Bimetallic Cu/Pt Oxygen Reduction Reaction Catalyst for Fuel Cells Cathode Materials

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Abstract: The oxygen reduction reaction (ORR) is a key process for the operation of fuel cells. To accelerate the sluggish kinetics of ORR, a wide range of catalysts have been proposed and tested. In this work, a nano-dispersed copper-impregnated platinum catalyst prepared by electrodeposition of platinum on a poly[Cu(Salen)] template followed by polymer destruction is described. In addition to the high activity of the thus prepared catalyst in the oxygen reduction reaction surpassing that of both polycrystalline platinum catalyst and the commercial carbon-platinum catalyst (“E-TEK”), it showed remarkable tolerance to the presence of methanol in solution.

Keywords: oxygen reduction reaction; bimetallic catalyst; template synthesis; Cu salen polymer complex

1. Introduction

The oxygen reduction reaction (ORR) plays a crucial role in the operation of a variety of electrochemical systems, such as metal–air batteries, fuel cells, and electrochemical sensors [1–5]. The performance of these devices often suffers from sluggish kinetics of ORR at the electrode–solution interface. To overcome this issue, much effort on preparation of a proper catalyst has been made. Most of commercial ORR catalysts use noble metals on carbon support (Pt/C, Ru/C, Ir/C) [6–11] or their alloys (Pt/Ru) [12,13]. Unfortunately, noble metal catalysts are quickly poisoned by various impurities, which are always present in practical systems [14]. The catalyst tolerance to the presence of poisoning impurities can be enhanced by combination of noble and transition metals [15]. In such mixed catalysts, various transition metals and their oxides are used, including Pt–TiO2 [16], Pt–Co [17–20], Pt–Pb [21], Pt–W [22], and Pt–Ni [23,24]. The activity, efficiency and lifetime of the catalysts are significantly influenced by their chemical composition as well as by the morphology of the catalytic layer. The catalytic activity is enhanced in highly porous systems and systems composed of meso- and nano-sized active particles due to increase in the catalyst surface area and the surface energy of such systems [25,26]. One of the most common methods of preparation of nano-structured mixed systems is the template synthesis [1,27–30], where an active component of the catalyst is deposited on a porous material used as a template. An example of such porous template are polymer films of metal complexes with Schiff bases formed on a conductive substrate [31]. The polymer template can be easily destroyed by thermolysis [32] or alkaline hydrolysis [33,34], resulting in removal of the organic ligand matrix and formation of metal oxide with high surface area. The metal atoms are uniformly distributed in the initial polymer films, so the resulting material has a uniform structure composed of nano-particles of metal hydroxides or oxides [32–34]. In this work, we report a template synthesis...
of a novel bimetallic Pt/Cu catalyst by electrodeposition of platinum particles on poly[Cu(Salen)] films used as a template, followed by hydrolytic decomposition of the polymer matrix. The efficiency, stability, and methanol tolerance of the Pt/Cu catalyst were studied, and the catalyst composition and preparation method were optimized.

2. Results and Discussion

2.1. Catalyst Synthesis and Characterization

The bimetallic catalyst Pt/Cu was prepared by reduction of K$_2$PtCl$_6$ on the pre-polymerized [Cu(Salen)] template matrix (see Supplementary Information) followed by the template removal from the resulting poly[Cu(Salen)]/Pt.

According to previous reports, similar nickel-based polymer, poly[Ni(salen)], undergoes destruction of organic part upon electrochemical oxidation of the polymer film in alkaline solutions [33]. However, the copper complex was proved to be more stable according to EQCM/CV study. Unlike poly[Ni(salen)], which swelling during the first cycle of potential sweep was followed by the polymer degradation [35], cycling of poly[Cu(salen)]/Pt in the same potential range (1–1.8 V (vs. reversible hydrogen electrode (RHE)) (Figure 1a) resulted in electroactivity drop accompanied by mass stabilization (Figure 1c) after the initial mass increase due to the polymer swelling. Therefore, the hydrolysis of poly[Cu(salen)]/Pt by preliminary reported procedure resulted only in the decrease of the polymer electroactivity with no physical destruction of the polymer template (Figure 1a).

**Figure 1.** Alkaline hydrolysis of the Pt modified poly[Cu(Salen)] film in the oxygen-saturated 0.2 M NaOH solution with mass control by EQCM (a) cyclic voltammograms and (b) the polymer mass change in the potential range of 1–1.8 V (vs. RHE); (c) cyclic voltammograms and (d) the polymer mass change in the wide potential range of 0.2–1.8 V (vs. RHE).
Extension of the potential sweep window from 1–1.8 V to 0.2–1.8 V (vs. RHE) (Figure 1c) produces an ORR wave at around 0.7 V (vs. RHE). In the first three voltammetry cycles a sharp increase of the film mass is observed, followed by the weight decrease, indicating the destruction of the polymer film in alkaline solution (Figure 1d). While the organic template is dissolved in the solution, Cu atoms remain partially on the surface of the platinum particles in the form of copper oxide (see text below). The resulting bimetallic catalyst is denoted as Pt/Cu.

The activity of the metallic catalysts is influenced by their composition as well as the size, shape, and distribution of their particles on the surface and in the active layer volume [36]. The composition and the morphology of the bimetallic catalyst Pt/Cu were optimized to reduce the platinum loading while maintaining the catalyst activity for ORR in alkaline medium at the proper level. Eight different compositions were tested with the platinum loading controlled by the charge of electrodeposition (Table S1, Figure S3). The morphology of the catalyst depends on the morphology and porosity of the polymer template, which in turn is determined by the properties of the solvent in which the polymer was synthesized [37]. As salen complexes are known to undergo electrochemical polymerization in weak or non-coordinating solvents, acetonitrile (AN) and propylene carbonate (PC) were explored as the solvents for the synthesis of the template, resulting in two series of bimetallic catalysts, Pt/Cu (AN) and Pt/Cu (PC) respectively (see Table S1 for the complete list of the samples).

The activity of Pt/Cu (AN) catalyst, assessed as the half-wave potential of ORR, becomes equal to the commercial E-TEK-based catalyst, prepared by the standard method, with two times higher Pt loading (Figure 2, Table 1). Though larger Pt loading significantly increases the activity of the catalyst by shifting the half-wave potential for ORR by 70 mV, this also increases the catalyst cost. Much better performance showed Pt/Cu(PC), which has activity surpassing that of commercial E-TEK catalyst at lower Pt loading: the positive shift of the half-wave for ORR by 20 mV was observed at 100 times lesser platinum loading (Table S1, Figure 2, sample 4 vs. sample 1 and E-TEK). In addition, synergistic effect of platinum and copper deposited from the polymer template was confirmed by the comparison of the electrocatalytic activity of Pt/Cu (PC) with poly[Cu(Salen)] and Pt deposited on an electrode without a polymer template (see Supplementary Information, Table S2, for detailed description of loading optimization and comparison of the performance with model systems and literature data).

![Figure 2. CV curves of Pt/Cu and Pt catalyst modified RDE electrode in oxygen-saturated 0.2 M NaOH electrolyte, 1000 rpm (catalyst samples differs by platinum loading and template preparation solvent; description of the samples is given in Table 1).](image-url)

To explain the observed difference between Pt/Cu (AN) and Pt/Cu (PC), a morphological study of the catalysts was performed by means of the scanning electron microscopy (SEM). Similar to the electropolymerized films of nickel salen complexes [38], the surface of poly[Cu(Salen)](AN) polymer complex (Figure 3a,b) is smooth and has no visible porosity. On the contrary, the poly[Cu(Salen)](PC) film (Figure 3b) is porous with pore diameters of 100 nm or less. When K$_2$[PtCl$_6$] is reduced at...
poly[Cu(Salen)](PC) polymer matrix, the reduction occurs first on the sites with the highest surface energy, the nano-sized pores, and thus the metal nanoparticles (average diameter is $31 \pm 10$ nm) are formed. Due to the high porosity of the template (hence the large number of the nucleation sites for metal deposition), the nanoparticles of platinum are evenly distributed throughout the polymer surface (Figure 3g), as can be evidenced from the SEM images of Pt/Cu (PC) bimetallic catalyst (Figure 3d). Unlike poly[Cu(Salen)](PC), the smooth surface of poly[Cu(Salen)](AN) template results in occasional (and more rare) formation of the seeds of the reduced metal resulting in larger diameter of the metal particles ($60 \pm 20$ nm) and their lesser number per unit area (Figure 3h). Energy Dispersive X-ray (EDX) analysis results confirmed the presence of Pt and Cu in the samples.

Figure 3. Cont.
The Pt spectrum consisted of two peaks of Cu 2p3/2 (70.9 eV and 74.2 eV) on the Pt spectrum, corresponding to Pt 4d levels of Pt metal at 71.9 eV [46], while the characteristic peaks of Pt/Cu nanoparticles appear at 70.9 eV [44,47]. The negative shift of the peaks in Cu–Pt catalysts compared to Pt should be attributed to the electron transfer from Cu to Pt by their intimate contact [44]. As the result, obtained data match well to the literature data for other mixed Cu–Pt catalysts [48–50] and the observed Pt spectrum is close to the spectrum of the Pt/Cu catalyst reported in [43,44]. Thus, XPS data confirm that during the hydrolysis of poly[Cu(Salen)] copper is not washed out of the film, but remains in several forms in the composition of the mixed Pt/Cu (PC) catalyst.

Table 1. Description of the samples, presented on Figure 2.

| Sample Number, Solvent | Pt Deposition Charge, Q, mC | Pt Loading, g | Pt Loading, g cm⁻² | E_{H2}, V |
|------------------------|-----------------------------|---------------|---------------------|----------|
| 1, acetonitrile         | 73                          | 3.69 × 10⁻⁵   | 5.3 × 10⁻⁴          | 0.87     |
| 2, acetonitrile         | 19                          | 9.70 × 10⁻⁶   | 1.4 × 10⁻⁴          | 0.85     |
| 3, acetonitrile         | 7                           | 3.38 × 10⁻⁶   | 4.83 × 10⁻⁵         | 0.82     |
| 4, propylene carbonate  | 1.1                         | 5.6 × 10⁻⁷    | 8.0 × 10⁻⁶          | 0.89     |
| E-TEK (prepared according to [36]) | | 1.97 × 10⁻⁶ | 2.8 × 10⁻⁵ | 0.78 |

According to the XPS data, the alkaline hydrolysis led to a significant change in the composition of the catalyst surface compared to the template polymer film. The Pt:Cu:O:N ratio on the surface of the Pt/Cu (PC) mixed catalyst was found to comprise 9:1:3:0.3, indicating removal of almost all organic backbone of the polymer. The XPS Cu spectrum of the mixed catalyst did not contain any peaks at 943.5 eV and 936.4 eV characteristic for [Cu(Salen)] complex [39]. On the contrary, the spectrum (Figure 4a) consisted of two peaks of Cu⁰ with binding energies characteristic for the metallic copper (931.7 eV, Cu 2p3/2 and 951.5 eV, Cu 2p1/2) and Cu²⁺ peak, typical for the copper hydroxide (933.8 eV, Cu 2p3/2) [41].

The oxygen spectrum (Figure 4c) contains the main peak with a binding energy of 530.7 eV corresponding to O²⁻ in copper hydroxide [41]. The second peak on the spectrum at 531.8 eV may be assigned to O²⁻ in platinum dioxide [42]. The amount of platinum on the surface of the catalyst significantly exceeds both the amount of copper and the amount of oxygen (Figure 4b). The first pair of peaks (70.9 eV and 74.2 eV) on the Pt spectrum corresponded to Pt⁰ in the metallic platinum [43], and the second pair (72.3 eV and 75.2 eV) had binding energies similar with Pt²⁺ in the CuPt alloy at the mixed catalyst surface [44] (Figure 4b). The peak at 75.6 eV possibly corresponds to Pt⁴⁺ in PtO₂ [45]. Presence of the platinum hydroxide at the catalyst surface was additionally proved by the presence of the platinum hydroxide peak on the oxygen spectrum (Figure 4c). The characteristic Pt peaks of bare Pt metal are located at 71.9 eV [46], while the characteristic peaks of Pt–Cu nanoparticles appear at 70.9 eV [44,47]. The negative shift of the peaks in Cu–Pt catalysts compared to Pt should be attributed to the electron transfer from Cu to Pt by their intimate contact [44]. As the result, obtained data match well to the literature data for other mixed Cu–Pt catalysts [48–50] and the observed Pt spectrum is close to the spectrum of the Pt/Cu catalyst reported in [43,44]. Thus, XPS data confirm that during the hydrolysis of poly[Cu(Salen)] copper is not washed out of the film, but remains in several forms in the composition of the mixed Pt/Cu (PC) catalyst.
2.2. Kinetics of the ORR

The kinetics of the ORR on the Pt/Cu (PC) mixed catalyst was studied on the rotating disk electrode. The four-electron character of the redox process was found from the slope of the $j^{-1}(\omega^{-1/2})$ dependence by means of the Koutecký–Levich equation according to the standard procedure [51] (Figure 5 and Figure S4). The number of electrons $n$ close to four is indicative of oxygen to water reduction rather than oxygen to hydrogen peroxide reduction. This is typical for Pt catalysts [52,53], but not for transition metals catalysts, which show mixed two-electron and four-electron reductions with $n$ between 2 and 4 [54]. The observed four-electron pathway of the ORR shows that copper does not block or change the electrochemical behavior of platinum in Pt/Cu (PC). The transferred electron number is typical for other Pt/Cu catalysts [55–57].

2.3. Stability of the Mixed Catalyst

The stability of the catalytic response of Pt/Cu (PC), as the best from the synthesized catalysts, was estimated from the catalytic ORR current in a potentiostatic mode on Pt/Cu (PC) modified electrode in an oxygen saturated alkaline solution. Pt/Cu (PC) catalyst activity shows gradual decrease and the catalytic current reaches 50% of the initial level after 3 h of continuous operation (Figure 6). The observed half-life of the catalyst is thus at the same level or better than the stability of commercial platinum catalysts [58,59]. Washing of the Pt/Cu (PC) catalyst by deionized water after 75% loss of the initial activity recovers its activity by 37% (Figure 6). This suggests that the decrease in activity is caused by the adsorption of impurities on the surface of the catalyst rather than by the mechanical destruction of the catalytic layer.
The leakage of the catholite to the anode space is a major problem of fuel cells. As a result, the catalyst is poisoned by a mixture of the fuel and the oxidant formed in the anodic space. This problem is particularly important for methanol fuel cells, as Pt-based ORR catalysts can promote methanol oxidation, which leads to a decrease of the cathodic current. The contact of methanol with a platinum catalyst may also lead to surface poisoning by aldehydes and other organic impurities that are formed during the oxidation of methanol. Therefore, a practically important parameter of a catalyst for a fuel cell is its tolerance to methanol admixtures.

The CV and chronoamperometry study of the tolerance of Pt/Cu (PC) catalyst to methanol was carried out in a solution of 0.2 M NaOH containing methanol additives. A methanol oxidation wave can be observed on the CV of 0.5 M methanol solution in 0.2 M aqueous NaOH (Figure 7a) at Pt/Cu (PC) modified electrode. However, the oxidation of methanol becomes possible only for positive direction potential sweep, though the methanol oxidation potential (ca. 0.8 V vs. RHE) is passed already on negative direction potential sweep. This implies that the significant polarization of the electrode surface is required to enable methanol sorption prior to oxidation. Taking into account that Pt/Cu (PC) has half-wave potential of 0.9 V and potential of 0.7 V for diffusion-limited current of ORR in 0.2 M NaOH, effective oxygen reduction without interference from methanol oxidation becomes possible.

Figure 5. (a) Rotating disc voltammograms and (insert) Koutecký–Levich plots for the oxygen reduction on the Pt/Cu (PC) (sample 4 from Table 1) electrode at different potentials in O2-saturated 0.2 M NaOH solutions, (b) electron transfer number profile obtained from Koutecký–Levich plot.

Figure 6. Stability of the Pt/Cu (PC) catalyst in O2-saturated 0.2 M NaOH electrolyte in potentiostatic mode at 0.7 V (vs. RHE) and 1000 rpm.

2.4. Stability of the Mixed Catalyst in the Presence of Methanol in the Electrolyte

The oxygen spectrum (Figure 4c) contains the main peak with a binding energy of 531.8 eV, which can be attributed to Pt0 in the metallic platinum. The second peak on the spectrum at 70.9 eV and 74.2 eV correspond to Pt2+ in the CuPt alloy at the catalyst surface. The characteristic binding energies of peaks (72.3 eV and 75.2 eV) on the Pt spectrum corresponded to Pt0 in the metallic platinum. Presence of the platinum hydroxide at the catalyst surface was additionally proved by the characteristic Pt peak at 75% loss of the initial activity recovers its activity by 37% (Figure 6).

The stability of the catalytic response of Pt/Cu (PC), as the best from the synthesized catalysts, was estimated from the catalytic ORR current in a potentiostatic mode at 0.7 V (vs. RHE) and 1000 rpm.
Indeed, addition of methanol had little effect on the current of oxygen reduction during chronoaamperometry study \((E = 0.7 \text{ V vs. RHE})\) (Figure 7b), which indicates a good tolerance to the presence of methanol in the solution. After 2000 seconds of continuous operation, the current value comprised 65% of the initial value, which is a good indicator, since under similar conditions the current drop for the E-TEK catalyst was 50% \([60]\). Compared to other analogues published in \([61,62]\), the stability of the mixed Pt/Cu catalyst in the presence of methanol is also higher.

The high methanol tolerance of the Pt/Cu electrocatalyst can be explained by combination of particle size and surface inhomogeneity effects. Maillard et al. \([63]\) found that ORR electrocatalysts with smaller metal particle sizes demonstrate enhanced methanol tolerance. It is established that at least three adjacent Pt sites in the proper crystallographic arrangement are necessary to activate the chemisorption of methanol for the methanol oxidation \([64–67]\), while only two adjacent Pt sites are necessary for the competing process of the oxygen adsorption. For the Pt/Cu electrocatalyst, where Pt surface is partially covered by methanol-tolerant Cu, the probability of finding three neighboring Pt atoms on the surface is lower compared to the pure Pt surface. It could hinder methanol adsorption on the catalyst and thus ensure little methanol effect on the current of oxygen reduction reaction.

3. Materials and Methods

3.1. General Remarks

In all electrochemical studies, a three-electrode electrochemical cell was used. The electropolymerization of [Cu(Salen)] was performed using the rotating disk glassy carbon electrode (RDE) with an area of 0.07 cm\(^2\) as a working electrode and a platinum plate (1 cm\(^2\)) as an auxiliary electrode. For experiments in aqueous solutions, a silver chloride reference electrode (SSCE) \((\text{Ag/AgCl (KCl sat.)})\) was used; while in non-aqueous solutions, a silver nitrate reference electrode \((\text{Ag/AgNO}_3 (0.01 \text{ M, CH}_3\text{CN}))\) \((0.35 \text{ V vs. SSCE})\) was used. The potential of SSCE reference electrode vs. reversible hydrogen electrode (RHE) potential in 0.2 M NaOH solutions used in the study comprises 0.890 V. All electrochemical studies were performed on Metrohm Autolab PGSTAT12 with Autolab Rotating Disk Electrode (Eco-Chemie, Utrecht, The Netherlands).

Morphology and elemental composition of the polymer and mixed catalyst were studied by the SEM/EDX method on the SUPRA 40VP (Carl Zeiss, Oberkochen, Germany) and Zeiss Merlin (Carl Zeiss, Germany) scanning electron microscopes. The X-ray photoelectron spectroscopy (XPS) of the materials was carried out on the Thermo Fischer Scientific Escalab 250Xi Spectrometer with nonmonochromatic
AIKα radiation (photon energy 1486.6 eV). A total energy resolution of the experiment was about 0.3 eV. Spectra of the samples were recorded in the constant pass energy mode at 20 eV, using a 650 mm diameter analysis area. Investigations were carried out at room temperature in an ultrahigh vacuum of the order of 1–10⁻⁹ mbar.

Commercial salicylaldehyde (Sigma-Aldrich, >97%), ethylenediamine (Sigma-Aldrich, purum p.a.) and copper(II) acetate tetrahydrate (Sigma-Aldrich, purum p.a.), K₂PtCl₆ (Sigma-Aldrich), propylene carbonate (99.7%, Sigma-Aldrich), acetonitrile (Cryochrome, cryogenically purified, water content <0.05%), CH₃OH (99%, Vekton), conc. HCl (reagent grade, NevaReactiv), and NaOH (extra pure, Wagent) were used without further purification. The commercially available Pt catalyst E-TEK used as a benchmark was prepared according to [36].

3.2. Catalyst Preparation

[Cu(Salen)] (Figure 8) complex was synthesized according to the known procedure by condensation of salicylaldehyde with ethylenediamine followed by metalation with copper(II) acetate tetrahydrate [68].

![Figure 8. Monomer [Cu(Salen)].](image)

Electropolymerization of [Cu(Salen)] from a monomer solution of 10⁻³ M [Cu(Salen)] and 0.1 M Et₄NBF₄ in acetonitrile or propylene carbonate was carried out by cyclic voltammetry in the potential range of 0–0.9 V (vs. Ag|AgNO₃) for four cycles at a potential sweep rate of 20 mV/s.

To incorporate Pt particles into the poly[Cu(SalEn)] film, the electrodes were cycled in a nitrogen saturated solution of 6.4 mM K₂PtCl₆ in 0.6 M aq. HCl from the open circuit potential to −0.3 V (vs. SSCE) with a potential sweep rate of 50 mV s⁻¹, and then the film was kept in a potentiostatic mode for the desired time at the potential of −0.3 V (vs. SSCE). The Pt loading was calculated according to Faraday’s law from the charge passed during the Pt electrodeposition.

Finally, the modified polymer was oxidatively hydrolyzed according to Kuznetsov et al. [33] in an oxygen saturated 0.2 M aq. NaOH by 150 cycles of potential sweep in the range of 2.1–0 V (vs. RHE) with sweep rate of 50 mV s⁻¹. Optimization of platinum loading in the mixed catalyst was carried out by varying the time of potentiostatic deposition step, with automatic termination of the experiment after reaching the desired charge value, which was chosen within the range from 72 µC to 1 µC.

E-TEK based catalyst was prepared as a Nafion-based ink and cast onto the GC electrode surface according to the method, described in [36]. Pt loading in the E-TEK based catalyst was determined from the ink volume, and E-TEK supplier specification.

3.3. Electrochemical Measurements

3.3.1. Cyclic Voltammetry

To confirm the activity of the mixed catalyst in the oxygen reduction reaction, cyclic voltammograms for oxygen reduction at the catalyst were registered at RDE in the potential range of 1.2–1.8 V (vs. RHE) at a set of rotation speeds (0, 500, 831, 1000, 1247, 1747, 2331, 2500, 3000, 3500, 4000 rpm)) and a sweep rate of 20 mV s⁻¹ in a 0.2 M solution of NaOH saturated with either argon or oxygen.

The number of electrons participating in the oxygen reduction reaction was calculated by the Koutecký–Levich equation as follows [51]

\[
\frac{1}{j} = \frac{1}{j_L} + \frac{1}{j_k} = \frac{1}{j} = \frac{1}{B \omega^{1/2}} + \frac{1}{j_k}
\]  

(1)
\[
B = 0.62nFD^{2/3} \omega^{-1/6}C_O; \quad j_k = nFkC_O
\]

where \( j \) is the overall current density, \( j_L \) is the diffusion-limiting current density, \( j_k \) is the kinetic-limiting current, and \( \omega \) is the electrode rotation rate (rpm), \( F \) is the Faraday constant (96,485 C mol\(^{-1}\)), \( n \) is the transferred electron numbers in the ORR, \( C_O \), \( D \) and \( \nu \) are the oxygen concentration, the oxygen diffusion coefficient and the kinematic viscosity for the solution, which for 0.2 M NaOH solution comprise \( 1.2 \times 10^{-6} \text{ mol cm}^{-3} \), \( 222 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1} \) \cite{69}, and 0.016 cm\(^2\) s\(^{-1}\) respectively.

### 3.3.2. Electrochemical Quartz Microbalance

Electrochemical quartz microbalance (EQCM) was used to find the optimum potentials for Pt deposition at poly[Cu(Salen)] and the polymer matrix hydrolysis. All measurements were carried out with in situ weight control during electrochemical experiment using a QCM200 Quartz Crystal Microbalance Analog Controller with QCM25 Crystal Oscillator (Stanford Research Systems, Sunnyvale, CA, USA). A platinum crystal with an area of 1.37 cm\(^2\) was used as a working electrode. The mass changes were calculated from the crystal resonant frequency according to the Sauerbray equation \cite{70}. The rigidity or the coating, necessary for Sauerbray equation application, was controlled by monitoring the crystal motional resistance.

### 3.4. Stability

#### 3.4.1. Study of a Catalyst Stability

Stability was studied in an oxygen saturated aq. solution of 0.2 M NaOH in a potentiostatic mode at a potential of 0.7 V (vs. RHE) for 60,000 s. After the experiment, the catalyst was washed with deionized water and immersed in the alkali solution again. The second part of the experiment was carried out under the same conditions for 65,000 s.

#### 3.4.2. Study of the Tolerance of the Catalyst to the Presence of Methanol

Methanol tolerance was studied with two additions of CH\(_3\)OH, each of them increased methanol concentration in the solution by 0.25 M. Measurements were carried in an aqueous solution of 0.2 M NaOH in the potentiostatic mode at a potential of −0.3 V for 2300 s.

### 4. Conclusions

In summary, an efficient Cu/Pt ORR catalyst for application in fuel cells has been developed. The catalyst shows high tolerance towards methanol poisoning and catalytic efficiency exceeding that of the commercial Pt/C catalyst (see Table S2 for details). The high durability of the catalyst is attained by homogenous distribution of copper domains across Pt surface, which decreases the number of active sites available for methanol sorption. This is achieved by the deposition of Pt on a poly[Cu(Salen)] polymer matrix used as a template. The highly developed surface attained during this process secures the high efficiency of the catalyst.

**Supplementary Materials:** The following are available online at http://www.mdpi.com/2073-4344/10/6/667/s1:
- Figure S1: (a,b) electrodeposition of poly[Cu(Salen)], 10-3 M [Cu(Salen)] in acetonitrile or propylene carbonate, 0-0.9 V (vs. Ag/AgNO\(_3\)), 20 mV/s; (d, e) electrodeposition of Pt particles, 6.4 mM K2PtCl\(_6\) in 0.6 M aq. HCl, −0.3 V (vs. SSCE), 50 mVs\(^{-1}\); Table S1: Load of Pt and monomer solvent solution; Figure S2: (a,b) SEM images of Pt particles, (c) distribution of Pt particles in the Pt/Cu(PC) catalyst; Figure S3: CV curves of poly[Cu(Salen)], Pt/Cu (PC), E-TEK and Pt catalyst modified RDE electrode in oxygen-saturated 0.2 M NaOH electrolyte, 1000 rpm; Figure S4: Koutecky–Levich plot at different potentials in oxygen-saturated 0.2 M NaOH electrolyte, (a) Pt/Cu(AN) catalyst, (b) E-TEK catalyst; Table S2: Electron transfer number calculated from slopes of Koutecky-Levich plots for different catalyst.

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