Polymer of Intrinsic Microporosity as Binders for both Acidic and Alkaline Oxygen Reduction Electrocatalysis

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In this work a new polymeric binder (PIM-1) to prepare and characterize composite material to form cathodes for the oxygen reduction reaction has been investigated and discussed. The new binder is a Polymer of Intrinsic Microporosity (PIM), a family of organic compounds with molecularly rigid (glassy) structure with good mechanical and chemical stability. Their influence on electrocatalytic behaviour of a commercial electrocatalyst during the oxygen reduction reaction in acidic and alkaline media has been investigated and discussed compared to the behaviour of common cationic and anionic polymer binders, using rotating disk electrode (RDE) techniques. Polymers of intrinsic microporosity perform similarly well, and sometimes better (due to rigidity and gas permeation), when compared to commercial binders. Thus, polymers of intrinsic microporosity do represent a very promising and versatile alternative as binder in electrocatalysis.

Introduction

Nowadays, for our lives and wellbeing, energy is fundamental and this energy mainly comes from fossil fuels. Fossil fuels belong to the class of non-renewable energy sources and their combustion produces CO_2, NO_x and SO_2, increasing pollution

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and greenhouse gases issues. On the other hand, renewable energy sources are those sources which are replenished on human timescale. This category comprises wind energy, solar energy, geothermal energy, hydropower, and bioenergy, but till now their use is not sufficient to reverse the actual increasing in fossil fuel exploitation. A significant contribution to the fossil fuels consumption is due to the transport sector.[1] Thus, to revert the actual situation it is necessary to find a valuable alternative especially for the automotive industry. In this context, a well-suited candidate is hydrogen. Hydrogen is not present as a natural resource on earth but can be produced from water using renewable energy sources.[2] Actually, hydrogen produced by water electrolysis (WaEl) using renewable energy sources, the so-called Green Hydrogen, can be "burnt" in fuel cells (FCs) to produce electrical energy and water. This is the paradigm of the Circular Economy: from water to hydrogen (WaEl), from hydrogen to water (FC).[3–6] To achieve this, new materials for active composite electrodes must be investigated to optimize the energy efficiency of the electrodes in both FC and WaEl systems. Moreover, with the aim of "merging" the two systems (FC and WaEl) to produce a single device able to perform both processes, the so-called reversible fuel cell (RFC), the electrode material must be very versatile, not only because it must withstand the chemical and mechanical harsh conditions of the reaction environment, but also because it should ideally work in both alkaline and acidic media. RFCs working at low temperature typically use a polymeric electrolyte, acidic or alkaline, on both sides of the composite electrodes, formed by catalyst powder, electronic conductor and gluing agent. In this view, also the membrane electrode assembly (MEA) must be implemented to allow gases to go in and out. Indeed, in RFCs at both electrodes, the chemical reactions involve a three-phase boundary at which the three main "actors" of the process, namely gas (hydrogen or oxygen), electrolyte and electron-active material (metals, etc.), must meet to exchange electrons, thus realizing a triple contact. Clearly, the larger the triple contact area, the faster the electron transfer. Hence, it is of

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paramount importance to design and develop materials that allow the formation of a triple contact area as wide as possible. Such materials can include zeolites, clays, metal-organic frameworks, porous carbons or metallic clusters.[7–9] In addition, the triple contact can be successfully realized employing gas diffusion electrodes (GDE), which constitute the core of the RFC. GDE shows a porous sandwich structure, composed by three layers:[10,11] (i) the gas diffusion layer (GDL), mainly based on carbon; (ii) the catalyst layer (CL), composed by the catalyst dispersed on carbon matrix; and (iii) the current collector (CC). Therefore, the addition of a specific binder, as gluing agent, is fundamental to prepare a mechanically stable electrode that guarantees the formation of a large area of triple contact. Generally, these binders are non-conductive polymers (e.g., PVDF, PBI or PTFE) for the GDE surface facing the gas side of a RFC, whereas ion-conductive polymers (e.g., Nafion® ionomer) are used for the other surface that is in contact with the polymeric electrolyte. It is worth underlining that it's a good practice to use a conductive ionomer of the same chemical structure and charge of the polymer composing the solid electrolyte i.e., cationic for proton exchange membrane RFC (PEMRFC) and anionic for anion exchange membrane RFC (AEMRFC). The specific mechanical properties, gas transfer features, and solubility of these binders determine the overall performance of the whole fuel cell.[12,13] Paulus et al.[14] evidenced how the diffusion resistance of electroactive species in the pores of Nafion® can strongly hamper the kinetics performance of the system itself. They stated that only with less than 0.2 μm thickness of Nafion® film on the catalyst particles it is possible to perform an electrochemical kinetics characterization by RDE technique.

Notably, the preparation and formation of MEA represent one of the crucial steps that can affect the entire performance of the RFC. The above-mentioned arguments clearly indicate the strategy for preparing new gluing agents. The polymer must:

- be stable in the harsh condition of the anodic and cathodic chamber of RFCs;
- allow a faster diffusion of gasses in and out RFC;
- enlarge the triple boundary phase region;
- allow a fast and simple formation of the GDE, independently whether it is used in a PEMRFC or an AEMRFC.

In this context, polymers of intrinsic microporosity (PIMs) used as binder to prepare the GDE can be the appropriate choice to increase the stability and performance of electrodes applied in FC, electrolysers and RFC.[15–19] PIMs are an interesting, promising and relatively new class of substances with many applications in different fields. They are organic compounds which are formed via condensation (polymerization) reactions among different precursors, typically a rigid compound, like 2,6,(7)-diamino-9,10-dimethylethanoanthracene or 5,5',(6),(6')-diamino-3,3,3',3'-tetramethyl-1,1'-spirobisindane, coupled with Tröger's base or other compounds. The peculiarity of PIMs is their high structural rigidity that causes an inefficient packing, resulting in the presence of a large number of voids with dimension around 0.3–2.0 nm,[20,21] thus leading to a very high specific surface area i.e., up to 1000–2000 m² g⁻¹.[22,23] PIMs are

structurally rigid because in the chemical structure there are no single bonds and there is no way the molecule could fold or change shape. Moreover, they show high thermal stability, since they do not decompose up to 260 °C, and they can be even vacuum carbonized at 500 °C still retaining their microporosity without structure collapse.[24] In addition, they possess good chemical stability, both in acidic and alkaline media, high mechanical strength, easy handling and processability.[25] Several Authors[26,27] delved deeper in assessing PIM-1's stability under harsh conditions, evidencing its successful hydrolysis only under severe circumstances, such as in highly concentrated acids ($H_2SO_4 > 95\%$/glacial acetic acid at 150 °C for 24–48 h) or bases (20% NaOH for a prolonged period of about 360 h.[28] Hence, to the authors' best knowledge, PIM-1 polymer may be considered highly stable, especially if operating in mild environments and at low temperatures.

Furthermore, most of PIM compounds are fully soluble in common organic solvents (such as chloroform, isopropanol, and acetonitrile) at room temperature, leading to an easy preparation of inks containing the electrocatalytic powder to be employed either to investigate the behaviour of the catalyst or to develop new MEA. The most studied applications of PIMs regard gas separation.[29–32] Thanks to their rigid structure and microporosity, they exhibit fast ion transport, high permeability and selectivity toward many different gases (in particular H_2).[25] In addition to gas separation and gas storage applications, PIMs are also exploited as active components in optical sensors or as ionic diodes.[33] More recently, they have been also exploited in electrochemical applications[18,34] as in electrocatalysis. For instance, Sun et al.[35] reported a novel ionomer based on the strategical incorporation of fluorinated and phosphonated groups in the PIM's local side chains, resulting in promising performances when added to MEA. Particularly, a lower mass transfer resistance was observed with a peak power density much greater than those of commercially available porous binders. Besides, another study by Tan et al.[36] shed light on the design of innovative PIMs modified with ethanoanthracene, benzo-methanoanthracene or dimethylbiphenyl moieties evidencing exquisite sub-nanometric pore structure, which can play a critical role in reaching fast ion transport and molecular selectivity. However, some degradation phenomena and crossover of organic molecules was observed when used in redox flow batteries, therefore further studies are required to fully elucidate the subsequent battery's decay.

Furthermore, PIMs are very versatile, since they can be used as films deposited onto the electrode surface or to embed the catalyst particles in the micropores. In any case, PIMs can give many advantages that comprise enhanced electrocatalyst stability, introduction of molecular selectivity and they can promote the formation of a triple interphase.[21,37] Marken et al.[38] studied the effect of PIMs as protecting binders on stability and durability of electrocatalytic powder and supports of FCs, as they can suffer from dissolution, Ostwald ripening, nanoparticles aggregation, migration and support corrosion when FCs operate. Moreover, PIMs have been studied to increase the concentration of reacting gases in proximity of the electrode surface, due to their capacity of creating a reacting-
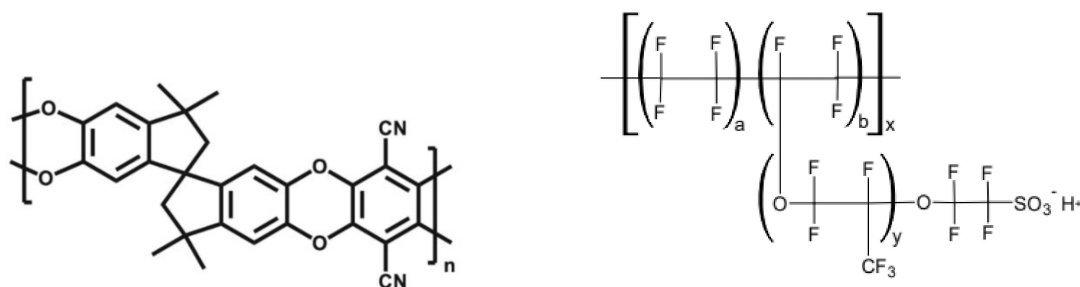
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Figure 1. PIM-1 and Nafion® molecular structures.

gas supersaturated environment, characterized by the presence of very small bubbles as close as possible to the electrode surface but not in direct contact with it.[39] Finally, in the very recent years, PIMs have found actual applications in real electrochemical systems with industrial applicability, in particular for energy storage,[40,41] selective electrocatalysis,[42] and as catalyst binder.[43–45]

In this work, PIM-1 (represented in Figure 1 together with Nafion® structure) has been electrochemically characterized as gluing agent added to inks containing an electrocatalytic powder: Pt on Vulcan XC-72. Different slurries have been drop-casted onto the surface of a glassy carbon (GC) disk of a rotating disk electrode (RDE), used as cathode for the oxygen reduction reaction (ORR) in alkaline and acidic media, far from the environment in which the nitrile group can be easily hydrolyse.[46,47]

The characterization was carried out preparing slurries with different content of PIM-1 and comparing the catalytic activity of electrodes containing PIM-1 with electrodes formed by the same electrocatalytic powder (Pt on Vulcan XC-72) but with two different binders: a cationic and an anionic one. The aims were: (i) to investigate the effects of the different PIM-1 concentrations on the electrochemical behaviour of the catalyst; (ii) to study the effect of alkaline or acidic media on the electrocatalyst in the presence of the three different binders; (iii) to verify the performance of the selected catalytic powder mixed with PIM-1, both in acidic and alkaline environment, in comparison with the same catalytic system mixed to benchmark binders.

This comparative study aims to highlight the possibility of substituting the commercial available binders with PIM-1, to rapidly prepare GDEs or MEAs for RFCs, independently on the pH values at which the electrochemical system will operate. PIM-1 has been chosen among the PIMs family due to its highest oxygen and hydrogen permeability.[19]

Experimental Section

PIM-1 was synthetized as described in the literature.[48] All solutions were prepared using MilliQ water (Millipore) to dilute $HClO_4$ (Sigma–Aldrich) or KOH (Fluka). The ink was prepared by dissolving 1 mg of Pt on Vulcan XC-72 (Pt E-Tek®, 30% of Pt) in 1 mL of chloroform (Sigma–Aldrich). The investigated binding agents were:

- PIM-1, dissolved in chloroform (Sigma–Aldrich), 0.15% in weight;

- Nafion® 117, as cationic ionomer dissolved in isopropanol (Sigma–Aldrich), 0.15% in weight;
- AS-4 Tokuyama, as anionic ionomer dissolved in isopropanol (Sigma–Aldrich), 0.15% in weight.

The selected binder, which present pore dimension very similar (1-2 nm) in order to prevent any possible diffusive limitations, was added to the ink using the adequate volume to obtain different binder-to-powder ratio, see Table 1. The obtained slurry was sonicated for 15 minutes and 30 μL (10 μl for 3 times) were drop-casted onto 5 mm diameter GC disk of RDE tip (0.05 mg_{Pt} cm^{-2}) and let it dry overnight, covered by a beaker to avoid dust or any other possible impurities. RDE tip surface was pre-treated before ink deposition. GC surface was lapped using sandpapers of increasing grit and lastly a 0.05 μm alumina slurry. To investigate the effect of the binder amount, different electrodes (#=number), with different binder-to-powder ratio, were prepared (see Table 1), and tested in aqueous 0.1 M $HClO_4$ or 0.1 M KOH.

All electrochemical characterizations were conducted with a Taccusel RDE rotor connected to an EG&G PAR 263 A potentiostat/galvanostat driven by Corrware (Scribner). GC rod and saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. In KOH, a double bridge with 0.5 M KNO_3 was used together with the SCE. In the present work, all the potentials are referred to the reversible hydrogen electrode (RHE).

Table 1. The different modified electrode prepared and tested.

#	Binder	Binder/Pt E-Tek®	Tested in
1	Nafion®	1:100	0.1 M $HClO_4$
2		1:70	
3		1:50	
4		1:25	
5	Tokuyama	1:100	0.1 M KOH
6		1:70	
7		1:50	
8		1:25	
9	PIM-1	1:100	0.1 M $HClO_4$
10		1:70	
11		1:50	
12		1:25	
13	PIM-1	1:100	0.1 M KOH
14		1:70	
15		1:50	
16		1:25	

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The conversion has been carried out using the following equation [Eq. (1)]:

$$E_{RHE} = E_{SCE} + 0.244 + 0.059 \times pH \quad (1)$$

where E_{RHE} is the potential referred to RHE; E_{SCE} is the experimental potential vs. SCE; pH = 1 or pH = 13 have been used for 0.1 M HClO₄ and 0.1 M KOH, respectively. Before each run, the solution was deaerated with N₂, for 15 minutes, to obtain the "zero" CV, ranging the potential from 1.1 V to 0.1 V vs. RHE at 5 mV·s⁻¹ twice (4 half-cycles), at 1400 RPM. Then the solution was purged with O₂ for 15 minutes and the above-described CV measurement was repeated at 800, 1000, 1200, 1400, 1600, and at 1800 RPM. All the experiments were carried out at 25 °C. The RDE tip was immersed in the relevant solution and the experiment started immediately. The tip remained in the solution at pH 13 or 1 for about 2 hours.

The onset potentials were determined as the intersection point between x-axis and line obtained by interpolating the experimental data of the RDE measurements after the current rising (magenta line in Figure 2B). All the currents discussed in this paper, normalized by the geometric area, have been corrected by subtracting the "zero" CV current obtained in N₂ degassed solution.

Results and Discussion

The aim of this work is to highlight the possibility of replacing the largely used commercial binders in MEAs and GDEs. Usually, alcoholic solutions of cationic or anionic ionomers are employed to prepare the slurries used as precursors of MEA formation. Herein, we investigate PIM-1 as a microporous binding agent for both alkaline and acidic environments. The investigation is carried out analysing the catalytic activity, by RDE technique, of Pt E-Tek® mixed with: (i) Nafion® ionomer; (ii) Tokuyama ionomer; (iii) PIM-1 solution. The typical figures of merit obtained by this study are: electron transfer number for ORR, onset potentials of ORR and Tafel slope. Moreover, to allow for a better comparison among different binders, we decided to use the kinetically controlled current density at 0.8 V vs. RHE,[14] where no mass-transport effects are present, normalized for the Pt load. RDE experiments and Koutecky–

Levich (K–L) analysis have been employed to obtain the electrochemical parameters described above. The K–L equation is [Eq. (2)]:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_L} = \frac{1}{j_k} + \frac{1}{0.62 \, n \, F \, D^{2/3} \, v^{-1/6} \, c_0} \cdot \frac{1}{\omega^{1/2}} \quad (2)$$

where j is the recorded current density at a given RPM (mA cm⁻²); j_k is the kinetic-limited current density (mA cm⁻²); j_L is the mass-transfer-limited current density (mA cm⁻²); n is the electron transfer number for mole of oxygen; F is the Faraday constant (C·(mol of e⁻)⁻¹); D is the diffusion coefficient of the oxygen (cm²s⁻¹); v is the kinematic viscosity (cm²s⁻¹); c_0 is the oxygen concentration in the bulk electrolyte (mol cm⁻³); ω is the RPM in rad·s⁻¹. The electron transfer number per molecule of oxygen, n, is obtained from the slope of Equation (1) [Eq. (3)].

$$n = \frac{1}{0.62 \, slope \, F \, D^{2/3} \, v^{-1/6} \, c_0} \quad (3)$$

using D, v and c_0 from Ref. [49].

The RDE plots in the kinetic regime have been used to obtain the Tafel slopes and the mass activity (MA, mA·mg_Pt) at 0.8 V vs. RHE for the different investigated electrodes.

In Figure 2A and B, typical 3rd half CV cycles, carried out with PIM-1 and Nafion® in 0.1 M HClO₄ and PIM-1 and Tokuyama in 0.1 M KOH, are presented together with the bare GC curve (black line). For the sake of clarity only the ratio 1:70 using a rotation rate at 1600 RPM is here presented. These plots, for all the investigated electrodes listed in Table 1, are used to extrapolate the onset potentials, listed in Table 2.

It is clear, from onset potential values of Table 2, that the presence of PIM-1 does not reduce, alter or impede the ORR in comparison to the most employed Nafion® or Tokuyama, which conversely shows a very constant onset potential, independently on the amount used in the slurry preparation. Indeed, Nafion® and Tokuyama confirm their good behaviour in acidic
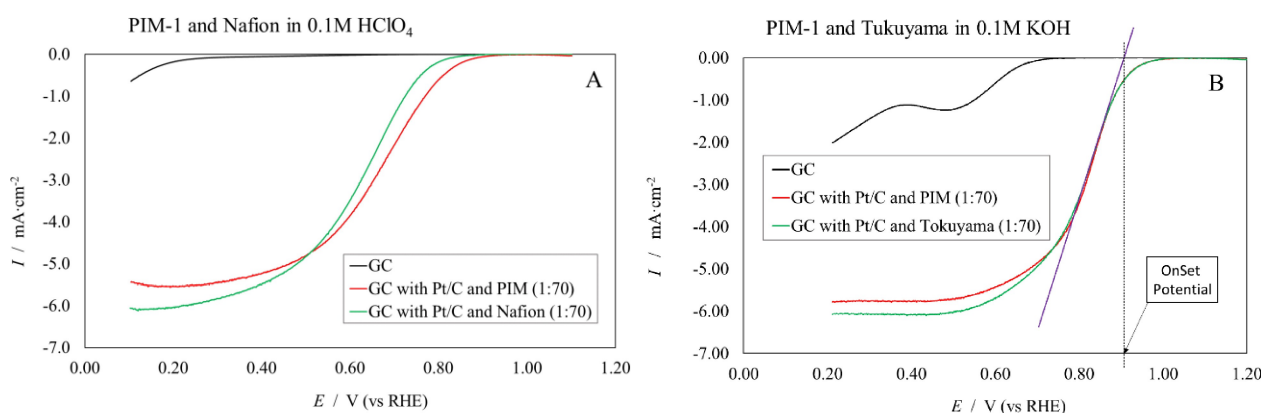

Figure 2. A) RDE data for PIM-1 and Nafion® in 0.1 M HClO₄ with the same amount of electrocatalytic powder, Pt E-Tek®. **B)** RDE data for PIM-1 and Tokuyama® in 0.1 M KOH with the same amount of electrocatalytic powder, Pt E-Tek®. Magenta line evidences the onset potential for these electrodes. Binder to Pt E-Tek® ratio 1:70. Scan rate is 5 mV s⁻¹. Rotating speed is 1600 RPM.

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Table 2. Electron transfer number for the different investigated electrodes.

| #	Binder/Pt E-Tek®		n. e⁻	std. dev.	Onset potential
1	1:100	Nafion in 0.1 M HClO₄	3.91	0.03	0.853
2	1:70		4.02	0.09	0.765
3	1:50		3.72	0.20	0.804
4	1:25		4.53	0.34	0.736
5	1:100	Tokuyama in 0.1 M KOH	4.15	0.02	0.959
6	1:70		4.04	0.02	0.964
7	1:50		3.59	0.02	0.973
8	1:25		3.65	0.03	0.949
9	1:100	PIM-1 in 0.1 M HClO₄	4.50	0.09	0.907
10	1:70		3.53	0.03	0.872
11	1:50		3.36	0.06	0.895
12	1:25		4.15	0.07	0.820
13	1:100	PIM-1 in 0.1 M KOH	4.04	0.07	0.951
14	1:70		3.57	0.03	0.955
15	1:50		4.02	0.01	0.915
16	1:25		4.59	0.15	0.903

and alkaline media, respectively, when used as binders with an active electrocatalytic powder, as Pt E-Tek®. Furthermore, this study gives also evidences of the better behaviour of Tokuyama® with respect to Nafion®, highlighted by the highest onset potentials (see column 5th rows 1st to 8th, Table 2).

Regarding the proposed new binder, PIM-1 in acidic environment is clearly better than Nafion®, especially in terms of onset potentials, as clearly visible from values in Table 2 (column 5th, rows 1st to 4th and 9th to12th). On the other hand, PIM-1 seems to lead toward a decreasing of the Pt E-Tek® electrocatalytic activity with the increasing of gluing agent amount used to prepare the slurries, as emerges from the comparison of onset potentials (see column 5th rows 11th to14th), probably due to the difficulty of H⁺ to diffuse inside the PIM-1 pores.[19] We can speculate that increasing the amount of PIM-1 in the slurry we increase both the hydrophobicity of the layer around the electrocatalytic particles deposited on RDE tip and the path length ions have to cross to reach the electrocatalyst,

thus reducing the mobility of the electroactive species and, in turn, the activity of the electrode.

In alkaline environment PIM-1 behaves very similar to Tokuyama® and better than in the acidic conditions. This is evidently connected to the ORR mechanism in alkaline environment, in which the electron transfer rate is fast, as widely described in the literature.[50] Specifically, by increasing the PIM-1 amount in the slurry, a reduction of the onset potential values (i.e., increasing of overpotentials) is visible, however the deactivation of the catalyst is limited and the onset potential decreases of about 50 mV at most.

These effects are also highlighted comparing Figures 3A and B, in which the more scattered RDE curves for PIM-1 are clearly observable, realistically due to a partial loss of catalytic powder from the GC surface. Besides, K—L analysis allows for the determination of important electrode reaction parameters, strictly connected with the activity of the electrocatalytic powder mixed with the selected binder in the slurries during
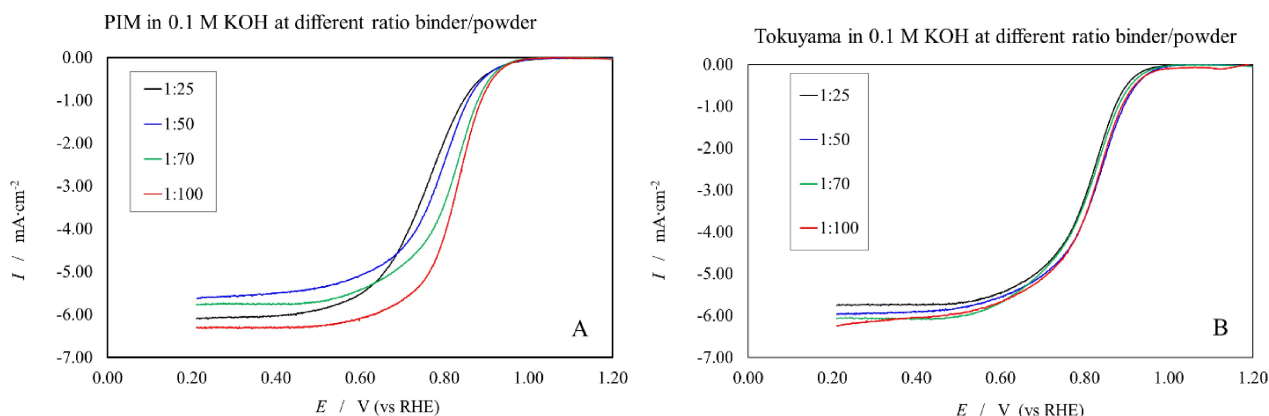
Figure 3. RDE data for PIM-1, **A**, and Tokuyama®, **B**, in 0.1 M KOH saturated with O₂. Scan rate is 5 mV s⁻¹. Rotating speed is 1600 RPM.

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the electrode preparation and used for ORR in acidic and alkaline media. Figures 4A–D show the K–L analysis only for electrodes #2, #6, #10 and #14, carried out in acidic and alkaline environments, respectively. From slopes of K–L plots, the electron transfer number for the investigated electrodes (see Table 1) has been calculated and listed in Table 2.

Electron transfer number (Table 2, column 4th) clearly demonstrates the similar behaviour of PIM-1 when compared with the two commercial binders: the obtained value for PIM-1 is almost 4 in both acidic and alkaline environment, evidencing a 4-electrons pathway reaction for ORR, thus resulting in the possibility of substituting cationic or anionic ionomers as gluing agent in MEA and GDE preparation.

Tafel slopes obtained at low overpotential and mass activity (mA·mg$_{Pt}$) at 0.8 V vs. RHE are presented in Table 3. It is evident the best behaviour of Tokuyama®, both in term of Tafel slopes and MA, with Tafel slope values ranging from 73 to 97 mV·dec^{-1}, almost constant and independent on binder amount, with the only exception in the case of a lower binder amount. In this case, Nafion® and PIM-1 seem to behave better than Tokuyama® (see Table 3, values in column 4th, rows 1st, 5th, 9th and 13th). In addition, Nafion® seems to be the most sensible to binder amount variations, presenting a very low values for MA at all the investigated ratios.

On the other way round, PIM-1 shows a very promising behaviour in alkaline medium, comparable with the anionic binder, both in terms of Tafel slopes, which range from 73 to 112 mV·dec^{-1}, and MA values, even if it demonstrates a

dependence on the total amount used to prepare the slurry containing the electrocatalytic powder. Notably, the present study highlights the increasing of Tafel slope values together with the reduction of the MA by increasing the PIM-1 amount, in both the investigated environments (see Table 3, columns 4th and 5th from row 9th to 16th). This behaviour is in line with the comments relative to the trend of the ORR onset potentials discussed previously. In any case, PIM-1 used to prepare ink containing Pt E-Tek® at the ratio of 1:100 and 1:70 leads to the formation of composite electrodes stable and with similar or better activity for ORR if compared to benchmark gluing agents.

In conclusion PIM-1, used as binder, does not hinder or reduce the electrocatalytic activity of Pt E-Tek® for ORR in acidic and alkaline media. The lower MA values of PIM-1 in acid (see Table 3 column 5th row from 9th to 12th) can be ascribable to the interaction of H$^+$ with the chemical constituents of the PIM-1 backbone.[19] This effect can be largely overcome using Polymers of Intrinsic Microporosity with different chemical structures and void/pore dimensions.[19]

Conclusions

The aim of this work is to highlight the possibility of substituting commercial gluing agent employed to prepare MEA and GDE for FCs and WaEl with polymer of intrinsic microporosity, a new family of polymers with high process-ability, non-toxicity, mechanically rigidity (glassy), and chemi-
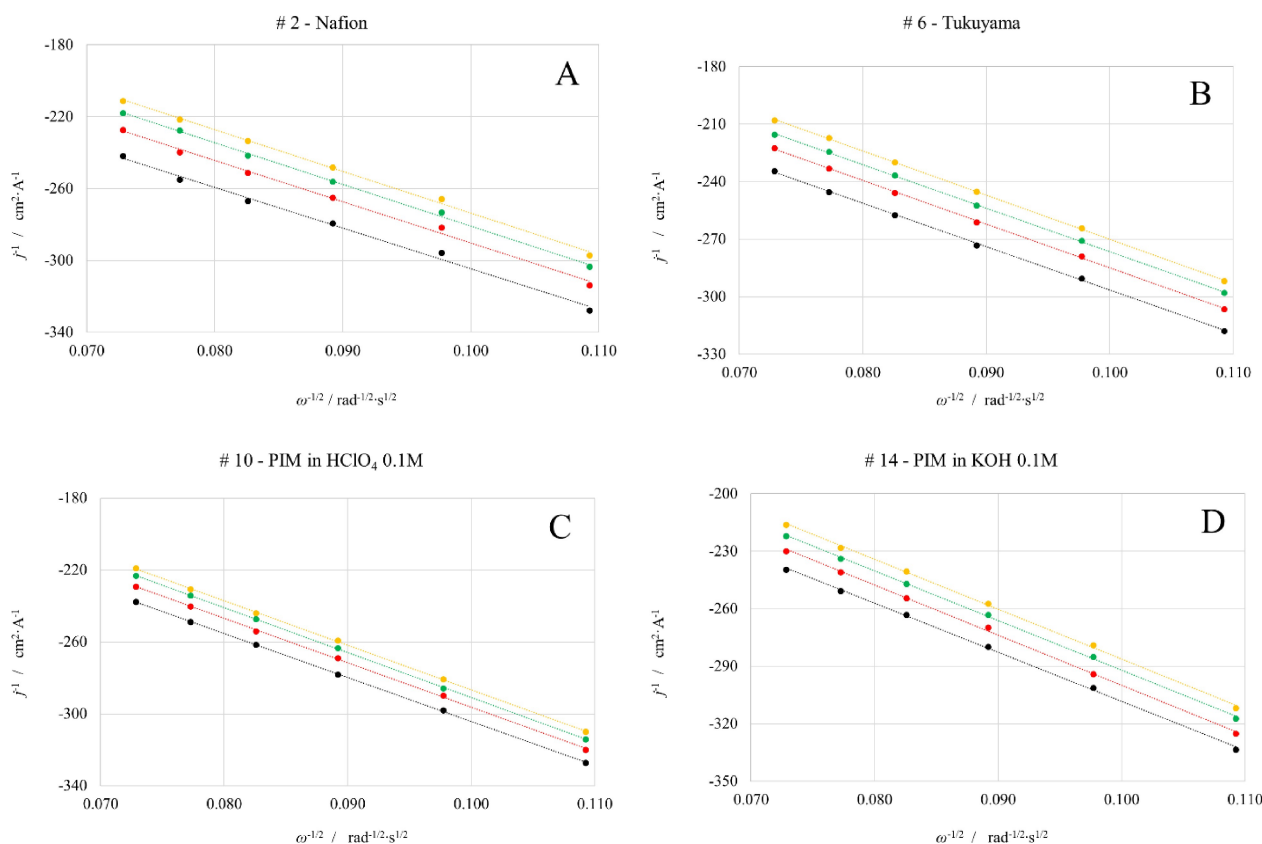

Figure 4. K–L analysis for electrodes #2, #6, #10 and #14.

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Table 3. Tafel slopes at low overpotentials and mass activity @0.9 V *vs.* RHE for the electrodes listed in Table 1.

#	Binder/Pt E-Tek®	Experimental condition	Tafel Slope/mV dec^{-1}	Mass Activity @0.8 V/mA mg$_{Pt}$
1	1:100	Nafion in 0.1 M HClO$_4$	0.066	6.10
2	1:70		0.087	1.00
3	1:50		0.093	1.97
4	1:25		0.093	0.83
5	1:100	Tokuyama in 0.1 M KOH	0.097	19.47
6	1:70		0.079	17.47
7	1:50		0.082	19.50
8	1:25		0.073	17.10
9	1:100	PIM-1 in 0.1 M HClO$_4$	0.056	9.90
10	1:70		0.089	3.26
11	1:50		0.102	4.90
12	1:25		0.105	1.92
13	1:100	PIM-1 in 0.1 M KOH	0.073	22.00
14	1:70		0.072	18.13
15	1:50		0.101	12.90
16	1:25		0.112	10.23

cally stability. These PIMs can be synthesized with different chemical structures for the backbone, thus allowing for a fine control of voids and pores dimension that, in turn, can affect the O$_2$ and H$_2$ diffusion producing a binding agent more versatile than the commercial one. With respect to other commercially available binders, PIM-1 presents a non-charge rigid structure, without fixed charge organic moieties, thus allowing for their utilization in both mild acidic and alkaline environment, far from the pH condition of nitrile groups hydrolysis, due to the easier anions and cations transfer through PIM-1's voids and pores. This rigidity in the polymer chains, due to the lack of single bond around which moieties can rotate, is peculiar for these family of polymer and absent in the case of Tokuyama® and Nafion®. This feature leads to the impossibility for PIM-1's contorted structure to efficiently fold and pack, thus allowing for a better mobility of gasses and ions inside the polymeric matrix. PIM-1 investigated in this work has shown the same behaviour, sometimes even better, of the two widely used ionomer gluing agents, namely Nafion® and Tokuyama®, in affecting the activity of the catalytic powder (Pt ETek®), which has been electrochemically characterized in acidic and alkaline environments toward ORR. All the electrochemical parameters investigated by using RDE and K–L analyses pointed out how PIM-1 does not deeply affect the activity of Pt ETek®, evidencing only a slight decrease of the performance by increasing the PIM-1 amount, especially in acidic medium. Further studies will be devoted to investigating the possible interaction of PIMs with gases at high current densities.

In conclusion, the use of PIM-1 as binding agent to prepare MEAs and GDEs to be used in FCs, WaEls, and RFCs, working at different pH values, seems to be possible and even advantageous, since we were able to show that with a porous non-charge binding agent it is possible to prepare a single catalytic ink that can be used for both acidic and alkaline environments.

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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