Iron Phthalocyanine Knitted Polymers as Electrocatalysts for the Oxygen Reduction Reaction

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ABSTRACT Knitted iron phthalocyanine based porous polymer networks (K-FePcs) were prepared in a single step using solvent knitting strategies with commercial iron phthalocyanine as building monomer. The incorporation of different aryl co-monomers (biphenyl and 1,2,4,5-tetraphenylbenzene) to FePc allowed quantitative yields, high porosities and excellent ORR activity. The reversible Fe(III)/Fe(II) redox potential of FeN₄ centers of the knitted polymer networks in N₂ saturated electrolyte solution (i.e. ca. 0.8 V vs RHE) were shown as good descriptors of their ORR activity. **K-FePc2Ph** presented the highest amount of FeN₄ active sites and an adequate degree of steric hindrance to maintain the isolation between catalytically active sites. Moreover, it displayed comparable current density limits, and superior mass activity and half-wave potential (i.e. 0.88 V vs RHE) than those of 20% Pt/C benchmark catalyst, while keeping higher stability towards methanol oxidation. **K-FePc2Ph** can be an interesting alternative to Pt based ORR electrocatalysts.

INTRODUCTION

Over the past years, numerous attempts to replace platinum-based electrocatalysts for the oxygen reduction reaction (ORR) on the cathodes of fuel cells have been made. For instance, high temperature pyrolytic approaches rendered highly active, non-noble metal (M) catalytic MN_xC centers, although these synthetic methods lack the accurate atomic control to replicate specific monodisperse metal coordination environments and availability.¹⁻⁴ More recently, research has focused on the development of more sustainable nitrogen rich biomimetic macrocycles with adjusted FeN₄C centers, as they are considered one of the most active sites for this reaction.⁵⁻⁸ Among them, iron phthalocyanines (FePcs) have been found particularly suitable as low cost non-precious electrocatalysts for ORR due to their ability to perform the reaction through a direct four-electron pathway from very low overpotentials.⁹ Yet, FePc's poor intermolecular conductivity, which hampers the necessary electron transfer processes, and its lack of electrochemical stability difficult their application. Moreover, self-aggregation of Pc reduces the intermetallic distance and O₂ accessibility, slowing the electron transfer properties for the ORR. The incorporation of different Pcs on the surface of conductive materials, such as porous carbons, carbon nanotubes or reduced graphene can greatly diminish these drawbacks and they have been extensively studied.¹⁰⁻¹⁴ The coupling of different tetrafunctionalized phthalocyanines pioneered in the preparation of conjugated 3D microporous polymers with elevated surface areas and outstanding catalytic activity towards ORR.¹⁵⁻¹⁷ Nevertheless, the use of precious metals and the need of previous functionalization of the Pc

precursors (involving several synthetic steps) limit their practical use.

Knitting strategies have been well established to yield hyper-cross-linked porous aryl polymers from cheap and accessible aromatic monomers.^{18,19} More recently, this approach has been extended towards the use of metal complexes as monomers, where the coordination environment of the final polymer network was preserved.^{20,21} Furthermore, the capability of using different aromatic co-monomers can provide higher degree of steric hindrance maintaining isolation between catalytically active sites.

In this work, the solvent knitting strategy has been used to prepare, for the first time; iron phthalocyanine (FePc) based porous knitted polymer networks from commercial unfunctionalized FePc in quantitative yields, as a new generation of non-pyrolyzed, non-noble metal ORR electrocatalysts. This strategy allows obtaining porous and robust networks in a single synthetic step without using a pre-functionalized phthalocyanine as previously reported for other Pc-containing porous networks.

Either by using Friedel-Crafts reaction, with -CH₂- spacers from the external cross-linker such as dimethoxymethane,¹⁸ or by using Scholl reaction, through aryl-aryl couplings,¹⁹ we were able to prepare structurally different knitted FePc polymer networks (Scheme 1). Thus, the new polymers exhibit diverse chemical composition, different thermal and porous properties but preserved FePc redox properties and activity towards ORR, while improving the stability.

Scheme 1. Synthetic strategy for knitted FePcs porous networks with different linkers

MATERIALS AND METHODS

Materials

Iron (II) phthalocyanine (FePc) was purchased from TCI with a purity >98%; Biphenyl (2Ph) was supplied by Fluka with a purity >98%; Anhydrous FeCl_3 was purchased from Alfa Aesar with 98% of purity; Anhydrous AlCl_3 and dichloroethane (DCE) (extra dry) were supplied by Across Organics with purities >98.5% and >99.8% respectively. Formaldehyde dimethyl acetal (FDA) and solvents were supplied by Aldrich with analytical grade. 1,2,4,5-tetraphenylbenzene (5Ph) was synthesized according with the procedure reported.²² For conductive ink preparation Nafion 117 (5% solution in alcohols) was purchased from Aldrich while carbon black super P (CB) was from Alpha Aesar.

Polymer Synthesis

K-FePc: A solution of 0.200 g (0.35 mmol) of iron phthalocyanine in 15 mL of anhydrous dichloroethane was placed in a Schlenk and purged with nitrogen over 20 min. Then, 3.5 mmol of formaldehyde dimethyl acetal (FDA) and 3.5 mmol of FeCl_3 were carefully added. The mixture was stirred for 48 h at 80°C . The resulting dark green precipitate was collected by filtration and washed with ammonia under stirring for 4 h to remove unreacted FeCl_3 . Then, the suspension was neutralized with HCl and after filtration, the green solid was washed with hot methanol for 24 h. Finally, the polymer was washed with water and THF under stirring. A green product was obtained as fine powder and was dried at 80°C overnight. Yield: 40%

K-FePc2Ph and K-FePc5Ph: A solution of 0.200 g (0.35 mmol) of iron phthalocyanine and 0.35 mmol of biphenyl (for K-FePc2Ph) or 0.35 mmol of 1,2,4,5-tetraphenylbenzene (for K-FePc5Ph) in 30 mL of anhydrous dichloroethane was placed in a Schlenk. The solution was purged with nitrogen over 20 min and then 3.5 mmol of FDA and 3.5 mmol of FeCl_3 were carefully added. The mixture was stirred for 48 h at 80°C . The resulting dark green precipitate was collected by filtration and washed following the same protocol described for K-FePc. Green solids were obtained in quantitative yields.

Conjugated knitting polymer cK-FePc2Ph: A solution of 0.200 g (0.35 mmol) of iron phthalocyanine and 0.35 mmol of biphenyl in 10 mL of chloroform were placed in a Schlenk and purged with nitrogen over 20 min. Then 2.5 mmol of AlCl_3 were carefully added and the mixture was stirred 48 h at 40°C . The resulting dark green precipitate was collected by filtration and washed for 4 h with a solution of HCl in water (4 mL of HCl in 50 mL of water), 12 hours with water and 1 h with

THF water under vigorous stirring. Green solid was obtained in quantitative yield.

Characterization

The solid-state ^{13}C -NMR spectra were recorded in a Bruker AV-400-WB using a 4 mm triple channel probe with ZrO rotors and Kel-F plug at room temperature and at 100.32 MHz. In all cases, the speed of rotation was set at 10 KHz. The spectra were collected using a spectral width of 35 kHz and the chemical shift refers to the CH_2 signal of adamantane (29.5 ppm) as a secondary reference to TMS as the primary reference.

Fourier Transform Infrared Spectra (FT-IR) were recorded on Bruker IFS 66VS Spectrometer ($10,000$ – 50 cm^{-1}).

Raman spectra were recorded at ambient conditions for a 785 nm laser excitation wavelength with a Renishaw invia Raman microscope. The exposure time was 10 s and 25 scans were accumulated. The power used was 5% with grating time 1200 l/min and optical microscope magnification of 50X.

Elemental Analyses were obtained with a LECO CHNS-932 elemental analyzer (C, H, N).

Iron content was determined by quantitative TXRF analysis using a benchtop S2 PicoFox TXRF spectrometer Bruker Nano (Germany) equipped with a multilayer monochromator with 80% of reflectivity at 17.5 keV (Mo $\text{K}\alpha$), a Mo X-ray source working at 50 kV and 600 μA and a XFlash SDD detector with an effective area of 30 mm^2 .

Nitrogen adsorption isotherms were measured at 77 K using a Micromeritics ASAP 2020 M surface and porosity analyzer. Prior to measurement, the samples were degassed for 12 h at 130°C . Specific surface areas were determined by BET technique and the pore size distribution by NLDFT methods.

Thermogravimetric analysis (TGA) data were obtained on a TA Q-500 analyzer under air atmosphere using around 4–5 mg of sample under a flow of 60 mL/min. The samples were heated from 50 to 850°C at $10^\circ\text{C}/\text{min}$.

Absorption spectra were carried out in a UV-VIS-NIR Varian Cary 500 Scan spectrophotometer.

Scanning electron microscopy (SEM) micrographs were obtained with a Hitachi SU-8000 microscope operating at 0.5 kV. The samples were prepared by dispersing the powder onto a double-sided adhesive surface.

EDX-analysis was made in a FEI microscope NOVA Nano-SEM 230 model equipped with an EDAX-Ametek detector, metalized by gold.

Electrochemical Properties

The catalyst ink dispersion was prepared by sonication for 30 min of 4 mg of the Knitted polymer with 4 mg Carbon black (Super P) into 500 μL isopropanol solvent containing 34 mg of 5 wt% Nafion. Then, 8 μL of the mixture were dropped onto a polished glassy carbon electrode (5 mm in diameter). The loaded electrodes were placed in a 60°C oven for 30 min to dry and then were left to cool down before testing. The corresponding catalyst loading was $0.16\text{ mg}\cdot\text{cm}^{-2}$.

A typical three-electrode system was employed to evaluate the electrochemical properties of the as-prepared catalysts. Specifically, glassy carbon, Pt wire and Ag/AgCl (in 3.5 M KCl solution) were used as the working, counter and reference electrode, respectively. All potentials were referred to the reversible hydrogen electrode by applying Eq. 1 to the obtained Voltage vs Ag/AgCl electrode.

$$V_{\text{RHE}} = V_{\text{Ag/AgCl}} + 0.205 + 0.059 \times \text{pH} \quad \text{Eq.1}$$

All electrochemical measurements, including cyclic voltammograms (CV), linear sweep voltammetry (LSV) and chronoamperometry, were performed using an Autolab PGSTAT302 N potentiostat at 25 °C in 0.1 M KOH solutions, previously purged with either high purity nitrogen or oxygen for at least 1 hour. Both CV and LSV were recorded at 10 mVs⁻¹ scan rate and the potential window ranged from -0.9 to 0.1 V vs Ag/AgCl (3.5 M KCl). Chronoamperometry tests were performed at constant applied potential of 0.35V vs Ag/AgCl (3.5 M KCl) at 1600 rpm in O₂ saturated 0.1 M KOH were run to check. In long-term stability tests *i-t* curves were run for 20000 s while for methanol crossover studies methanol (0.3 M) was injected after running 1500 s. Cycling stability was performed by continuously running 1000 CV at 50 V/s. CVs in N₂ saturated solution at 0 rpm and LSVs in O₂ at 1600 rpm were recorded before and after the cycling.

To elaborate the Koutecky–Levich (KL) plots from equation 3, rotating disk working electrodes (RDE) were scanned catodically at 10 mV/s with different rotation speeds (i.e. from 250 to 2000 rpm)

$$\frac{1}{J} = \frac{1}{J_K} + \frac{1}{J_L} \quad \text{Eq.2}$$

$$\frac{1}{J} = \frac{1}{J_K} + \frac{\nu^{1/6}}{0.620nFAC_{O_2}D_{O_2}^{2/3}} \cdot \frac{1}{\omega^{1/2}} \quad \text{Eq. 3}$$

where J , J_K , and J_L are, respectively, the measured, kinetic and diffusion limiting current densities, ν is the kinematic viscosity (0.01004 cm².s⁻¹), n is the number of transferred electrons in the ORR process; F is the Faraday constant (96485 C.mol⁻¹); A is geometric surface area of the electrode; C_{O_2} is the oxygen concentration in the electrolyte solution (1.39·10⁻³ mol.L⁻¹), D_{O_2} is the diffusion coefficient of oxygen in the solution (1.9·10⁻⁵ cm².s⁻¹) ω is the angular rotation speed (rad.s⁻¹). The mass activity was obtained by normalizing the kinetic current (I_K) to the electrode mass. I_K was derived by multiplying J_K (obtained from the KL plot at 0.9 V vs RHE) by the geometric area of the glassy carbon electrode. All LSVs have been corrected to discard the influence of the double layer capacitance on the ORR performance by subtracting the LSV data measured in N₂-saturated solution from those obtained in O₂-saturated.

Double layer capacitance C_{dl} was calculated after recording different CVs at various scan rates at potentials where there is no Faradaic current.¹⁵⁻¹⁷ According to the Eq. 4 C_{dl} is calculated from the slope of the capacitive current vs r .

$$C_{dl} = J/r \quad \text{Eq. 4}$$

where r is the scan rate. Electrochemically active surface area (ECSA) was calculated using the Eq. 5

$$\text{ECSA} = C_{dl}/C_s \quad \text{Eq. 5}$$

where C_s is the specific capacitance value for a flat standard with 1 cm² of real surface area. A 40 μF/cm² as the average value was taken¹⁵

RESULTS AND DISCUSSION

Synthesis and characterization of iron phthalocyanine knitted polymers

Using standard solvent knitting conditions based on Friedel-Crafts reaction,¹⁸ FePc was firstly heated at 80 °C in DCE in presence of FDA, as external linker, and using FeCl₃ as catalyst to yield the knitting polymer **K-FePc** (Scheme 1) with a moderate 40% yield. The incorporation of a second aromatic monomer biphenyl, (2Ph) or 1,2,4,5-tetraphenylbenzene, (5Ph) in the reaction media, yielded this time the knitting copolymers **K-FePc2Ph** and **K-FePc5Ph** in quantitative yields. Finally, by using FePc and 2Ph under the Scholl reaction conditions, (i.e., AlCl₃ as catalyst, chloroform as solvent and moderated temperature of 40 °C)¹⁹ a predominantly conjugated polymer network, **cK-FePc2Ph**, mainly based on direct aryl-aryl couplings, was formed as shown by solid-state ¹³C-NMR (Figure 1a) with the absence of the broad signal at 35 ppm. This signal corresponds to the aliphatic carbons from the linker (-CH₂- groups) and can be noticed in **K-FePc2Ph** and **K-FePc5Ph** ¹³C-NMR spectra (Figure 1a). Moreover, all polymer networks showed the characteristic intense signals between 145 and 120 ppm attributed to the imine and aromatic carbons.

Figure 1. a) Solid state ¹³C-NMR; b) UV-vis-NIR; c) N₂ adsorption (full circles)/desorption (empty circles) isotherms and d) SEM image of K-FePc2Ph, K-FePc5Ph and cK-FePc2Ph; e) EDX analysis of K-FePc2Ph, carbon (red), iron (yellow).

The presence of the FePc units was also confirmed by FT-IR (Figure S1), Raman spectroscopy (Figure S2) and UV-Vis-NIR spectroscopy (Figure 1b). Figure S1 shows the IR spectra of **K-FePc2Ph** compared with the original FePc monomer. The spectra show the five representative strong bands of the FePc ring at 1331, 1117, 1288, 1078 and 729 cm⁻¹,²³ and a broad adsorption band between 1610 and 1720 cm⁻¹ attributed to the biphenyl units as it was previously observed for knitted polymers prepared from 2Ph monomer.²⁴ Raman spectra were recorded for all knitted polymers and FePc powder (Figure

S2). All polymers contained the characteristic signals corresponding to FePc (Table S1) showing the preservation of the metal macrocycle. Additionally, two new bands assigned to the linker and aromatic monomer of the polymeric network appeared at ca. 1406 and 1446 cm^{-1} associated to C=CH bending and to deformations of C-H groups, respectively. The solid UV-VIS spectra (Figure 1b) of the **K-FePcs2Ph** polymer networks also confirmed the presence of the PcFe units with an intense Q band centered at 684 nm.²⁵

Chemical composition of the aromatic copolymer networks were analyzed by elemental analysis (EA) and total-reflection X-Ray Fluorescence (TXRF) and are shown in Table S2. For copolymers containing biphenyl, 1: 3 ratio, FePc: 2Ph, were found while copolymer **K-FePc5Ph** showed a 1: 2 ratio, FePc: 5Ph. The results revealed the lower reactivity of the iron complex monomer compared to the aromatic ones. In fact, as mentioned above, when FePc was used in the absence of aromatic linkers the corresponding **K-FePc** yield decreased drastically. Knitted copolymer networks exhibited iron contents between 4.4 and 6.6% with N: Fe ratio close to 8 suggesting the preservation of the FeN₄ coordination center during the synthetic process.

TGAs showed high thermal stability with decomposition patterns in one-step for all polymers, as consequence of a high cross-linking degree (Figure S3). Nevertheless, a small decrease in thermal stability for **K-FePc2Ph** and **K-FePc5Ph** copolymers compared to the monomer was found due to presence of aliphatic linkers. The elimination of these units in **cK-FePc2Ph** increased the thermal stability with a decomposition temperature of 350 °C, further corroborating the absence of -CH₂- linking units.

The morphology observed by SEM microscopy showed irregular particulate structures for the three co-polymers (Figure 1d and S4). However, mapping analysis for Fe and C elements by means of energy-dispersive X-ray (EDX) analysis, confirms the homogeneous dispersion of iron in the sample (Figure 1e and S5). The porous structure of the K-FePcs was evaluated by N₂ adsorption-desorption isotherms at 77 K (Figure 1c) and the parameters are recorded in Table S3. The reduced surface area of ca. 62 m²/g for K-FePc homopolymer network suggested the low contribution of an extended polymer network vs the external surface area. On the other hand, all co-polymer curves showed similar shape revealing the prevalence of microporous networks with a small contribution of certain mesoporosity.²⁶ Specific surface areas of ca. 427, 353 and 175 m².g⁻¹ for **K-FePc2Ph** and **K-FePc5Ph** and **cK-FePc2Ph**, respectively, were within the range of those of other conjugated porous polymers based on functionalized phthalocyanines (118-580 m².g⁻¹)^{15,16,27-30} Interestingly, the absence of CH₂ linkers that reduced the flexibility of the structure in **cK-FePc2Ph**, yielded lower surface area than the non-conjugated **K-FePc2Ph**, which provided the highest surface area of the studied knitted polymer networks. The pore distributions, calculated by N₂-DFT method (Figure S6), indicated a similar distribution of micro and mesopores for copolymers **K-FePc2Ph** and **K-FePc5Ph**, which could proportionally allow better access to higher amount of active sites in the microporosity than **cK-FePc2Ph**, which essentially showed mesopores.

Electrocatalytic activity

The ORR electrocatalytic performance for **FePc** monomer and **K-FePc** polymer networks was examined by CV after loading on the glassy carbon electrode a constant mass of ink containing FePc material, CB and Nafion® as a binder. As increasing amounts of carbon material (i.e. up to 50%) into the catalyst ink increases the electrical conductivity of the samples improving the local electron transfer,^{8,14} the amount of CB was set to 50%. All samples showed a small reversible redox peak in N₂ saturated electrolyte solution close to 0.8 V vs RHE (Figure 2a). This redox peak is associated to the Fe (III/II) redox potential of the FeN₄ active site, which has been correlated to the Fe-O₂ binding energy, and considered as a descriptor for the ORR activity.⁸ Interestingly, **K-FePc2Ph** (the knitted polymer with highest surface area) resulted in the largest amount of accessible redox sites while the more conjugated and rigid polymer network, **cK-FePc2Ph** with lower surface area, led to a less reversible FeN₄ redox center regardless its relatively higher amount of iron content.

Figure 2. a) Cyclic voltammetry curves (10 mV/s) in N₂ saturated 0.1 M KOH of the monomer **FePc** (green) and the knitted polymer networks, **K-FePc2Ph** (black) **K-FePc5Ph** (grey), **cK-FePc2Ph** (red) mixed with 50 wt% CB; b) CVs of Knitted polymer **K-FePc2Ph** mixed with 50 wt% CB in N₂- saturated 0.1 M KOH (black) and O₂-saturated 0.1 M KOH (red).

A pronounced cathodic signal in O₂-saturated electrolyte (at ca. 0.885, 0.865, 0.900 and 0.902 V vs RHE) for **K-FePc2Ph**, **K-FePc5Ph**, **cK-FePc2Ph** and **FePc** monomer respectively, revealed high electrocatalytic activity towards ORR (Figure 2b and S7) with very low overpotentials compared to the benchmark catalyst Pt 20% (0.9112 vs RHE). It is worth mentioning that the absence of heat treatment after the polymerization helped the preservation of the coordination environment of the FeN₄ centers.^{9,10}

Linear sweep voltammetry (LSV) in O₂ saturated 0.1 M KOH solution was used on a rotating disk electrode (RDE) to further analyze the K-FePc co-polymer electrocatalysts. In LSV, the ORR process is characterized by polarization curves holding flat plateau currents from which the limiting current density value (J_L) and half-wave potential ($E_{1/2}$) can be obtained. Figure 3a compares the LSV curves of the monomer and K-FePc polymer networks mixed with 50 wt% CB, to that of commercial (20 wt%) Pt/C catalyst benchmark in O₂ saturated 0.1 M KOH solution, at a scan rate of 10 mV/s with a rotation speed of 1600 rpm. As it can be seen, all FePc samples exhibited similar high onset potential (E_{onset}) and very high $E_{1/2}$ revealing how knitting of FePc into a 3D networks barely affects the potential at which ORR occurs (Table S4). In particular, the half-wave potential reached 0.88 V (vs RHE) for **K-FePc2Ph**, **cK-FePc2Ph** and **FePc**, which is 30 mV higher than that of 20%

Pt/C (i.e. 0.85 V vs RHE) showing their excellent ORR activity. Moreover, **K-FePc2Ph** displayed the highest J_L , close to that of Pt catalyst, in agreement with the reversible ORR descriptors showing the available FeN_4 redox centers.

Figure 3. a) LSV curves of **K-FePc2Ph**, **K-FePc5Ph**, **cK-FePc2Ph**, **FePc** and **Pt/C (20%)** in O₂-saturated 0.1 M KOH electrolyte at 1600 rpm. b) Comparisons of E_{ONSET} , $E_{1/2}$ Mass activity and averaged number of electrons transferred in the ORR process for **FePc** monomer, **K-FePc** Knitted polymer networks and 20% **Pt/C**.

LSV curves at different rotation rates were also investigated to further assess the kinetics and the apparent number of electrons transferred during the ORR (n). J_L significantly increased with the rotation rate, as high rotation speed improves O₂ diffusion to the electrode surface (Figure 4a and Figure S8). K–L plots of K-FePc polymer networks derived from LSV curves, according to equations 2 and 3, displayed good linearity and parallelism, suggesting first-order reaction kinetics towards dissolved oxygen concentration (Figure 4b and Figure S9).

The average number of electrons transferred in the ORR process (Table S4, Figure 3b) was calculated from the slope of K–L curves for **K-FePc5Ph**, **K-FePc2Ph**, **cK-FePc2Ph**, **FePc** and **Pt/C**.⁵ The achieved average n values for the knitted polymers **K-FePc2Ph**, **K-FePc5Ph**, **cK-FePc2Ph** and **FePc** monomer were 3.7, 3.2, 3.3 and 3.4, respectively. The results show that despite all knitted polymers have an important contribution of a 4-electron pathway, a coexistence of 2 e- and 4 e- reduction processes occur and therefore, some H₂O₂ production. Yet, **K-FePc2Ph** was the most efficient FePc polymer based catalyst. Related FePc based conjugated microporous polymers showed n values higher than 3.9, with amounts of produced H₂O₂ below 5%.^{15,16} The evaluated n at different voltages for **K-FePc2Ph** knitted polymer (from 3.62 to 3.72, Figure S10), suggests higher amounts of produced H₂O₂. For instance, conjugated CoPc based porous polymers having n values close to 3.6 produced 20% of H₂O₂. In our case, larger particles size or lower surface area (and active electrochemical surface area, see below), which worsen mass transportation towards catalytic sites, could decrease the n value. Compared to other non-pyrolyzed MN_x coordination-frameworks, the new electrocatalyst showed superior activity^{31,32} whereas very close performance was found for phthalocyanine based conjugated microporous polymer approached *via* Sonogashira–Hagihara coupling reaction.^{15,16} While these conjugated porous polymers provided relevant insights on the efficiency of FePc centers in a polymer network with different spacers or combined with other metal centers (i.e Co, Zn) thanks to their very controlled location of the FeN_4 centers, our knitted polymer offered new cost efficient way to produce electrocatalysts. Moreover, low molecular weight FePc polymers and exfoliated amorphous conjugated FePcs polymers adsorbed on gra-

phene^{14,17} were recently obtained exhibiting higher mass activities, and onset and half-wave potentials, in agreement with recent reports showing increased performance of nanostructured electrocatalysts on energy generation related reactions.³⁵⁻³⁷ In all cases, the ultrathin surfaces allowed more exposed catalytic sites and easier mass transportation.

The accessibility to the catalytic sites through the porous network also influenced the ORR performance of knitted polymers. The active electrochemical surface area (ECSA) for **K-FePc2Ph** electrodes (ca. 7.4 m²/g) was estimated from its double layer capacitance (Figure S11). The results were in the range, but somewhat lower than those reported for conjugated porous phthalocyanines (i.e. 9-13 m²/cm²), whose ordered structure minimized bottle-neck sites.^{15,16} Nevertheless, **FePc** monomer, (i.e., with no linked co-monomer contribution that might alleviate partial self-aggregation) showed lower J_L and mass activity at 0.9 V (vs RHE) than those knitted polymers containing a biphenyl group, i.e., **K-FePc2Ph**, **cK-FePc2Ph** (Figure 3a). On the other hand, the lower iron content resulting from the weighty character of 5Ph vs 2Ph reduced the mass activity in **K-FePc5Ph**, while the more rigid **cK-FePc2Ph** polymer network, with lower surface area, led to a less reversible FeN_4 redox center, limiting the J_L . Therefore, an adequate linker should be carefully chosen to be bulky enough to maintain a proper intermetallic distance while providing high concentration of available FeN_4 centers.

Besides the ORR activity, long term stability and fuel crossover (e.g. methanol) can greatly affect the overall performance of the cathode electrocatalysts, as it is seen for the Pt/C benchmark.^{33,34} Thus, we also evaluated the stability of **K-FePc2Ph** with 50% CB for methanol crossover by testing the chronoamperometric response at constant voltage of -0.35 V, in O₂ saturated 0.1 M KOH electrolyte at 1600 rpm. The i - t curves were then compared to those of 20% Pt/C catalyst and FePc monomer with 50% CB. **K-FePc2Ph** polymer network exhibited quite stable amperometric response after the addition of methanol at 1500 s showing its excellent stability towards methanol (Figure 4c). In contrast, a sharp drop of the current response of ca. 70% followed the introduction of methanol on the 20% Pt/C benchmark catalyst. Moreover, the knitted polymer **K-FePc2Ph** also showed improved stability during the electrocatalytic ORR process compared to FePc monomer just dispersed on CB, where partial leaching of the FePc might arise. Long-term stability was further explored for **K-FePc2Ph** by continuously cycling the sample over 1000 times. LSV curves at 1600 rpm in O₂ saturated 0.1 M KOH solution performed before and after the test showed identical performance indicating negligible loss of activity (Figure 4d). Moreover, CVs in N₂ saturated 0.1 M KOH solution, before and after the cycling were performed in order to control the active redox sites, with similar identical results indicating little damage has been made on the redox active centers (inset in Figure 4d). It should be noted, that longer i - t experiment (up to 20000 s) showed some activity loss (ca. 17%, Figure S12), but lower than that found for FePc conjugated porous polymers (29.9%), and very close to 19.4% found for a mixed FeCoPc conjugated porous polymer.¹⁶

Figure 4. a) LSV curves of **K-FePc2Ph** at different rotation speeds from 250 to 2000 rpm; b) K-L plot of **K-FePc2Ph**; c) Amperometric $i-t$ curves of **FePc** monomer, **K-FePc2Ph**, and 20% **Pt/C** electrodes recorded at 1600 rpm in O_2 -saturated 0.1 M KOH solution d) Long term stability test of **K-FePc2Ph**: LSV performed in O_2 -saturated 0.1 M KOH solution at 1600 rpm and 10 mV/s before and after cycling 1000 times (at 50mV/s) Inset: CV curves of **K-FePc2Ph** in N_2 -saturated 0.1 M KOH solution at 0 rpm and 10 mV/s, before and after 1000 CV cycles.

CONCLUSIONS

In conclusion, we successfully prepared, through a simple one-pot knitting strategy, **K-FePc** polymer networks from commercial **FePc**, which result in highly efficient ORR electrocatalysts. The synthetic strategy allows preparing a new family of Pc-containing porous polymers in a very simple way without the need of Pc monomer pre-functionalization before polymerization. Pc-containing polymers with a wide variety of structures and different properties can be obtained by changing the co-monomer or crosslinking agent, while the ORR properties of **FePc** prevail. Among the evaluated polymer networks, **K-FePc2Ph** demonstrated superior ORR activity showing the highest limiting current density, mass activity and half-wave overpotential. Additionally, compared to the commercial 20 % **Pt/C** benchmark catalyst, comparable J_L and superior half-wave overpotential (i.e. 30mV), mass activity and stability for methanol crossover were also found. These results are in agreement with the use of the reversible Fe (III/II) redox potential of the FeN_4 centers as descriptors for the ORR activity of the new knitted polymer networks. Moreover, the knitting synthetic strategy might offer an interesting approach to get new non-pyrolytic, precious metal-free ORR polymer network electrocatalysts based on aromatic macrocycles with controlled FeN_4C and carefully chosen co-monomer linkers capable to maintain an appropriate intermetallic distance while providing high concentration of available FeN_4 centers.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Tables S1-S4 contain structural characterization data and electrochemical data (pdf)

Figures S1 to S6 are characterization information: Raman, FT-IR, TGA, SEM and EDX analysis and Pore Distribution (pdf)

Figures S7-S12 contain information of electrochemical properties (pdf)

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