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ORIGINAL PAPER

Electrochemical reduction of oxygen with iron phthalocyanine in neutral media

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Abstract Recent interest in electricity production using microbial fuel cells makes it important to better understand O_2 reduction in neutral solutions with non-precious metal catalysts. Higher O_2 reduction activity was obtained using iron phthalocyanine supported on Ketjen black carbon (FePc-KJB) than with a platinum catalyst in neutral pH. At low overpotentials, a Tafel slope close to -0.06 V/dec in both acid and neutral pH suggested that the mechanism of O_2 reduction on FePc is not changed with the change of pH, and the reaction is mainly controlled by Fe^{II}/Fe^{III} redox couple. This behaviour gives us new insight into catalysis using FePc, and further supports the use of FePc as a promising catalyst for the oxygen reduction applications in neutral media.

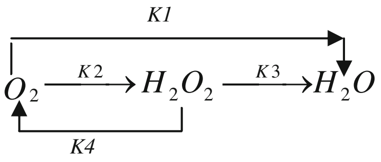
Keywords Microbial fuel cells · Oxygen reduction · Iron phthalocyanine · Redox couple · EIS

1 Introduction

Renewable energy production and the use of biofuels are attracting more attention due to continuously increasing demands on energy and limited energy reserves. Research on biological fuel cells, either using living microorganisms (microbial fuel cells; MFCs) or enzymes (enzymatic biofuel cells) has been increasing [1–6]. The common point for all the biological systems is need for near-neutral operating conditions, especially when using bacteria. In MFCs, microbes are used as biocatalysts on the anode to oxidise the organic matter and produce electrons. However, platinum is still often used as a catalyst for oxygen reduction. The use of Pt is not cost effective, and the operational conditions of neutral pH and relatively low temperatures (compared to hydrogen fuel cells) cause poor kinetics of oxygen reduction and limit MFC performance.

Transition metal macrocycles have been of great interest for electrochemical reduction of oxygen since the work of Jasinski on metal phthalocyanines in the 1960s [7]. The molecular structure of metal phthalocyanine is shown in Fig. 1. Extensive studies on metal macrocycles for oxygen reduction have been carried out in either strongly acidic or alkaline solutions [8–17]. These catalysts have shown highly selective catalytic activity for oxygen reduction in the presence of methanol and CO in direct methanol fuel cells (DMFC) and hydrogen fuel cells [18–26]. The chemical stability of these catalysts in acidic conditions is low due to the demetalisation of the macrocycle rings. However, metal macrocyclic catalysts are stable in neutral and alkaline media. This suggests their application in MFCs and other biological fuel cells operating at neutral pH will be more feasible than in these other fuel cells.

Oxygen reduction proceeds through parallel two- and four-electron reaction pathways, which can be expressed as:



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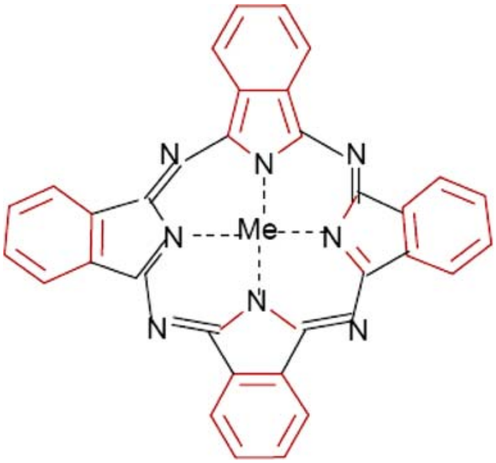

Fig. 1 Schematic diagram of molecular structure of metal phthalocyanine (MePc)

$$O_2 \xrightarrow{K_2} H_2O_2 \xrightarrow{K_3} H_2O$$

It has been reported that iron phthalocyanine (FePc) has the ability to promote direct $4e^-$ oxygen reduction to water, while CoPc promotes O_2 reduction to H_2O_2 by a $2e^-$ pathway [27–29]. This $4e^-$ pathway is more desirable as it avoids the production of hydrogen peroxide which can damage the electrode structure.

Some preliminary studies on the application of metal macrocycles to MFCs have produced promising results with two different materials: cobalt tetramethoxyphenylporphyrin (CoTMPP); and FePc [30–32]. In our previous study on oxygen reduction catalysts used to improve MFC performance, we demonstrated that metal macrocycles had a higher activity towards oxygen reduction in neutral pH than Pt [32, 33]. However, oxygen reduction under circumneutral pH conditions with different catalysts in general has not been well studied compared to the performance of these catalysts under acidic or alkaline conditions. In this study, we therefore focused on better electrochemical characterization of oxygen reduction using FePc compared to Pt under neutral pH conditions, using cyclic voltammetry, galvanostatic steady-state polarisation and electrochemical impedance spectroscopy (EIS) techniques for characterizing kinetics and reaction mechanisms.

2 Experimental

2.1 Preparation of metal phthalocyanine catalysts

The carbon supported metal phthalocyanine catalysts were prepared by impregnating commercial metal macrocyclic compounds (used as received), iron phthalocyanine (FePc, TCI America), cobalt phthalocyanine (CoPc, Aldrich) on carbon nano-particles (Ketjenblack EC 300, Akzo Nobel). Carbon supported Pc catalysts were prepared using the method described by Ladouceur et al. [34]. The obtained catalysts were completed by pyrolysis at 800 °C in argon for 2 h followed by cooling to ambient temperature with argon. The molecular structure of a metal phthalocyanine (MePc) is shown in Fig. 1, highlighting the characteristic N4-chelate structure. A commercially produced carbon supported Pt catalyst (Etek, 20 wt%) was used as a relative reference for comparing catalyst activities.

2.2 Preparation of electrodes

Electrodes for electrochemical studies were prepared using 20% wet-proofed Toray 90 carbon paper (Etek). Catalyst ink containing 10 wt% Nafion (5% Nafion solution, Aldrich) as the binder was painted to the carbon paper to the desired loading. The loading was 1 mg cm^{-2} for metal macrocycles, and 0.5 mg cm^{-2} for Pt.

2.3 Electrochemical study of oxygen reduction

A three-electrode H-cell was used for electrochemical tests in neutral pH, as previously described [33]. The working electrode was a gas-diffusion electrode with the surface area of 0.64 cm^2 exposed to air, and the counter electrode was a platinum foil. An Ag/AgCl (3 M NaCl, EE009, Cypress System) electrode was used as the reference electrode. All electrode potentials given here are with reference to an Ag/AgCl electrode (0.208 V vs. normal hydrogen electrode, NHE), unless stated otherwise. The electrolyte was 0.05 M phosphate buffered nutrient medium (PBM, pH 7.0) [32]. Electrochemical tests were carried out in a temperature-controlled room at 30 °C. The working electrode was immersed in PBM solution overnight in order to fully hydrate the electrode while at the same time the open circuit potential was measured. The electrolyte for oxygen reduction carried out in acid was 0.5 M H_2SO_4.

Cyclic voltammetry, linear sweep voltammetry and galvanostatic polarisation were used for the characterisation of the oxygen reduction reactions with various catalysts in neutral and acid solutions. Electrochemical impedance spectroscopy was performed with amplitude of 5 mV in the frequency range 10 kHz to 0.1 Hz and was carried out at different potentials. Computer controlled potentiostats, a Gill AC (ACM Instruments Ltd., UK) and a PCI4/750 Potentiostat/Galvanostat (Gamary Instruments, Warminster, PA, USA) were used for the electrochemical measurements.

3 Results and discussion

3.1 Oxygen reduction on FePc in acidic media

In order to better understand factors affecting performance of catalysts under neutral pH conditions, we examined oxygen reduction in acidic medium (0.5 M H_2SO_4). The voltammograms for oxygen reduction in acid show that the Pt catalyst had a higher oxygen reduction current, and thus higher catalytic activity, in acid solution than FePc. However, onset potentials for Pt (0.874 V) and FePc (0.862 V) were comparable (Fig. 2a) indicating similar activation energy with the catalysts. Stability of FePc in acid was examined by soaking the electrode in the acid solution for up to 15 days after first test. The results are shown in Fig. 2b. It is known that demetalisation of metal macrocycle compounds occurs when pH lower than 3. The central metal ion is ‘knocked off’ from the N4-ring, and hence the activity of the catalyst decreases accordingly [35]. Although the activity was decreased after 15 days, FePc was still relatively stable comparing to other macrocycle compounds (data not shown here). Therefore, it is to expect that FePc would have reasonable stability in neutral media. A redox peak associated with Fe^{II}/Fe^{III} couple observed around 0.9 V vs. Ag/AgCl (0.7 V vs. SHE), in the CV obtained in N_2 saturated 0.5 M H_2SO_4 (Fig. 3) was observed, which could be related to the oxidation status, of the iron centre in the N4-ring.

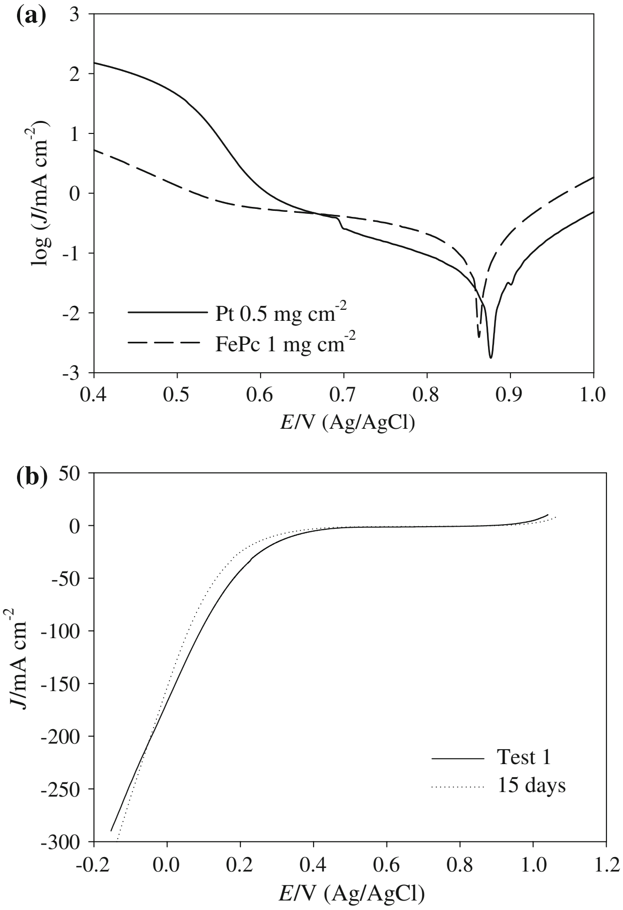

Fig. 2 Oxygen reduction in 0.5 M H_2SO_4, (**a**) on Pt and FePc-KJB (**b**) Stability studies of FePc, scan rate: 1 mV s^{-1}

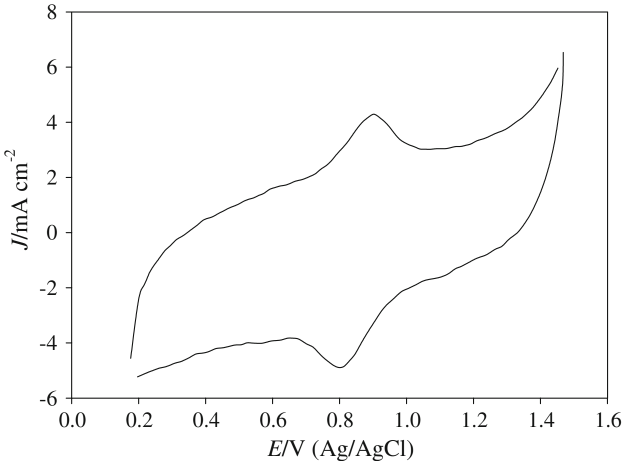

Fig. 3 Cyclic voltammogram of FePc in 0.5 M H_2SO_4 saturated with N_2, scan rate: 20 mV s^{-1}

3.2 Oxygen reduction with FePc in neutral media

Oxygen reduction with FePc and CoPc in neutral pH was carried out in 0.05 M PBM with various catalysts. Figure 4 demonstrates the polarisation curves obtained from galvanostatic polarisation study from the current density up to 4 mA cm^{-2}. In the low overpotential range (i.e. potential more positive than 0.1 V) the Pt catalyst produced a higher current response, and FePc showed comparable performance. In the potential more negative than 0.1 V, higher

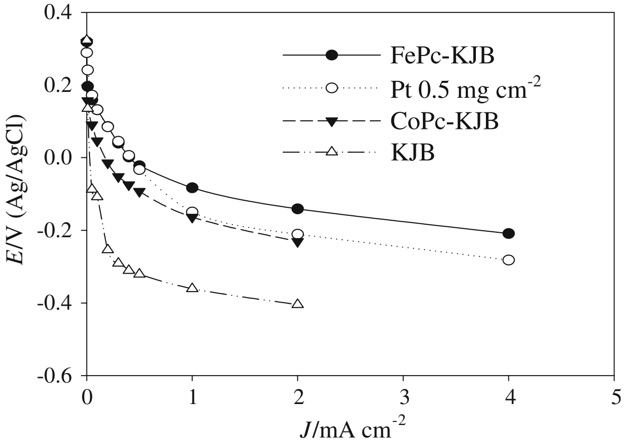

Fig. 4 Galvanostatic polarisation curves for O_2 reduction on various catalysts. Catalyst loading 1 mg cm^{-2}, in 0.05 M phosphate buffer, pH 7.0, T = 30 °C

Table 1 Comparison of potentials of galvanostatic polarisation for O_2 reduction on carbon supported FePc and Pt catalysts in neutral pH

Current density J/mA cm^{-2}	FePc V	Pt V
0.30	0.040	0.045
0.50	−0.023	−0.033
1.00	−0.083	−0.150
2.00	−0.141	−0.211
4.00	−0.209	−0.282

oxygen reduction current was obtained. These results are consistent with our previous study [33]. In neutral pH, it is seen that oxygen reduction current is significantly decreased (two orders of magnitude lower than in acid), and the onset potentials are shifted in the negative direction by about 0.4 V. According to a study by Zagal et al., the effect of pH on the potential change is −0.059 V/pH [36]. Assuming pH was the only variable changed in the system here, a 0.413 V shift towards negative direction would therefore be expected for a pH change from 0 to 7. Pt and FePc showed reasonable catalytic activity for oxygen reduction compared to non-catalyzed Ketjen black carbon. Oxygen reduction using Ketjen black carbon had an onset potential of 0.344 V, while Pt and FePc-KJB onset potentials were more positive at 0.452 V and 0.429 V, respectively. The comparison between the potentials obtained on Pt and FePc-KJB, with galvanostatic polarisation at the same current density is shown in Table 1. More positive O_2 reduction potentials were achieved with FePc-KJB than Pt in the high current density region indicating a promising application of FePc in neutral pH.

3.3 Tafel study

Tafel plots of log (J/mA cm^{-2}) vs. E are given in Fig. 5 for oxygen reduction on FePc and Pt in neutral solutions. The values of Tafel slope in acid and neutral media are listed in Table 2. Oxygen reduction occurred by different mechanisms in low and high current density regions. In the low current density region, the Tafel slope for Pt changed from −0.058 V/dec in the pH 0 acid solution to −0.118 V/dec in pH 7 solution. For O_2 reduction on Pt in acid, with a Tafel slope of −0.060 V/dec, there was no detectable amount of peroxide measured indicating that O_2 reduction occurred by the four-electron pathway [37]. The change of Tafel slope from close to −0.060 V/dec to −0.120 V/dec suggests a change on the rate determining step, and therefore a change of reaction mechanism on Pt.

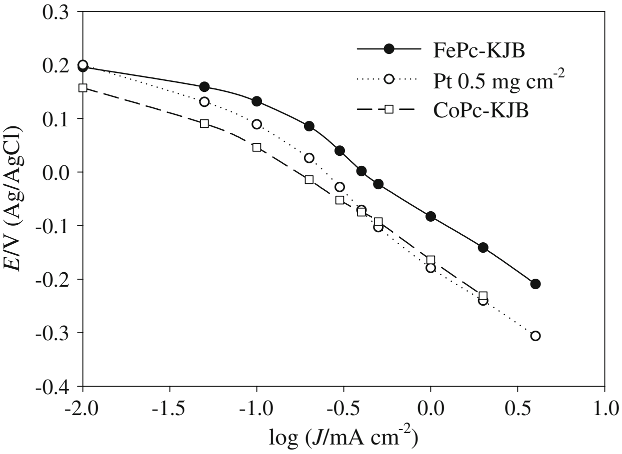

Fig. 5 Tafel plot from Galvanostatic polarisation for O_2 reduction on various catalysts. Catalyst loading 1 mg cm^{-2}, in 0.05 M PBM, pH 7.0, T = 30 °C

In contrast to that observed with Pt, the Tafel slope for FePc did not change with pH. The Tafel slopes in the low polarisation region were −0.058 V/dec in acid and −0.062 V/dec in neutral solutions, respectively, indicating less pH dependence for oxygen reduction using the FePc catalyst.

A mechanism developed by Beck [38] proposed that the metal macrocycle reacts with oxygen according to the redox reaction.

$$Me^{II} + O_2 \rightarrow Me^{III}O_2{}^{-} \tag{1}$$

$$Me^{III}O_2{}^{-} + e^{-} \xrightarrow{H^{+}} \text{product} + Me^{III} \tag{2}$$

$$Me^{III} + e^{-} \rightarrow Me^{II} \tag{3}$$

During the adsorption of O_2, the metal ion is oxidised and the O_2 molecule is reduced. It is likely that with FePc, in the low polarisation region, the Fe^{II}/Fe^{III} redox couple controls the rate of O_2 reduction. The redox peak in the CV shown earlier in Fig. 3 further provides support for this redox mechanism. Zagal et al. [36] studied O_2 reduction on water soluble Fe phthalocyanine absorbed on graphite electrodes. Equation 2 was suggested as the rate determining step at low overpotential. Studies by several researchers suggest the transfer coefficient α has a value near 0.5 at $pH < 10$ [11, 35], which may explain the stable Tafel slopes observed for FePc at pH 0 and 7. It was reported by Zagal et al. that compounds with Me^{II}/Me^{III} redox couples close to the onset of O_2 reduction, such as FePc, a small Tafel slope of −0.060 V/dec at low overpotentials was observed and the four-electron reduction of O_2 was also promoted in that region [39]. However, this mechanism does not hold for high polarisation region. The Tafel slopes changed from −0.163 to −0.127 V/dec on FePc from pH 0 to pH 7; while the slopes changed from −0.094 to −0.171 V/dec on Pt from pH 0 to pH 7. The O_2 reduction processes at high polarisation region can be:

Table 2 Tafel slopes of oxygen reduction on metal phthalocyanine and Pt in 0.5 M H_2SO_4 and 0.05 M PBM pH 7

Tafel slope	pH 7, 0.1 M PBM, 30 °C V/dec		Eo/V	pH 0, 0.5 M H_2SO_4 V/dec		Eo/V
FePc 40%	−0.062	−0.127	0.429	−0.058	−0.163	0.862
CoPc	−0.108	−0.203	0.321	−0.029	−0.209	0.886
Pt	−0.118	−0.171	0.451	−0.058	−0.094	0.945
Ketjen black	−0.299	−0.145	0.344	−0.077	−0.200	0.879

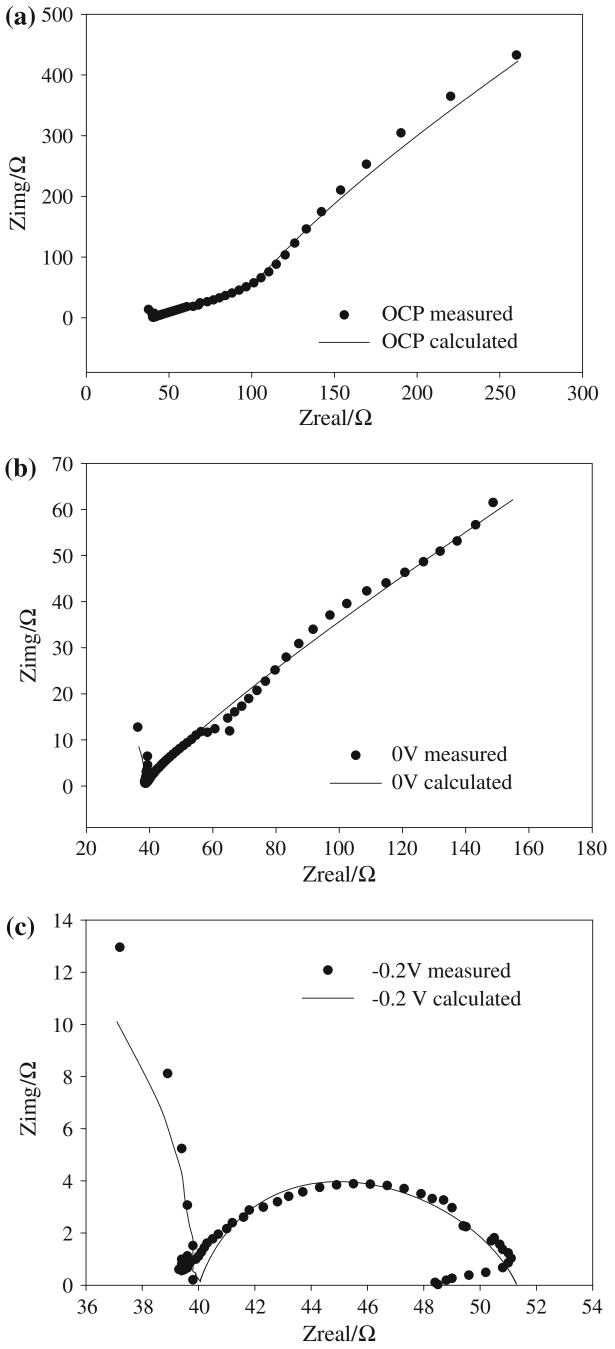

Fig. 6 Nyquist plots of oxygen reduction on FePc in 0.05 M PBM, pH 7 at various potentials. **a** OCP 0.192 V, **b** 0 V, **c** −0.2 V

$$\mathrm{Me^{II}} + \mathrm{O_2} \leftrightarrow \mathrm{Me^{III}} - \mathrm{O_2}^- \tag{4}$$

$$\mathrm{Me^{III}} - \mathrm{O_2}^- + e^- \leftrightarrow \mathrm{Me^{II}} - \mathrm{O_2}^- \tag{5}$$

$$\mathrm{Me^{II}} - \mathrm{O_2}^- \rightarrow \text{products} \tag{6}$$

The Tafel slope close to −0.120 V/dec suggests a first one-electron transfer step as the rate determining step, which according to Zagal et al. [35] was the reduction of the charge transfer complex $\mathrm{Fe^{III}} - \mathrm{O_2}^-$, Eq. 5.

3.4 EIS study on oxygen reduction in neutral pH

An EIS study was carried out at different potentials in order to study the internal resistance of the system and reaction kinetics. Figure 6 shows the Nyquist plots for O_2 reduction on FePc at 0.192, 0 and −0.2 V in pH 7 solution. The shape of plots changed at different potentials, suggesting different electrochemical processes occurring on the electrode. The processes that could be involved on the electrode surface that would produce these changes [40] include:

(1) Diffusion of O_2 through the gas phase in the pores (of porous carbon supported catalyst) and the electrolyte to the reaction site.
(2) Adsorption or heterogeneous surface reaction of the oxygen, together with oxygen diffusion.
(3) Charge transfer.
(4) Diffusion of reduction products into the bulk electrolyte.

Using the equivalent circuit shown in Fig. 7, a constant phase element (CPE) associated with double layer charge and adsorption of ions is suggested due to the non-homogeneous surface of the electrode. An inductance was added for the physical inductance of the electric circuit. The

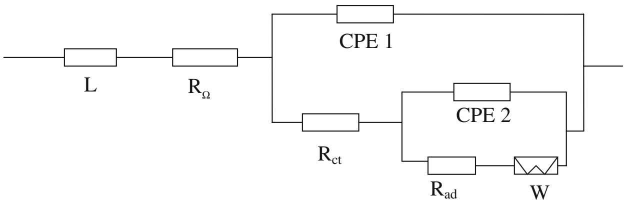

Fig. 7 Equivalent circuit for O_2 reduction on gas diffusion electrode using FePc catalyst in 0.05 M PBM, pH 7

Table 3 EIS parameters for O_2 reduction on the gas diffusion electrode using 0.05 M PBM pH 7 at various potentials (see Fig. 7 for equivalent circuit and parameter definitions)

E/V	$R_{ohm/\Omega}$	CPE 1 S s^n	n 1	$R_{ct/\Omega}$	CPE 2 S s^n	n 2	$R_{ad/\Omega}$	W S $s^{0.5}$	L/H
−0.2	39.7	0.0035	0.77	11.3	0.012	0.60	0.10	0.01	1E−8
0	39	0.005	0.65	40	0.038	0.48	2.10	0.07	5.3E−6
0.191	40	0.0067	0.59	131.8	0.011	0.94	3.16	1.8E−6	1E−6

charge transfer resistance, which is related to reaction kinetics, has a high dependence on potentials. For oxygen reduction on FePc in neutral medium, charge transfer between the redox couple Fe^{II}/Fe^{III} is the main process controlling the reaction. As the rate-determining step of the proposed mechanism of O_2 reduction involves species adsorption, a complex element accounting for adsorption represented by a second CPE and a resistance (R_{ad}) and a diffusion related Warburg component (W) in parallel should be considered in the equivalent circuit.

At low overpotentials, a straight line is observed in Fig. 6a, b, which indicates a capacitive impedance and typical semi-infinite diffusive character, related to double-layer charge-discharge process and the adsorption of reactants expressed in terms of a CPE, as well as diffusion of the adsorbing species. At more negative potentials (ca. −0.2 V) an inductive arc was observed at low frequency. This implies a change in the mechanism and kinetics of the O_2 reduction [41], which is reflected by a different Tafel slope. The transition to an inductive arc may have resulted from the limited diffusion of dissolved oxygen through the electrolyte within the narrow pores [42].

Parameters calculated from the equivalent circuit for O_2 reduction on the gas diffusion electrode are listed in Table 3, and the fit of these parameters to the equivalent circuit are shown in Fig. 6. The calculated impedance values agreed with the measured data, indicating that suggested equivalent circuit was an acceptable model for this system.

4 Conclusions

In this study, further electrochemical studies of oxygen reduction in neutral medium with non-Pt catalysts, particularly FePc supported on KJB carbon, were carried out. Higher O_2 reduction activity was obtained on FePc-KJB than Pt in neutral pH. The mechanism of O_2 reduction using FePc was unaffected regardless the change of pH in low overpotential region, while the mechanism was different for Pt and other non-Pt catalysts. A Tafel slope of −0.06 V/dec at low overpotentials suggests that the reaction for FePc is mainly controlled by the Fe^{II}/Fe^{III} redox couple. EIS study on the O_2 reduction on FePc suggests different electrochemical process occurring at different potential regions, and provides further understanding on the reaction process and mechanisms. The comparable performance to Pt in neutral pH obtained from FePc indicates FePc to be a promising low cost catalyst for O_2 reduction in the biological fuel cell applications in neutral media.

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