, J. Olauson, F. Remouit, M. Bergkvist, M. Grabbe and R. Waters, *Renewable Sustainable Energy Rev.*, 2015, **44**, 356.
2 N. Pearre, K. Adye and L. Swan, *Appl. Energy*, 2019, **242**, 69.
3 A. R. Dehghani-Sanij, E. Tharumalingam, M. B. Dusseault and R. Fraser, *Renewable Sustainable Energy Rev.*, 2019, **104**, 192.
4 A. B. Yaroslavtsev, I. A. Stenina and D. V. Golubenko, *Pure Appl. Chem.*, 2020, **92**, 1147.
5 B. Pandey, Y. K. Prajapati and P. N. Sheth, *Int. J. Hydrogen Energy*, 2019, **44**, 25384.
6 Y. Gao, J. Jiang, Y. Meng, F. Yan and A. Aihemaiti, *Energy Convers. Manage.*, 2018, **171**, 133.
7 A. A. Lytkina, N. V. Orekhova and A. B. Yaroslavtsev, *Inorg. Mater.*, 2018, **54**, 1315.
8 R. Nagappan and M. Sanjeev, *Chem. Rev.*, 2019, **119**, 11945.
9 S. P. Filippov and A. B. Yaroslavtsev, *Russ. Chem. Rev.*, 2021, **90**, 627.
10 K. Nijmeijer and S. Metz, in *Sustainability Science and Engineering*, Elsevier, 2010, vol. 2, ch. 5, pp. 95–139.
11 Z. Jia, B. Wang, S. Song and Y. Fan, *Renewable Sustainable Energy Rev.*, 2014, **31**, 91.
12 R. A. Tufa, E. Curcio, W. van Baak, J. Veerman, S. Grasman, E. Fontananova and G. Di Profio, *RSC Adv.*, 2014, **4**, 42617.
13 N. C. Darre and G. S. Toor, *Curr. Pollut. Rep.*, 2018, **4**, 104.
14 J. Choi, P. Dorji, H. K. Shon and S. Hong, *Desalination*, 2019, **449**, 118.
15 R. A. Tufa, S. Pawlowski, J. Veerman, K. Bouzek, E. Fontananova, G. di Profio, S. Velizarov, J. G. Crespo, K. Nijmeijer and E. Curcio, *Appl. Energy*, 2018, **225**, 290.
16 S. J. Peighambardoust, S. Rowshanzamir and M. Amjadi. *Int. J. Hydrogen Energy*, 2010, **35**, 9349.
17 Y. Mei and C. Y. Tang, *Desalination*, 2018, **425**, 156.
18 H. Tian, Y. Wang, Y. Pei and J. C. Crittenden, *Appl. Energy*, 2020, **262**, 114482.
19 F. Kotoka, I. Merino-Garcia and S. Velizarov, *Membranes*, 2020, **10**, 160.
20 I. G. Wenten, K. Khoiruddin, P. T. P. Aryanti and A. N. Hakim, *J. Membr. Sci. Res.*, 2016, **2**, 42.
21 J. Ran, L. Wu, Y. He, Z. Yang, Y. Wang, C. Jiang, L. Ge, E. Bakangura and T. Xu, *J. Membr. Sci.*, 2017, **522**, 267.
22 A. Campione, L. Gurreri, M. Ciofalo, G. Micale, A. Tamburini and A. Cipollina, *Desalination*, 2018, **434**, 121.
23 P. Yu. Apel, O. V. Bobreshova, A. V. Volkov, V. V. Volkov, V. V. Nikonenko, I. A. Stenina, A. N. Filippov, Yu. P. Yampolskii and A. B. Yaroslavtsev, *Membr. Membr. Technol.*, 2019, **1**, 45.
24 A. Merkel, D. Voropaeva, H. Fárová and A. Yaroslavtsev, *Int. Dairy J.*, 2020, **108**, 104737.
25 D. Y. Voropaeva, S. A. Novikova, T. L. Kulova and A. B. Yaroslavtsev, *Ionics*, 2018, **24**, 1685.
26 X. Chen and P. M. Vereecken, *Adv. Mater. Interfaces*, 2019, **6**, 1800899.
27 C. M. Costa, Y.-H. Lee, J.-H. Kim, S.-Y. Lee and S. Lanceros-Méndez, *Energy Storage Mater.*, 2019, **22**, 346.
28 D. Yu. Voropaeva, S. A. Novikova and A. B. Yaroslavtsev, *Russ. Chem. Rev.*, 2020, **89**, 1132.
29 J. G. Hong, B. Zhang, S. Glabman, N. Uzal, X. Dou, H. Zhang, X. Wei and Y. Chen, *J. Memb. Sci.*, 2015, **486**, 71.
30 E. Yu. Safronova and A. B. Yaroslavtsev, *Pet. Chem.*, 2016, **56**, 281 (*Membr. Membr. Tekhnol.*, 2016, **6**, 3).
31 Y. Shi, C. Eze, B. Xiong, W. He, H. Zhang, T. M. Lim, A. Ukil and J. Zhao, *Appl. Energy*, 2019, **238**, 202.
32 J. Sheng, A. Mukhopadhyay, W. Wang and H. Zhu, *Mater. Today Nano*, 2019, **7**, 100044.
33 I. Stenina, D. Golubenko, V. Nikonenko and A. Yaroslavtsev, *Int. J. Mol. Sci.*, 2020, **21**, 5517.
34 X. Cheng, J. Zhang, Y. Tang, C. Song, J. Shen, D. Song and J. Zhang, *J. Power Sources*, 2007, **167**, 25.
35 M. Ahmed and I. Dincer, *Int. J. Energy Res.*, 2011, **35**, 1213.
36 U. Chakraborty, *Appl. Energy*, 2016, **163**, 60.
37 E. Güler, W. Baak, M. Saakes and K. Nijmeijer, *J. Membr. Sci.*, 2014, **455**, 254.
38 D. Pintossi, C.-L.Chen, M. Saakes, K. Nijmeijer and Z. Borneman, *npj Clean Water*, 2020, **3**, 29.
39 Y. Lee, H. J. Kim and D.-K. Kim, *Energies*, 2020, **13**, 904.
40 S. Mehdizadeh, Y. Kakihana, T. Abo, Q. Yuan and M. Higa, *Membranes*, 2021, **11**, 27.
41 X. Yan, W. Zheng, X. Ruan, Y. Pan, X. Wu, G. He and J. Chin, *Chem. Eng.*, 2016, **24**, 558.
42 S. Mondal, I. M. Griffiths and G. Z. Ramon, *J. Membr. Sci.*, 2019, **588**, 117166.
43 I. A. Stenina and A. B. Yaroslavtsev, *Membranes*, 2021, **11**, 198.
44 W. Y. Hsu and T. D. J. Gierke, *J. Membr. Sci.*, 1983, **13**, 307.
45 V. V. Nikonenko, A. B. Yaroslavtsev and G. Pourcelly, in *Ionic Interactions in Natural and Synthetic Macromolecules*, eds. A. Ciferri and A. Perico, John Wiley & Sons, Inc., New Jersey, 2012, ch. 9, pp. 267–336.
46 C. Yin, J. Li, Y. Zhou, H. Zhang, P. Fang and C. He, *J. Phys. Chem. C*, 2018, **122**, 9710.
47 S. P. Fernandez Bordín, H. E. Andrada, A. C. Carreras, G. E. Castellano, R. G. Oliveira and V. M. Galván Josa, *Polymers*, 2018, **155**, 58.
48 R. K. Nagarale, G. S. G. Vinod and K. Shahi, *Adv. Colloid Interface Sci.*, 2006, **119**, 97.

49 M. Geise, M. A. Hickner and B. E. Logan, *ACS Appl. Mater. Interfaces*, 2013, **5**, 10294.
50 D. V. Golubenko, G. Pourcelly and A. B. Yaroslavtsev, *Sep. Purif. Technol.*, 2018, **207**, 329.
51 H. Strathmann, A. Grabowski and G. Eigenberger, *Ind. Eng. Chem. Res*., 2013, **52**, 10364.
52 Y.- M. Miao, Y.-X. Jia, R.-Q. Guo and M. Wang, *J. Membr. Sci*., 2018, **557**, 67.
53 V. Zabolotskii, N. Sheldeshov and S. Melnikov, *Desalination*, 2014, **342**, 183.
54 N. Kononenko, V. Nikonenko, D. Grande, C. Larchet, L. Dammak, M. Fomenko and Yu. Volfkovich, *Adv. Colloid Interface Sci*., 2017, **246**, 196.
55 N. D. Pismenskaya, E. V. Pokhidnia, G. Pourcelly and V. V. Nikonenko, *J. Membr. Sci*., 2018, **566**, 54.
56 A. B. Yaroslavtsev, I. A. Stenina, T. L. Kulova, A. M. Skundin and A. V. Desyatov, in *Comprehensive Nanoscience and Nanotechnology*, 2nd edn., eds. D. L. Andrews, R. H. Lipson and T. Nann, Academic Press, 2019, vol. 5, pp. 165–206.
57 K. A. Mauritz and R. B. Moore, *Chem. Rev*., 2004, **104**, 4535.
58 G. Cognard, G. Ozouf, C. Beauger, L. Dubau, M. López-Haro, M. Chatenet and F. Maillard, *Electrochim. Acta*, 2017, **245**, 993.
59 A. B. Yaroslavtsev and Yu. P. Yampolskii, *Mendeleev Commun.*, 2014, **24**, 319.
60 Yu. P. Yampolskii, N. A. Belov and A. Yu. Alent'ev, *Russ. Chem. Rev*., 2019, **88**, 387.
61 A. Kusoglu and A. Z. Weber, *Chem. Rev.*, 2017, **117**, 987.
62 S. Fujinami, T. Hoshino, T. Nakatani, T. Miyajima, T. Hikima and M. Takata, *Polymer*, 2019, **180**, 121699.
63 A. K. Sahu, S. Pitchumani, P. Sridhar and A. K. Shukla, *Bull. Mater. Sci*., 2009, **32**, 285.
64 S. S. Ivanchev, V. S. Likhomanov, O. N. Primachenko, S. Ya. Khaikin, V. G. Barabanov, V. V. Kornilov, A. S. Odinokov, Yu. V. Kulvelis, V. T. Lebedev and V. A. Trunov, *Pet. Chem.*, 2012, **52**, 453 (*Membr. Membr. Tekhnol*., 2012, **2**, 3).
65 E. V. Polunin, Yu. E. Pogodina, I. A. Prikhno and A. B. Yaroslavtsev, *Mendeleev Commun*., 2019, **29**, 661.
66 J. Li, M. Pan and H. Tang, *RSC Adv*., 2014, **4**, 3944.
67 Y.-C. Park, K. Kakinuma, H. Uchida, M. Watanabe and M. Uchida, *J. Power Sources*, 2015, **275**, 384.
68 X. Luo and S. Holdcroft, *J. Membr. Sci*., 2016, **520**, 155.
69 E. Moukheiber, G. De Moor, L. Flandin and C. Bas, *J. Membr. Sci*., 2012, **389**, 294.
70 A. Vishnyakov and A. V. Neimark, *J. Phys. Chem. B*, 2014, **118**, 11353.
71 N. A. Kononenko, M. A. Fomenko and Yu. M. Volfkovich, *Adv. Colloid Interface Sci*., 2015, **222**, 425.
72 E. Yu. Safronova, A. K. Osipov and A. B. Yaroslavtsev, *Pet. Chem*., 2018, **58**, 130 (*Membr. Membr. Tekhnol*., 2018, **8**, 34).
73 R. Hammer, M. Schönhoff and M. R. Hansen, *J. Phys. Chem. B*, 2019, **123**, 8313.
74 I. A. Prikhno, E. Yu. Safronova, I. A. Stenina, P. A. Yurova and A. B. Yaroslavtsev, *Membr. Membr. Technol*., 2020, **2**, 265.
75 A. O. Volkov, D. V. Golubenko and A. B. Yaroslavtsev, *Sep. Purif. Technol*., 2021, **254**, 117562.
76 T. Xu, *J. Membr. Sci*., 2005, **263**, 1.
77 F. A. Zakil, S. K. Kamarudin and S. Basri, *Renewable Sustainable Energy Rev*., 2016, **65**, 841.
78 C. Y. Wong, W. Y. Wong, K. Ramya, M. Khalid, K. S. Loh, W. R. W. Daud, K. L. Lim, R. Walvekar and A. A. H. Kadhum, *Int. J. Hydrogen Energy*, 2019, **44**, 6116.
79 G. D. Gebreeyessus, *Appl. Water Sci*., 2019, **9**, 135.
80 P. Karthikeyan and S. Meenakshi, *J. Environ. Chem. Eng*., 2020, **8**, 103717.
81 V. Di Noto, N. Boaretto, E. Negro and G. Pace, *J. Power Sources*, 2010, **195**, 7734.
82 A. Saccà, A. Carbone, I. Gatto, R. Pedicini, A. Freni, A. Patti and E. Passalacqua, *Polym. Test*., 2016, **56**, 10.
83 A. Balwani and E. M. Davis, *ACS Appl. Polym. Mater*., 2020, **2**, 40.
84 E.Yu. Safronova, I. A. Stenina and A. B. Yaroslavtsev, *Pet. Chem*., 2017, **57**, 299 (*Membr. Membr. Tekhnol*., 2017, **7**, 77).
85 M. Adamski, N. Peressin, S. Holdcroft and B. G. Pollet, *Ultrason. Sonochem*., 2020, **60**, 104758.
86 E. Yu. Safronova, G. Pourcelly and A. B. Yaroslavtsev, *Polym. Degrad. Stab*., 2020, **178**, 109229.
87 A. B. Yaroslavtsev, I. A. Stenina, E. Yu. Voropaeva and A. A. Ilyina, *Polym. Adv. Technol*., 2009, **20**, 566.
88 I. A. Stenina and A. B. Yaroslavtsev, *Membr. Membr. Technol.*, 2019, **1**, 137.
89 V. Di Noto, S. Lavina, E. Negro, M. Vittadello, F. Conti, M. Piga and G. Pace, *J. Power Sources*, 2009, **187**, 57.
90 E. Yu. Safronova, I. A. Stenina and A. B. Yaroslavtsev, *Russ. J. Inorg. Chem*., 2010, **55**, 13 (*Zh. Neorg. Khim*., 2010, **55**, 16).
91 K. Ketpang, K. Oh, S.-C. Lim and S. Shanmugam, *J. Power Sources*, 2016, **329**, 441.
92 M. Ercelik, A. Ozden, Y. Devrim and C. O. Colpan, *Int. J. Hydrogen Energy*, 2017, **42**, 2658.
93 J.-M. Thomassin, C. Pagnoulle, D. Bizzari, G. Caldarella, A. Germain and R. Jérôme, *e-Polymers*, 2004, **4**, 018.
94 E. V. Gerasimova, E. Yu. Safronova, A. A. Volodin, A. E. Ukshe, Yu. A. Dobrovolsky and A. B. Yaroslavtsev, *Catal. Today*, 2012, **193**, 81.
95 G. Xu, Z. Wei, S. Li, J. Li, Z. Yang and S. A. Grigoriev, *Int. J. Hydrogen Energy*, 2019, **44**, 29711.
96 S. A. Novikova, E. Yu. Safronova, A. A. Lysova and A. B. Yaroslavtsev, *Mendeleev Commun.*, 2010, **20**, 156.
97 I. A. Stenina and A. B. Yaroslavtsev, *Inorg. Mater*., 2017, **53**, 253.
98 Y. Liu, S. V. Sambasivarao, J. L. Horan, Y. Yang, C. M. Maupin and A. M. Herring, *J. Phys. Chem. C*, 2014, **118**, 854.
99 M. J. Martínez-Morlanes, A. M. Martos, A. Várez and B. Levenfeld, *J. Membr. Sci*., 2015, **492**, 371.
100 D. J. Kim, M. J. Jo and S. Y. Nam, *J. Ind. Eng. Chem*., 2015, **21**, 36.
101 I. A. Prikhno, K. A. Ivanova, G. M. Don and A. B. Yaroslavtsev, *Mendeleev Commun*., 2018, **28**, 657.
102 J. Li, G. Xu, X. Luo, J. Xiong, Z. Liu and W. Cai, *Appl. Energy*, 2018, **213**, 408.
103 E. Gerasimova, E. Safronova, A. Ukshe, Yu. Dobrovolsky and A. Yaroslavtsev, *Chem. Eng. J*., 2016, **305**, 121.
104 L. Li, J.-F. Drillet, Z. Mácová, R. Dittmeyer and K. Jüttner, *Russ J. Electrochem.*, 2006, **42**, 1193 (*Elektrokhimiya*, 2006, **42**, 1330).
105 J. L. da Silva Marques, A. P. S. Zanatta, M. Hattenberger and M. M. de Camargo Forte, *Polímeros*, 2018, **28**, 293.
106 S. Ghosh, S. Das and M. E. G. Mosquera, *Polymers*, 2020, **12**, 2993.
107 I. A. Stenina, P. A. Yurova, T. S. Titova, M. A. Polovkova, O. V. Korchagin, V. A. Bogdanovskaya and A. B. Yaroslavtsev, *J. Appl. Polymer Sci*., 2021, **138**, 50644.
108 H.-L. Lin, T.-L. Yu and F.-H. Han, *J. Polym. Res*., 2006, **13**, 379.
109 K.-J. Peng, J.-Y. Lai and Y.-L. Liu, *J. Membr. Sci.*, 2016, **514**, 86.
110 Y. Devrim, *J. Appl. Polym. Sci*., 2014, **131**, 40541.
111 Y. Kim, K. Ketpang, S. Jaritphun, J. S. Park and S. Shanmugam, *J. Mater. Chem. A*, 2015, **3**, 8148.
112 A. K. Sahu, K. Ketpang, S. Shanmugam, O. Kwon, S. Lee and H. Kim, *J. Phys. Chem. C*, 2016, **120**, 15855.
113 S. Sasikala, S. V. Selvaganesh, A. K. Sahu, A. Carbone and E. Passalacqua, *J. Membr. Sci*., 2016, **499**, 503.
114 N. Steffy, V. Parthiban and A. Sahu, *J. Membr. Sci.*, 2018, **563**, 65.
115 F. C. Teixeira, A. I. de Sá, A. P. S. Teixeira, V. M. Ortiz-Martínez, A. Ortiz, I. Ortiz and C. M. Rangel, *Int. J. Hydrogen Energy*, 2020, **46**, 17562.
116 K. Talukdar, P. Gazdzicki and K. A. Friedrich, *J. Power Sources*, 2019, **439**, 227078.
117 A. Stassi, I. Gatto, E. Passalacqua, V. Antonucci, A. S. Arico, L. Merlo, C. Oldani and E. Pagano, *J. Power Sources*, 2011, **196**, 8925.
118 S. Paul, S.-J. Choi and H. J. Kim, *Ionics*, 2021, **27**, 1653.
119 J. A. Asensio, E. M. Sánchez and P. Gómez-Romero, *Chem. Soc. Rev*., 2010, **39**, 3210.
120 D. Aili, J. Zhang, M. T. Dalsgaard Jakobsen, H. Zhu, T. Yang, J. Liu, M. Forsyth, C. Pan, J. O. Jensen, L. N. Cleemann, S. P. Jiang and Q. Li, *J. Mater. Chem. A*, 2016, **4**, 4019.
121 C. Wannek, I. Konradi, J. Mergel and W. Lehnert, *Int. J. Hydrogen Energy*, 2009, **34**, 9479.
122 J.-C. Chen, Y.-R. Hsiao, Y.-C. Liu, P.-Y. Chen and K.-H. Chen, *Polymer*, 2019, **182**, 121814.
123 Y. Devrim, H. Devrim and I. Eroglu, *Int. J. Hydrogen Energy*, 2016, **41**, 10044.
124 Y. Cheng, J. Zhang, S. Lu, H. Kuang, J. Bradley, R. De Marcod, D. Ailif, Q. Lif, C. Q. Cuia and S. P. Jiang, *Int. J. Hydrogen Energy*, 2018, **43**, 22487.
125 S. M. Suryani, Y. N. Chang, J. Y. Lai and Y. L. Liu, *J. Membr. Sci.*, 2012, **403**–**404**, 1.
126 L.-C. Jheng, A. A. Rosidah, S. L.-C. Hsu, K.-S. Ho, C.-J. Pan and C.-W. Cheng, *RSC Adv.*, 2021, **11**, 9964.
127 S. Hiraiwa, T. Yoshikawa, A. Oshima and M. Washio, *J. Photopolym. Sci. Technol.*, 2012, **25**, 481.
128 D. V. Golubenko, E. V. Gerasimova and A. B. Yaroslavtsev, *Int. J. Hydrogen Energy*, 2021, **46**, 16999.

129 Y. Zhu, L. Ding, X. Liang, M. A. Shehzad, L. Wang, X. Ge, Y. He, L. Wu, J. R. Varcoe and T. Xu, *Energy Environ. Sci.*, 2018, **11**, 3472.
130 S. Yu, X. Ma, H. Liu and J. Hao, *Polym. Bull.*, 2018, **75**, 5163.
131 J. Ponce-González, D. K. Whelligan, L. Wang, R. Bance-Soualhi, Y. Wang, Y. Peng, H. Peng, D. C. Apperley, H. N. Sarode, T. P. Pandey, A. G. Divekar, S. Seifert, A. M. Herring, L. Zhuang and J. R. Varcoe, *Energy Environ. Sci.*, 2016, **9**, 3724.
132 K. Yoshimura, A. Hiroki, H. C. Yu, Y. Zhao, H. Shishitani, S. Yamaguchi, H. Tanaka and Y. Maekawa, *J. Membr. Sci.*, 2019, **573**, 403.
133 Y. Zhang, W. Chen, T. Li, X. Yan, F. Zhang, X. Wang, X. Wu, B. Pang and G. He, *J. Power Sources*, 2021, **490**, 229544.
134 L. Zeng, Y. Liao, J. Wang and Z. Wei, *J. Power Sources*, 2021, **486**, 229377.
135 A. M. A. Mahmoud, K. Yoshimura and Y. Maekawa, *J. Membr. Sci.*, 2021, **620**, 118844.
136 J. E. Chae, S. Y. Lee, S. J. Yoo, J. Y. Kim, J. H. Jang, H.-Y. Park, H. S. Park, B. Seo, D. Henkensmeier, K. H. Song and H.-J. Kim, *Polymers*, 2021, **13**, 690.
137 S. Maurya, S. Noh, I. Matanovic, E. J. Park, C. Narvaez Villarrubia, U. Martinez, J. Han, C. Bae and Y. S. Kim, *Energy Environ. Sci.*, 2018, **11**, 3283.
138 H. Peng, Q. Li, M. Hu, L. Xiao, J. Lu and L. Zhuang, *J. Power Sources*, 2018, **390**, 165.
139 J. Wang, Y. Zhao, B. P. Setzler, S. Rojas-Carbonell, C. B. Yehuda, A. Amel, M. Page, L. Wang, K. Hu, L. Shi, S. Gottesfeld, B. Xu and Y. Yan, *Nat. Energy*, 2019, **4**, 392.
140 J. C. Douglin, J. R. Varcoe and D. R. Dekel, *J. Power Sources Adv.*, 2020, **5**, 100023.
141 H. A. Miller, M. V. Pagliaro, M. Bellini, F. Bartoli, L. Wang, I. Salam, J. R. Varcoe and F. Vizza, *ACS Appl. Energy Mater.*, 2020, **3**, 10209.
142 M. M. Nasef and E. S. A. Hegazy, *Prog. Polym. Sci.*, 2004, **29**, 499.
143 T. A. Sherazi, S. Ahmad, M. A. Kashmiri and M. D. Guiver, *J. Membr. Sci.*, 2008, **325**, 964.
144 E. Yu. Safronova, D. V. Golubenko, N. V. Shevlyakova, M. G. D'yakova, V. A. Tverskoi, L. Dammak, D. Grande and A. B. Yaroslavtsev, *J. Membr. Sci.*, 2016, **515**, 196.
145 T. T. Duy, S. Sawada, S. Hasegawa, Y. Katsumura and Y. Maekawa, *J. Membr. Sci.*, 2013, **447**, 19.
146 S. Sadeghi, L. I. Şanlı, E. Güler and S. A. Gürsel, *Solid State Ionics*, 2018, **314**, 66.
147 S. Hasegawa, A. Hiroki, Y. Ohta, N. Iimura, A. Fukaya and Y. Maekawa, *Radiat. Phys. Chem.*, 2020, **171**, 108647.
148 E. F. Abdrashitov, D. A. Kritskaya, V. C. Bokun, A. N. Ponomarev, K. S. Novikova, E. A. Sanginov and Y. A. Dobrovolsky, *Solid State Ionics*, 2016, **286**, 135.
149 Q. Qiu, J.-H. Cha, Y.-W. Choi, J.-H. Choi, J. Shin and Y.-S. Lee, *Desalination*, 2017, **417**, 87.
150 O. ul Haq, J.-H. Choi and Y.-S. Lee, *React. Funct. Polym.*, 2018, **132**, 36.
151 D. V. Golubenko and A. B. Yaroslavtsev, *Mendeleev Commun.*, 2017, **27**, 572.
152 D. V. Golubenko, B. Van der Bruggen and A. B. Yaroslavtsev, *J. Appl. Polym. Sci.*, 2020, **137**, 48656.
153 M. M. Nasef, *Chem. Rev.*, 2014, **114**, 12278.
154 A. N. Ponomarev, E. F. Abdrashitov, D. A. Kritskaya, V. Ch. Bokun, E. A. Sanginov and Yu. A. Dobrovol'skii, *Russ. J. Electrochem.*, 2017, **53**, 589 (*Elektrokhimiya*, 2017, **53**, 666).
155 J. Ma, J. Peng and M. Zhai, in *Radiation Technology for Advanced Materials: From Basic to Modern Applications*, eds. J. Ma, J. Peng and M. Zhai, Academic Press, 2019, ch. 7, pp. 207–247.
156 J. R. Varcoe and R. C. T. Slade, *Fuel Cells*, 2005, **5**, 187.
157 M. Bellini, M. V. Pagliaro, A. Lenarda, P. Fornasiero, M. Marelli, C. Evangelisti, M. Innocenti, Q. Jia, S. Mukerjee, J. Jankovic, L. Wang, J. R. Varcoe, C. B. Krishnamurthy, I. Grinberg, E. Davydova, D. R. Dekel, H. A. Miller and F. Vizza, *ACS Appl. Energy Mater.*, 2019, **2**, 4999.
158 T. J. Omasta, A. M. Park, J. M. LaManna, Y. Zhang, X. Peng, L. Wang, D. L. Jacobson, J. R. Varcoe, D. S. Hussey, B. S. Pivovar and W. E. Mustain, *Energy Environ. Sci.*, 2018, **11**, 551.
159 D. R. Dekel, *J. Power Sources*, 2018, **375**, 158.
160 F. Xu, Y. Su and B. Lin, *Front. Mater.*, 2020, **7**, 4.
161 G. Merle, M. Wessling and D. C. Nijmeijer, *J. Membr. Sci.*, 2011, **377**, 1.
162 S. M. Alia and Y. Yan, *J. Electrochem. Soc.*, 2015, **162**, F849.
163 H. A. Miller, F. Vizza, M. Marelli, A. Zadick, A. Zadick, L. Dubau, M. Chatenet, S. Geiger, S. Cherevko, H. Doan, R. K. Pavlicek, S. Mukerjee and D. R. Dekel, *Nano Energy*, 2017, **33**, 293.
164 Y. He, J. Pan, L. Wu, Y. Zhu, X. Ge, J. Ran, Z. J. Yang and T. Xu, *Sci. Rep.*, 2015, **5**, 13417.
165 L. Wang, J. J. Brink, Y. Liu, A. M. Herring, J. Ponce-González, D. K. Whelligan and J. R. Varcoe, *Energy Environ. Sci.*, 2017, **10**, 2154.
166 J. Hou, Y. Liu, Q. Ge, Z. Yang, L. Wu and T. Xu, *J. Power Sources*, 2018, **375**, 404.
167 Y. Wang, D. Zhang, X. Liang, M. A. Shehzad, X. Xiao, Y. Zhu, X. Ge, J. Zhang, Z. Ge, L. Wu and T. Xu, *J. Membr. Sci.*, 2020, **595**, 117483.
168 K. M. Meek, C. M. Reed, B. Pivovar, K.-D. Kreuer, J. R. Varcoe and R. Bance-Soualhi, *RSC Adv.*, 2020, **10**, 36467.
169 L. Wang, M. Bellini, H. A. Miller and J. R. Varcoe, *J. Mater. Chem. A*, 2018, **6**, 15404.
170 T. J. Omasta, L. Wang, X. Peng, C. A. Lewis, J. R. Varcoe and W. E. Mustain, *J. Power Sources*, 2018, **375**, 205.
171 Y. Zheng, T. J. Omasta, X. Peng, L. Wang, J. R. Varcoe, B. S. Pivovar and W. E. Mustain, *Energy Environ. Sci.*, 2019, **12**, 2806.
172 Y. Zheng, G. Huang, L. Wang, J. R. Varcoe, P. A. Kohl and W. E. Mustain, *J. Power Sources*, 2020, **467**, 228350.
173 F. Barbir, *PEM Fuel Cells: Theory and Practice*, 2nd edn., Academic Press, 2012.
174 I. A. Stenina and A. B. Yaroslavtsev, *Pure Appl. Chem.*, 2017, **89**, 1185.
175 M. C. Elvington, H. Colyn-Mercado, S. McCatty, S. G. Stone and D. T. Hobbs, *J. Power Sources*, 2010, **195**, 2823.
176 R. E. Rosli, A. B. Sulong, W. R. W. Daud, M. A. Zulkifley, T. Husaini, M. I. Rosli, E. H. Majlan and M. A. Haque, *Int. J. Hydrogen Energy*, 2017, **42**, 9293.
177 V. Vijayakumar, K. Kim and S. Y. Nam, *Appl. Chem. Eng.*, 2019, **30**, 643.
178 J. Mader, L. Xiao, T. J. Schmidt and B. C. Benicewicz, *Adv. Polym. Sci.*, 2008, **216**, 63.
179 M. A. Haque, A. B. Sulong, K. S. Loh, E. H. Majlan and R. E. Rosli, *Int. J. Hydrogen Energy*, 2017, **42**, 9156.
180 A. Kalathil, A. Raghavan and B. Kandasubramanian, *Polym.-Plast. Technol. Mater.*, 2019, **58**, 465.
181 N. N. Krishnan, D. Joseph, N. M. H. Duong, A. Konovalova, J. H. Jang, H.-J. Kim, S. W. Nam and D. Henkensmeier, *J. Membr. Sci.*, 2017, **544**, 416.
182 Harilal, R. Nayak, P. C. Ghosh and T. Jana, *ACS Appl. Polym. Mater.*, 2020, **2**, 3161.
183 T. Ossiander, C. Heinzl, S. Gleich, F. Schönberger, P. Völk, M. Welsch and C. Scheu, *J. Membr. Sci.*, 2014, **454**, 12.
184 Z. Yue, Y.-B. Cai and S. Xu, *Int. J. Hydrogen Energy*, 2016, **41**, 10421.
185 M. Hu, J. Ni, B. Zhang, S. Neelakandan and L. Wang, *J. Power Sources*, 2018, **389**, 222.
186 J. Yang, H. Jiang, L. Gao, J. Wang, Y. Xu and R. He, *Int. J. Hydrogen Energy*, 2018, **43**, 3299.
187 M. S. Kondratenko, I. I. Ponomarev, M. O. Gallyamov, D. Y. Razorenov, Y. A. Volkova, E. P. Kharitonova and A. R. Khokhlov, *Beilstein J. Nanotechnol.*, 2013, **4**, 481.
188 N. N. Krishnan, S. Lee, R. V. Ghorpade, A. Konovalova, J. H. Jang, H.-J. Kim, J. Han, D. Henkensmeier and H. Han, *J. Membr. Sci.*, 2018, **560**, 11.
189 A. A. Lysova, I. I. Ponomarev and A. B. Yaroslavtsev, *Solid State Ionics*, 2011, **188**, 132.
190 A. A. Lysova, A. B. Yaroslavtsev and I. I. Ponomarev, *Russ. J. Inorg. Chem.*, 2012, **57**, 1 (*Zh. Neorg. Khim.*, 2012, **57**, 3).
191 Y. Özdemir, N. Üregen and Y. Devrim, *Int. J. Hydrogen Energy*, 2017, **42**, 2648.
192 X. Sun, S. C. Simonsen, T. Norby and A. Chatzitakis, *Membranes*, 2019, **9**, 83.
193 E. Quartarone, S. Angioni and P. Mustarelli, *Materials*, 2017, **10**, 687.
194 S. Kumar, B. Sana, D. Mathew, G. Unnikrishnan, T. Jana and K. S. S. Kumar, *Polymer*, 2018, **145**, 434.
195 A. A. Lysova, I. A. Stenina, A. O. Volkov, I. I. Ponomarev and A. B. Yaroslavtsev, *Solid State Ionics*, 2019, **329**, 25.
196 A. A. Lysova, I. I. Ponomarev and A. B. Yaroslavtsev, *Mendeleev Commun.*, 2019, **29**, 403.
197 A. A. Lysova, P. A. Yurova, I. A. Stenina, I. I. Ponomarev, G. Pourcelly and A. B. Yaroslavtsev, *Ionics*, 2020, **26**, 1853.
198 P. Sun, Z. Li and S. Wang, *J. Membr. Sci.*, 2018, **549**, 660.
199 Iv. I. Ponomarev, I. I. Ponomarev, P. V. Petrovskii, Yu. A. Volkova, D. Yu. Razorenov, I. B. Goryunova, Z. A. Starikova, A. I. Fomenkov and A. R. Khokhlov, *Dokl. Chem.*, 2010, **432**, 168 (*Dokl. Akad. Nauk*, 2010, **432**, 632).
200 S. Balakondareddy and J. Tushar, *Eur. Polym. J.*, 2016, **84**, 421.
201 A. A. Lysova, Iv. I. Ponomarev, Yu. A. Volkova, I. I. Ponomarev and A. B. Yaroslavtsev, *Pet. Chem.*, 2018, **58**, 958 (*Membr. Membr. Tekhnol.*, 2018, **8**, 353).

202 A. Siria, M. L. Bocquet and L. Bocquet, *Nat. Rev. Chem*., 2017, **1**, 0091.
203 A. Alkaisi, R. Mossad and A. Sharifian-Barforoush, *Energy Procedia*, 2017, **110**, 268.
204 D. Curto, V. Franzitta and A. Guercio, *Appl. Sci*., 2021, **11**, 670.
205 A. H. Avci, D. A. Messana, S. Santoro, R. A. Tufa, E. Curcio, G. Di Profio and E. Fontananova, *Membranes*, 2020, **10**, 168.
206 A. P. Straub, A. Deshmukh and M. Elimelech, *Energy Environ. Sci.*, 2016, **9**, 31.
207 G. O'Toole, L. Jones, C. Coutinho, C. Hayes, M. Napoles and A. Achilli, *Desalination*, 2016, **389**, 39.
208 C. Lee, S. H. Chae, E. Yang, S. Kim, J. H. Kim and I. S. Kim, *Desalination*, 2020, **491**, 114501.
209 C. Tristán, M. Fallanza, R. Ibáñez and I. Ortiz, *Appl. Sci*., 2020, **10**, 7317.
210 A. Zoungrana and M. Çakmakci, *Int. J. Energy Res*., 2020, https://doi.org/10.1002/er.6062.
211 M. Vanoppen, E. Criel, G. Walpot, D. A. Vermaas and A. Verliefde, *npj Clean Water*, 2018, **1**, 9, https://doi.org/10.1038/s41545-018-0010-1.
212 J. Moreno, S. Grasman, R. Van Engelen and K. Nijmeijer, *Environ. Sci. Technol*., 2018, **52**, 10856.
213 S. I. Sharudin, P. S. Goh, A. F. Ismail and N. B. Cheer, *J. Membr. Sci. Res*., 2020, **6**, 168.
214 J. Veerman, R. M. De Jong, M. Saakes, S. J. Metz and G. J. Harmsen, *J. Membr. Sci*., 2009, **343**, 7.
215 D. A. Vermaas, M. Saakes and K. Nijmeijer, *Environ. Sci. Technol*., 2011, **45**, 7089.
216 E. Güler, R. Elizen, D. Vermaas, M. Saakes and K. Nijmeijer, *J. Membr. Sci*., 2013, **446**, 266.
217 E. Güler, R. Elizen, M. Saakes and K. Nijmeijer, *J. Membr. Sci*., 2014, **458**, 136.
218 E. Altıok, T. Z. Kaya, E. Güler, N. Kabay and M. Bryjak, *Water*, 2021, **13**, 814.
219 M. Tedesco, E. Brauns, A. Cipollina, G. Micale, P. Modica, G. Russo and J. Helsen, *J. Membr. Sci*., 2015, **492**, 9.
220 D. A. Vermaas, M. Saakes and K. Nijmeijer, *Fuel Energy Abstr.*, 2011, **385**, 234.
221 D.-K. Kim, C. Duan, Y.-F. Chen and A. Majumdar, *Microfluid. Nanofluid.*, 2010, **9**, 1215.
222 B. D. Kang, H. J. Kim, M. G. Lee and D.-K. Kim, *Energy*, 2015, **86**, 525.
223 M. M. Nasef and O. Güven, *Prog. Polym. Sci*., 2012, **37**, 1597.
224 T. R. Willson, I. Hamerton, J. R. Varcoe and R. Bance-Soualhi, *Sustainable Energy Fuels*, 2019, **3**, 1682.
225 D. V. Golubenko, E. Yu. Safronova, A. B. Ilyin, N. V. Shevlyakova, V. A. Tverskoi, L. Dammak, D. Grande and A. B. Yaroslavtsev, *Mater. Chem. Phys*., 2017, **197**, 192.
226 X. Tong, B. Zhang and Y. Chen, *J. Membr. Sci*., 2016, **516**, 162.
227 H. Susanto, M. Fitrianingtyas, A. M. Samsudin and A. Syakur, *Int. J. Energy Res*., 2017, **41**, 1474.
228 S. Pawlowski, R. M. Huertas, C. F. Galinha, J. G. Crespo and S. Velizarov, *Desalination*, 2020, **476**, 114183.
229 J. Moreno, V. Díez, M. Saakes and K. Nijmeijer, *J. Membr. Sci*., 2018, **550**, 155.
230 M. Vaselbehagh, H. Karkhanechi, R. Takagi and H. Matsuyama, *J. Membr. Sci*., 2017, **530**, 232.
231 J.-H. Han, N. Jeong, C.-S. Kim, K. S. Hwang, H. Kim, J.-Y. Nam, E. Jwa, S.-C. Yang and J. Choi, *Water Res.*, 2019, **166**, 115078.
232 J. Xia, G. Eigenberger, H. Strathmann and U. Nieken, *J. Membr. Sci*., 2018, **565**, 157.
233 J. Xia, G. Eigenberger, H. Strathmann and U. Nieken, *Processes*, 2020, **8**, 99.

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