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Research Article

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Template- and Surfactant-Free Room Temperature Synthesis of Pt/C and Pt<C->Rh/C Nanowires/Nanoparticles for Ethanol Electro-Oxidation

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**Using a simple and direct method**, without the use of surfactants and/or templates, it was possible to synthesize Pt<C->Rh nanowires, despite the formation of Pt<C->Rh nanoparticles as well. In addition, the addition of Rh into the Pt catalyst greatly improves the catalytic activity and stability of the material towards ethanol electro-oxidation in comparison to commercial Pt/C catalyst.

The synthesis of Pt<C->Rh alloy nanowires (NWs) using straightforward methodologies remains a challenge. Here, carbon-supported Pt and Pt<C->Rh nanowire catalysts were synthesised by chemical reduction at room temperature, without using surfactants or templates. The method of synthesis used yielded Pt/C NWs and a mixture of nanowires with some nanoparticles for the Pt<C->Rh/C catalysts (characterised using XRD, TEM, EDX, XPS, and XAS). The nanoparticles form due to differences in the surface energy and atomic radius between Pt and Rh. The binary NWs are found to be more active towards ethanol oxidation than the commercial Pt/C reference catalyst. Additionally, the Pt<C->Rh/C NW catalyst displays a specific activity 2.5-fold higher than the Pt/C NWs and Pt/C reference catalysts after 15^^min of chronoamperometric tests (at 0.5^^V). Thus, the synthesised carbon-supported Pt NWs and Pt<C->Rh nanowires-nanoparticles are promising alternatives for direct ethanol fuel cell anodes.

binary catalysts
electroactivity
ethanol
nanowires
oxidation

Introduction

The high fossil fuel consumption, allied with increasing environmental degradation, has led to the search for alternative energy sources.[1] In this sense, fuel cells (FCs) emerged as environmentally-friendly energy systems which can be applied to many applications, such as (i) portable devices, (ii) stationary applications, and (iii) vehicles.[1] Ethanol can be highly attractive to be used as fuel for FC systems as long as its chemical energy is directly converted to electrical energy in a low-temperature reaction.[2]

Ethanol offers several ideal properties such as (i) low toxicity, (ii) easy logistics, (iii) high production from renewable sources (fermentation of raw materials), and (iv) high energy density (8.0^^kWh^kg<M->1).[2,3] Besides, ethanol is less permeable through the polymeric membranes used in low-temperature FCs. These characteristics make ethanol a feasible and a good alternative for low-temperature FCs.[3] The ideal reaction occurring at the anode of a direct ethanol fuel cell (DEFC) comprises the total ethanol oxidation to CO2 and H2O, which involves C<C->C bond cleavage and 12 electrons (e<M->) transferred per ethanol molecule.[2]

However, one of the major problems regarding ethanol oxidation is the lack of efficient catalysts for promoting the total oxidation of ethanol to CO2. Despite recent advances, the complete breaking of the ethanol C<C->C bond in acidic solutions is still complicated.[4] This complex reaction leads to strongly adsorbed species (like CO) and by-products (mainly acetaldehyde and acetic acid). These species strongly adsorb at the catalyst surface, poisoning it, thus causing a considerable decrease in FC overall efficiency.[2,5] The most promising catalysts to fully oxidize ethanol involve alloying Pt with Rh. The addition of Rh can increase the yield of CO2 production by promoting a more efficient C<C->C bond cleavage, also facilitating the removal of strongly adsorbed CO-like species.[6,7]

The catalytic efficiency and selectivity of catalysts also depend on their size and shape.[8] The FC technology still suffers from the limited activity and stability of Pt nanoparticles (NPs), even for the best catalysts. These problems are derived from the loss of Pt electrochemical surface area (ECSA) over time, caused by the corrosion of the carbon support and the combined effects of Pt dissolution/aggregation/Ostwald ripening. Pt NPs possess high surface energies that induce severe Ostwald ripening or grain growth during the operation of the FC.[9] The one-dimensional (1D) structure of nanowires (NWs) can overcome the drawbacks presented by NPs due to their unique features, such as (i) high surface-area-to-volume ratio, (ii) long segments of smooth crystal planes, and (iii) fewer surface defect sites.[10,11]

Recently, Rh atoms were selectively deposited onto defective sites of Pt NWs, thus producing core-shell Rh@Pt NWs.[12] Rh atoms altered the structure of Pt defect sites and improved the ability of the catalyst to electro-oxidise the alcohol fuel. The Rh@Pt NWs catalyst completely oxidises methanol and promotes the cleavage of the C<C->C bond of ethanol. In another report, Pt<C->Rh NWs were synthesised using metallic acetylacetonates, tungsten hexacarbonyl, oleylamine, and cetyltrimethylammonium bromide at 190^°C. Combining the 1D structural and synergistic effect of both metals resulted in enhanced activity towards ethanol oxidation compared with commercial Pt/C. The Pt<C->Rh NWs/C displayed superior anti-poisoning ability and exhibited significantly excellent ability for C<C->C bond cleavage with significant C1 pathway selectivity for ethanol oxidation.[13]

The syntheses of Pt and Pt-based NWs generally involve the use of templates, surfactants, or stabilising agents, which are accompanied by laborious and time/energy-consuming pre-synthesis and further removal steps that limit their practical applications to some extent. Moreover, Pt<C->Rh NWs were made using metallic acetylacetonates and environmentally unfriendly organic solvents and reactants.[13] Thus, synthesising catalysts through simple and eco-friendly methodologies that require fewer steps should be encouraged, as it increases the forms of application of these materials and reduces the costs involved in manufacturing. Hence, we hypothesised that Pt<C->Rh NWs could be produced using a simple chemical reduction of metallic precursors onto carbon powder, as accomplished in our earlier study in which Pt NWs were prepared using a similar process.[10]

To test whether this hypothesis holds, we report the synthesis of Pt and Pt<C->Rh NWs supported on carbon Vulcan XC-72R powder at room temperature and using metallic salts as precursors. The activity of the Pt/C and Pt<C->Rh/C NWs towards ethanol oxidation was also studied and compared with commercial Pt/C catalyst (Johnson MattheyTM, named in the manuscript as Pt/C JM), aiming to develop catalysts that can be successfully applied as anodes for DEFCs. Notably, the NWs were obtained through a one-step method without adding any additional surfactant, template, or stabilising agent. We demonstrate that both the NW morphology and the binary catalyst composition have a synergistic effect on the catalytic activity of the catalysts.

Results and Discussion

Physical characterisation

The TEM image of the synthesised Pt/C in Figure^^1<figr1>(a) shows NWs well dispersed over the carbon support. These NWs are composed of several short arms of Pt with approximately 20 and 4^^nm in length and diameter, respectively. The excellent dispersion of the Pt NWs over the carbon support suggests a functional interaction between the metallic atoms and the exposed crystal planes of the carbon.[12] However, a deep examination of the sample showed some particles and their agglomeration to form the NWs (Figure^^S1).

The TEM image of the Pt<C->Rh/C NW catalyst in Figure^^1<xfigr1>(b) shows a much greater extent of agglomeration of the particles. Careful inspection using TEM images at different magnifications shows a mixture of short and thin NWs and NPs (Figure^^S2). Hence, the presence of Rh atoms seems to lessen the formation of NWs compared with Pt, probably due to differences in the reduction potentials and surface energies of both metals, as will be discussed hereafter.

The powder XRD patterns obtained for the Pt/C JM, Pt/C, and Pt<C->Rh/C catalysts are shown in Figure^^2<figr2>. The Pt/C JM catalyst showed a diffraction peak at 2θ=30.34°, which is ascribed to graphite carbon (PDF card no. 001-0646). For the Pt/C catalyst, the peaks at 2θ=39.91°, 46.44°, 67.75°, 81.60, and 86.21° are assigned to the face-centred cubic (fcc) phase of the polycrystalline Pt reflection planes (111), (200), (220), (311), and (222), respectively, in accordance with PDF card no. 004-0802.

The bimetallic Pt<C->Rh/C catalysts display similar XRD patterns as the pure Pt catalysts, showing that the fcc structure was maintained with the inclusion of Rh. Further inspection reveals a shift of the peaks to higher 2θ for the Pt<C->Rh/C catalysts, which is expected as the substitution of Pt atoms by Rh atoms with smaller radius results in the contraction of Pt crystal lattice and is attributed to the formation of a Pt<C->Rh alloy.[3] In addition, the Pt^:^Rh elemental ratio (47.3^:^52.7) taken from SEM-EDX measurements (Figure^^S5) is close to the nominal one (50^:^50), demonstrating the feasibility of the adopted synthesis method.

The survey XPS spectra of Pt/C and Pt<C->Rh/C NWs catalysts are shown in Figure^^3<figr3>, with the high-resolution XPS spectra of Pt 4^f and Rh 3d presented in Figures^^3<xfigr3>b--3d. As expected, the survey scans of the catalysts detected only emissions related to platinum, oxygen, rhodium, and carbon. The survey XPS spectra reveal that the surface composition of Pt<C->Rh/C NWs (Pt^:^Rh=42.7^:^57.3) agrees with the EDX measurements.

The XPS spectra of the Pt 4^f level for Pt/C NWs (Figure^^3<xfigr3>b) and Pt/C NWs (Figure^^3<xfigr3>c) were fitted with two spin-orbit spitted in two parts the band of Pt 4f5/2 at low energy and the high-energy band of Pt 4f7/2. For Pt/C NWs, the peaks at around 335.24 and 341.17^^eV are attributed to metallic Pt (Pt0), while the less intense doublets at around 71.47 and 74.82^^eV correspond to Pt 4f7/2 and Pt 4f5/2 peaks of Pt2+.[17,18] These data indicate that the Pt species supported on carbon consist of metallic Pt and PtO.

In the case of Pt<C->Rh/C NWs, the binding energy of the Pt signals has shifted negatively compared with Pt/C NWs (71.13 and 74.68^^eV for Pt 4f7/2 and Pt 4f5/2, respectively), indicating the modification of the electronic structure of Pt by the addition of Rh (Figure^^S3).[18--20] According to the *d*-band theory proposed by Hammer and Nørskov,[21] adding a second metal to the Pt can induce a shift to more negative values of the centre of the *d* band of Pt, weakening the binding between the Pt and the adsorbed intermediates.

The Rh 3d spectrum for Pt<C->Rh/C NWs (Figure^^3<xfigr3>d) also presents the contribution of two pairs, the binding energy of Rh 3d5/2 and Rh 3d3/2.[19] The most intense doublet at 304.76 and 309.46^^eV can be assigned to metallic Rh (Rh0), while the peak at 313.15^^eV corresponds to Rh oxides.[19]]

Alternatively, due to similar cell constants for Pt (3.924^^Å) and Rh (3.803^^Å) and the broadness of the peaks, we cannot eliminate the possibility that Pt and Rh are present as separate phases in the Pt<C->Rh samples, which will be investigated below. The mixing of Pt<C->Rh was further studied by EXAFS at the Pt L3 edge and the Rh K edge (Figure^^4<figr4>). Compared to Pt/C and Rh foil, the Pt<C->Rh/C shows decreased amplitude in 2.5--2.8^^Å at the Pt L3-edge and a peak splitting of the first shell at the Rh K edge, which results from the phase cancelling of multiple scatterers at a close distance. These differences at the Pt and Rh edges indicate the mixing of Pt and Rh in the Pt<C->Rh/C sample.

The extent of mixing of Pt and Rh was extracted by EXAFS fitting. The fits of Pt<C->Rh/C catalysts are shown in Figure^^S4, and the obtained structural parameters are listed in Table^^1<tabr1>. For the Pt<C->Rh/C catalyst, hetero-atomic scattering paths between Pt<C->Rh must be included to produce good fits. The fits for Pt L3 edge and Rh K edge were performed interactively by setting Pt<C->Rh and Rh<C->Pt in the same values for the bond length and it is mean square displacement, that is, RPt<C->Rh=RRh<C->Pt and σ2Pt<C->Rh=σ2Rh<C->Pt.

The mixing of Pt and Rh was then studied using the obtained coordination number. The extent of alloying of Pt (JPt) and Rh (JRh) were calculated using Equation^^(1), assuming narrow composition distributions over the particles.[22] <ffr1>

<ff1>JA=PA, observed/PA, random<ZS>(1)

Where for the calculus of PA, we used Equation^^(2).<ffr2>

<ff2>PA=NAB/NAA+NAB<ZS>(2)

P is the coordination number ratio of A<C->B scattering to the sum of A<C->B and A<C->A, and the P for random alloy (Prandom) is derived from the corresponding random alloy. For a perfect Pt1Rh1 solid solution, NPt<C->Pt=NPt<C->Rh and NRh<C->Rh=NRh<C->Pt, then both PPt, random, and PRh, random equal to 0.5. Thus, the calculated values of JPt and JRh are ~25^% and ~133^% for Pt<C->Rh/C catalyst (Table^^1<xtabr1>). Because JPt <100^% and JRh >100^%, no perfect Pt1Rh1 alloy was formed, and it is suggested that the interactions between atoms follow this order, Pt<C->Pt>Pt<C->Rh/Rh<C->Pt>Rh<C->Rh. Thus, the Pt<C->Rh NPs of Pt<C->Rh/C probably adopt a structure with a Pt-rich core and a Rh-rich shell.[15]

The existence of clustered Pt<C->Rh NWs and Pt<C->Rh NPs can be explained in terms of the surface energy difference between Pt and Rh. It is known that the compound with a higher reduction potential is reduced faster.[23] Here, Pt and Rh have similar reduction potentials, 0.755 and 0.758^^V *vs* standard hydrogen electrode (SHE), respectively.[24] Hence, the formation of Pt and Rh nanoparticles could occur simultaneously.

However, Rh has a higher surface energy than Pt (2.90 and 2.82^^J m<M->2) and a slightly smaller atomic radius (rRh=0.134^^nm and rPt=0.139^^nm) and, therefore, diffuses more slowly than Pt.[24] In this way, Pt nanoparticle seeds are formed initially. With the first nanoparticles formed, the growth of Pt nanowires begins and, in parallel, the formation of Rh nanoparticle seeds. As the growth of Pt nanowires is slow and Pt ions are still available in the reaction solution, these Pt ions meet Rh ions and form Pt<C->Rh nanoparticles. These observations agree with the higher amount of Pt<C->Rh nanoparticles observed in the TEM images (Figure^^1<xfigr1> and Figure^^S2) and the EXAFS data (Table^^1<xtabr1>), which indicate the existence of separate phases in the form of individual Pt or Rh NPs, and alloy nanoparticles.

Electrochemical characterisation

Figure^^5<figr5> shows the CO-monolayer stripping cyclic voltammetry data recorded on 0.5^^mol^L<M->1 H2SO4 at 20^^mV^s<M->1. CO-monolayer stripping voltammetry is frequently used to determine the tolerance of the catalysts to poisoning by CO. A more negative potential is related to improved CO oxidation. The voltammogram for Pt/C JM showed a single peak (peak III) at 0.82^^V. However, Pt/C and Pt<C->Rh/C NWs presented an additional peak, denoted as peak II, and a shoulder (peak I), both at lower potentials. The multiplicity of CO oxidation peaks for both synthesised catalysts is derived from CO adsorption on different crystallographic orientations.[23]

The small peak I at around 0.50^^V at all synthesised catalysts is related to a so-called pre-oxidation wave in which weakly adsorbed CO (bridge-bonded) is oxidised.[25] Peak II is attributed to the oxidation of weakly adsorbed CO on Pt (111) facets,[25] present in large quantities in Pt and Pt<C->Rh NWs, compared with commercial Pt nanoparticles, in which peak II is absent.

The CO oxidation onset potential (peak II) was, in the order: Pt<C->Rh/C (0.55^^V)<Pt/C (0.68^^V)<Pt/C JM (0.77^^V). A lower potential for CO-monolayer oxidation can be seen for NWs, especially for the Pt<C->Rh/C catalyst. This better activity is probably related to more pronounced intrinsic catalytic properties derived from an electronic effect on Pt atoms caused by the presence of Rh, which is also associated with the morphology of nanowires. Rh atoms act to promote the availability of the proper amount of oxygen for CO-monolayer oxidation that happens at lower potentials[26] due to a bifunctional mechanism operating at the bimetallic catalyst.

Moreover, the modification of Pt with Rh results in a down-shift of the Pt 5d-band centre caused by the lattice mismatch and electronic interaction between Pt and Rh atoms, as observed in XPS measurements (Figure^^S3). This claim may be supported by density functional theory (DFT) computations.[27--29] DFT calculations demonstrated that the activation barrier for the atomic oxygen bound is ~0.6^^eV lower for a Pt monolayer supported on Rh (111) than for the surface of pure Pt;[27] this was attributed to a shift of the *d*-band centre to lower energy caused by strain and vertical ligand effects.[28] In addition, using DFT calculations, Luo et^^al.[29] revealed that doping Pt (110) surface with a single Rh atom leads to a substantially lower activation barrier to C<C->C bond cleavage of 0.72^^eV compared to Pt (110) which required an activation barrier of 1.1^^eV. When combined with tensile strain, the tensile-strained Rh/Pt (110) surface leads to the lowest barrier (0.67^^eV). Therefore, the Pt reactivity or the adsorption strength between Pt and CO (Pt<C->CO) leads to faster oxidation of the CO-monolayer.[26] Hence, both bifunctional and electronic effects may also contribute to the enhanced kinetic towards CO oxidation on Pt<C->Rh catalysts and an improved water dissociation to form adsorbed OH, thus, increasing the CO<C->O coupling.[30] This trend is expected in this work, evidenced by the shape of the voltammogram and the lower strongly adsorbed CO onset potential of the Pt<C->Rh/C catalyst.

Although the commercial Pt/C JM catalyst displays the highest CO oxidation peak, the more positive onset potential indicates difficult oxidation of CO adsorbed on the Pt surface due to a high affinity between CO and Pt. Moreover, this oxidation peak (peak III) may be associated with a CO oxidation process occurring on isolated nanoparticles.[31]

The electrochemical surface area (ECSA) of the catalysts was calculated based on the area below the CO oxidation peak, assuming that the oxidation of a monolayer of linearly adsorbed CO involves a charge of 420^^μC^cm<M->2.[15] The ECSA values for NWs catalysts, displayed in Table^^2<tabr2>, were higher than those of the commercial Pt/C material, especially the bimetallic Pt<C->Rh catalyst, which obtained an area 1.56 times larger than the commercial Pt catalyst. This outcome suggests that Pt<C->Rh/C NWs possess more active sites than the other materials.

Figure^^6<figr6> shows cyclic voltammograms (Figure^^6<xfigr6>(a)) and derivative voltammograms (Figure^^6<xfigr6>(b)) for all catalysts in the presence of ethanol. According to Figure^^6<xfigr6>(a), the hydrogen adsorption region (Figure^^S6) is inhibited on all catalysts, suggesting strong adsorption of ethanol molecules with the active sites of the catalysts.[32,33]

Based on the current densities in the anodic scan, the EOR rate accompanies the following order: Pt<C->Rh/C>Pt/C>Pt/C JM. The Rh-containing catalyst displays a specific activity, measured at the anodic scan (ia), almost 2-fold higher than the commercial Pt catalyst (Table^^2<xtabr2>). Unlike CO-monolayer oxidation, for the EOR, the overall oxidation enhancement is related to the fact that Rh addition increases the ability towards the C<C->C bond cleavage.[5,34] The Rh species increase the yield of CO2 production by promoting a more efficient C<C->C bond dissociation,[35,36] also providing oxygen species at low potentials to further oxidation of intermediates produced in ethanol’s dissociative adsorption on the catalyst sites. Consequently, the EOR onset potential measured at 0.01^^mA^cm<M->2 is lower, as observed in Table^^2<xtabr2>.

Figure^^6<xfigr6>(b) shows the first derivative of the anodic sweep for Pt/C JM, Pt/C, and Pt<C->Rh/C catalysts, as described in detail by Murthy and Manthiram.[37] Currently, a dual-pathway mechanism on Pt catalysts is broadly accepted for acid or alkaline environments.[12,38,39] A pathway that leads to the C<C->C bond breaking, through COads oxidation to CO2, releasing 12 electrons per ethanol molecule oxidised, and the second path that leads to the formation, mainly, of acetic acid (releasing 4e<M->) and acetaldehyde (releasing 2e<M->), without the C<C->C bond breaking.[39]

All curves in Figure^^6<xfigr6>(b) display two positive peaks, which were more defined for the NW Pt/C and Pt<C->Rh/C catalysts. The current behaviour is similar for all catalysts between 0.2 and 0.4^^V, which is the region where ethanol dehydrogenation occurs. Peak II at around 0.82^^V is related to the oxidation of COads to CO2, which could be the rate-determining step (rds) for all catalysts. Peak I (about 0.73^^V) can be related to EOR through the C<C->C bond breaking (C1 pathway), and, therefore, the higher this peak, the greater the amount of CO2 produced. However, if this peak did not exist, as indicated by the dashed arrow, the formation of species without breaking the C<C->C bond (C2 pathway) would be dominant. Further increase in the potential around 0.83^^V leads to more coverage of Pt sites with OH, blocking the ethanol adsorption and decreasing the EOR, resulting in the third peak (peak III).

The Pt/C and Pt<C->Rh/C NWs catalysts showed a much higher peak I (Figure^^6<xfigr6>(b)) than the Pt/C JM catalyst in the derivative voltammograms, suggesting an improvement in selectivity for C<C->C bond breaking. It is worth noticing that a previous report from our group[10] revealed that the production of CO2 determined by FTIR measurements was higher on the Pt/C NWs catalyst than on the commercial Pt/C NP catalyst in all potentials studied. This feature can be associated with surface contraction for Pt nanowires. According to Nørskov and Hammer’s reports,[40,41] a down-shift of the d-band centre of Pt may occur due to a surface contraction strain, decreasing the adsorption strength of reactants on the catalyst surface. Wang and co-workers[42] reported a down-shift of the Pt 5*d*-band for Pt NWs compared to Pt NPs supported on carbon. Thus, the NW morphology may improve CO oxidation due to the weaker binding of CO, leading to an enhanced oxidation rate. Additionally, the interaction between Pt and Rh atoms, in which Rh modifies the Pt lattice, improves the C<C->C bond cleavage and ethanol oxidation,[3] thus explaining the best catalytic activity of the Pt<C->Rh/C catalyst.

The Pt/C JM catalyst showed low ethanol oxidation (compared with the Pt/C NW catalyst) since the higher II/I peak ratio should indicate that the C2 pathway dominates at this catalyst. This observation can result from the high affinity of Pt for intermediary carbonaceous species. The derivative current reaches its minimum value at ~0.96^^V for all catalysts since, at this point, OH species are strongly adsorbed at the catalyst’s sites, blocking the adsorption of ethanol from the bulk solution. The onset potential for ethanol oxidation (measured at the derivative current of 0.15^^mA) is similar for Pt/C and Pt<C->Rh/C catalysts, which are much lower than at the commercial Pt/C catalyst, with values of 0.50, 0.43, and 0.42^^V versus RHE for Pt/C JM, Pt/C, and Pt<C->Rh/C, respectively.

In addition, a direct comparison of the results published by different research groups becomes difficult due to different experimental conditions, such as the catalytic charge deposited on the working electrode, the alcohol concentration, and the scan rate, among others. Nevertheless, Table^^S1 compares the performance of some Pt-based bi and trimetallic NWs catalysts and the Pt<C->Rh/C catalyst developed in this work for ethanol oxidation. Notably, the Pt<C->Rh/C NWs catalyst showed mostly higher current densities for ethanol oxidation than the NW catalysts reported in the literature (Table^^S1). Wang et^^al.[43] reported the maximum mass currents of 520 and 1050^^mA^mg<M->1Pt for Pt48Pd52 and Pt22Pd27Cu51 NWs materials at the forward scan, which are lower than the values displayed by our binary catalyst (1332^^mA^mg<M->1Pt+Rh). The mass activity of our Pt<C->Rh/C NWs catalyst was also higher than the Pt1Fe0.20Sn0.46 NWs reported in the research of Wang et^^al.,[44] 1210^^mA^mg<M->1Pt. Another research group[45] reported a mass activity of 1550^^mA^mg<M->1Pt for their most active PtRh NWs/C catalyst. This activity is higher than the maximum mass activity observed in our study (1332^^mA^mg<M->1Pt+Rh); however, they used organic solvents and surfactants in their synthesis, which, as already discussed in this work, may lead to additional synthetic steps for the removal of these compounds.

Chronoamperometric tests were used to evaluate the stability of the catalysts at 0.5^^V (potential of technical interest). As can be seen in Figure^^7<figr7>, all catalysts show a quick decay of capacitive current at the beginning of the measurement. This decay is due to double layer loading and a poisoning effect caused mainly for COads intermediate species.[12,46] Both synthesised catalysts showed higher current density at the end of the experiment than the commercial Pt/C catalyst, indicating better EOR and less coverage of the catalyst surface by intermediate by-products.

Further, the Pt<C->Rh/C catalyst showed a current density almost 3.1-fold higher than the Pt/C commercial catalysts after 300^^min. These results were similar to those found in the literature. In all cases, the Pt<C->Rh/C catalysts showed higher current densities at the end of the chronoamperometric tests.[3,12--14] This better activity may be attributed to a bifunctional mechanism and electronic effects operating on this catalyst due to the presence of Rh, which develops oxygen-containing compounds at lower potentials, providing a great C<C->C bond dissociation activity and better resistance to poisoning by intermediate species. Therefore, these catalysts possess more free catalytic active sites leading to further ethanol oxidation.[12,47]

To complement the stability studies carried out for chronoamperometry, the polarisation curves taken before and immediately after consecutive cyclic voltammograms are displayed in Figure^^S7. Besides Pt/C NW catalysts, all catalysts showed a significant activity loss after accelerated degradation tests were conducted. After 1000 cycles, the superior stability of the activity of the Pt/C catalyst can be a result of the predominant 1D NW structure compared with the hybrid NWs-NPs morphology of the Pt<C->Rh/C catalyst, which makes Pt less vulnerable to dissolution, aggregation, or Ostwald ripening during system operation.[27]

Conclusion

Pt and Pt<C->Rh NWs supported on carbon Vulcan XC-72R powder using a simple, low-cost, template-free, and surfactant-less chemical reduction of metallic precursor’s method by formic acid were successfully synthesised. The developed catalysts were used to study the EOR in acidic media. TEM images confirmed the formation of Pt/C NWs and a mixture of nanowires with some nanoparticles for the Pt<C->Rh/C catalyst. The binary catalyst is formed by some separate Pt and Rh phases and by Pt<C->Rh alloy structures. The introduction of Rh atoms at the Pt lattice modified the properties of the materials, resulting in more active catalysts. All the synthesised NWs displayed improved catalytic activity compared with the commercial Pt/C Johnson Matthey (JM) catalyst, showing higher oxidation current densities and lower onset potentials for ethanol oxidation.

The Pt<C->Rh/C NW catalyst has the highest catalytic activity towards EOR, followed by Pt/C and Pt/C JM catalysts in sequence. Derivative voltammetry data suggest that the Pt<C->Rh/C catalyst efficiently oxidises ethanol. The reason is the Rh atoms can promote the breaking of the ethanol C<C->C bond, thus improving the intrinsic electrocatalytic activity of the catalyst. The results confirm the feasibility of the applied method to produce Pt<C->Rh/C catalysts since the use of Rh with Pt facilitates the removal of intermediate species from the catalyst surface, producing efficient catalysts to be applied as anodes for DEFCs.

Experimental Section

Nanowire syntheses

The Pt and Pt<C->Rh nanowires were synthesised through the chemical reduction of metallic precursors by the addition of formic acid (CH2O2, Sigma-Aldrich®, 98^%--100^%)[9,10,14] without the aid of surfactants, stabilising agents, and templates. The entire synthesis route was conducted in an aqueous solution under ambient temperature and pressure conditions. The Pt<C->Rh NWs were synthesised with a fixed atomic proportion of Pt and Rh (1^:^1) over the carbon support (Vulcan XC-72R), namely, Pt/C and Pt<C->Rh/C. The NWs were obtained using 40^^wt.% of metal loading in relation to the carbon support.

The synthesis of Pt and Pt<C->Rh NWs was carried out using hexachloroplatinic acid (Sigma-Aldrich®, 37.5^% of Pt) and rhodium (III) chloride hydrate (RhCl3.xH2O, Sigma-Aldrich®, 99.0^%) dissolved in an aqueous solution. First, for binary catalysts, suitable amounts of a hexachloroplatinic acid solution (33.58^^mM) and rhodium (III) chloride hydrate were dissolved in 4^^mL of ultrapure water in an ultrasonic bath for 30^^min. Afterwards, the dissolved solution was diluted with more ultrapure water, a total volume of 90^^mL. After that, 6.0^^mg of carbon powder (Vulcan XC-72R) were added to the solution and stirred for 15^^min. Then, formic acid was added, and the suspension was stirred for 15^^min.

The resulting suspension was stored for 72^^h to allow NWs growth and avoid agglomeration. After 72^^h, the suspension changed from black to colourless, confirming the reduction of metallic precursors, and the catalyst powder rested at the bottom of the reaction flask. After that, the resulting powder was filtered under vacuum, washed several times with ultrapure water, dried in an oven for 30^^min at 60^°C and finally stored for further analyses. The synthesised catalysts were compared with a commercial Pt/C Johnson Matthey catalyst, Pt/C JM.

Electrode preparation and electrochemical measurements

The electrochemical measurements were performed in a conventional three-electrode electrochemical cell using an Autolab Model PGSTAT 302^^N potentiostat/galvanostat. A reversible hydrogen electrode (RHE) prepared in the same electrolyte solution immersed in a Luggin capillary was used as the reference electrode, a Pt spiral wire as the counter electrode, and a glassy carbon disk (GC, 0.071^^cm2) as the working electrode. Measurements were performed in an O2-free solution of 0.5^^mol^L<M->1 H2SO4 (Sigma Aldrich, 98^%) saturated with high purity N2 (White Martins, 99.9^%) in the absence or presence of 0.5^^mol^L<M->1 ethanol (C2H6O, Sigma Aldrich, 99.5^%). All aqueous solutions used in this work were prepared with ultrapure water (Gehaka MS 2000 model system, 18.2^^MΩ·cm).

Before each measurement, the GC electrode was polished with a 0.3^^µm α-alumina suspension, then sonicated in an ultrasonic bath with 2-propanol and ultrapure water in sequence to remove surface residues and renew the electrode surface. Subsequently, 3.0^^mg of each catalyst was weighed and added to a solution composed of 1000^^µL of 2-propanol and 30^^µL of 5^^wt.% Nafion® (Sigma Aldrich) to prepare catalyst inks. The resulting suspension was then subjected to an ultrasonic bath for 20^^min to disperse and homogenise the powder catalysts in the solution. Finally, 5^^µL of the catalyst ink was deposited dropwise on the GC electrode surface and dried at room temperature to give a catalyst loading of 0.21^^mg^cm<M->2.

The catalysts were first pre-treated using 500 cyclic voltammetry scans between 0.05 and 0.80^^V to activate the catalytic sites for further reaction and obtain reproducible voltammograms. Then, two cyclic voltammetry scans at 20^^mV^s<M->1 between 0.05^^V and 1.30^^V were performed in the presence and absence of ethanol. Accelerated degradation tests were conducted by potential cycling between 0.05 and 1.30^^V versus RHE for 1000 cycles at 50^^mV^s<M->1 in N2-purged 0.5^^mol^L<M->1 H2SO4+0.5^^mol^L<M->1 ethanol solution at room temperature. Then, linear-sweep voltammetry (LSV) curves were compared before and after the accelerated degradation tests.

The chronoamperometric (CA) tests were conducted by fixing the potential at 0.5^^V (potential of technical interest) for 15^^min to visualise the stability and the catalyst’s resistance to poisoning by intermediate species derived from the EOR. Derivative voltammetry was done to obtain better information about the EOR mechanism. The derivative voltammograms were done from the derivative of the first cycle of the ethanol oxidation voltammogram, between 0.05 and 1.20^^V versus RHE at 20^^mV^s<M->1. Quasi-steady-state polarization curves were conducted in a potential window from 0.1 to 0.8^^V from potentiostatic currents measured after 200^^s polarisation at each potential; these curves were conducted after 1000 voltammetric cycles in the supporting electrolyte in order to assess the stability of the activity of the catalysts under study.

CO-stripping experiments were carried out in a 0.5^^mol^L<M->1 H2SO4 electrolyte. For this measurement, the same pre-treatment procedure described above was made. CO voltammograms were obtained after bubbling CO gas into the electrochemical cell for 5^^min, holding the potential at 0.05^^V versus RHE. The electrolyte was then sequentially purged with high-purity N2 for 25^^min to remove the remaining CO in the solution. After, a CO-stripping voltammogram (1 cycle) between 0.05^^V and 1.30^^V versus RHE at 20^^mV^s<M->1 was obtained. For the ECSA calculation, the area below the peak of CO oxidation was used, assuming that the oxidation of a monolayer of linearly adsorbed CO involves a charge of 420^^μC^cm<M->2.[15] The ECSA normalised all electrochemical results presented in this paper.

Physical characterisation

X-ray diffractograms of the catalysts were obtained using a Bruker D8 Advance, operating with Cu Kα radiation (λ=0.15406^^nm). The diffraction patterns were registered from 20 to 90° with a scan rate of 2°^min<M->1 (the equipment operated at 50^^kV and 100^^mA). The XRD patterns were compared with the JCPDS (Joint Committee of Powder Diffraction Standard) crystallographic cards. Transmission electron microscopy (TEM) measurements were carried out using an FEI Tecnai 12 microscope at an 80-kV accelerating voltage and a JEM 1400plus microscope at a 120-kV accelerating voltage to identify the morphology of the catalysts and their sizes. Energy-dispersive X-ray spectrometry (EDX) measurements were performed in an EDX LINK ANALYTICAL (Isis System Series 300) coupled to a ZEISS LEO 440 Scanning Electron Microscope. The analysed sample area was 320×320^^mm.

X-ray photoelectron spectroscopy (XPS) measurements were carried out using an Omicron spectrometer (CHA - Concentric Hemisferica analyzer), with a monochromatic Al Kα X-ray source radiation (hν=1486.6^^eV) at a base pressure of 5×10<M->9 mbar. Binding energies of the spectra were referenced against the C 1^^s component of adventitious carbon at 284.6^^eV. Peak energies were given with an accuracy of 0.1^^eV. The spectra were deconvoluted using a Levenberg-Marquardt algorithm of the CasaXPS software.

X-ray absorption spectroscopy (XAS) measurements were conducted at the B18 beamline at Diamond Light Source (United Kingdom). Each sample was ground and mixed with boron nitride before being compressed into a pellet. XAS spectra of the pellets were recorded in the transmission mode at the Pt L3-edge and in the fluorescence mode at the Rh K-edge. The spectra were collected in an H2 atmosphere at room temperature to reduce the surface oxidation of the metals, which facilitates data analysis. Pt or Rh foils were measured along with the samples in the reference channel for energy calibration. Data reduction and analysis of XAS spectra were conducted using the Demeter software package (ATHENA and ARTEMIS, respectively).[16] The edge step of each spectrum was normalised by subtracting the pre-edge with a linear function and the post-edge with a quadratic function. The energy shift was calibrated by choosing the zero crossings of the second derivative of the reference spectra as E0 and assigning it to the corresponding tabulated value provided by ATHENA. The Fourier transformation from extended X-ray absorption fine structure (EXAFS) spectra in the k-space to those in R-space was conducted within a Hanning window function of k=3--15^^Å<M->1 for the Pt edge data and of k=3.6--14^^Å<M->1 for the Rh edge data. The spectra in the R space are not phase corrected.

The EXAFS spectra were obtained by subtracting the corresponding XAS spectra with a background algorithm (AUTOBKG) provided by ATHENA. For fitting Pt<C->Rh/C, double dataset fitting was performed for the first coordination shell of the Pt edge and the Rh edge data, with the hetero-atomic scattering paths, Pt<C->Rh and Rh<C->Pt, sharing the same R and σ2. The amplitude reduction factors were determined to be 0.837 for Pt and 0.829 for Rh by fitting the corresponding foil spectra.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

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Figure^^1 TEM micrographs of the synthesised nanowires: (a) Pt/C NWs and (b) Pt<C->Rh/C NWs catalysts.

Figure^^2 XRD patterns of the Pt/C JM, Pt/C NWs, and Pt<C->Rh/C NWs catalysts.

Figure^^3 (a) Survey XPS spectra of Pt/C NWs and Pt<C->Rh/C NWs. High-resolution spectra of Pt 4^f for (b) Pt/C NWs and (c) Pt<C->Rh/C NWs. (d) High-resolution spectra of Rh 3d for Pt<C->Rh/C NWs.

Figure^^4 Magnitude of the Fourier transforms of Pt L3 edge and Rh K edge spectra of Pt<C->Rh/C NWs catalyst.

Figure^^5 CO-monolayer stripping voltammetry on Pt/C JM, Pt/C NWs, and Pt<C->Rh/C NWs catalysts in 0.5^^mol^L<M->1 H2SO4 at 20^^mV^s<M->1.

Figure^^6 (a) Cyclic voltammograms (second cycle) for the electrochemical oxidation of ethanol 0.5^^mol^L<M->1 dissolved in H2SO4 for the Pt/C JM, Pt/C NWs, and Pt<C->Rh/C NWs catalysts. ʋ=20^^mV^s<M->1 and T=25^°C. ia and ib represent peaks for ethanol oxidation at the anodic and cathodic scans. (b) First derivative voltammograms of anodic scans for ethanol oxidation on Pt/C JM, Pt/C, and Pt<C->Rh/C catalysts obtained in 0.5^^mol^L<M->1 H2SO4 + 0.5^^mol^L<M->1 ethanol at 20^^mV^s<M->1.

Figure^^7 Chronoamperometric curves were obtained for catalysts Pt/C JM, Pt/C, and Pt<C->Rh/C catalysts in 0.5^^mol^L<M->1 H2SO4 + 0.5^^mol^L<M->1 ethanol solution for 15^^min. The electrodes were polarised at 0.5^^V. T=25^°C.

Table^^1 Structural parameters of Pt<C->Rh/C catalyst obtained from EXAFS fitting.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Sample | Scattering path[a] | N[b] | R [Å][c] | σ2×102 [Å2][d] | J [%] | R factor [%] |
| <?IMA tbcolhmode=0?>Pt<C->Rh/C | Pt<C->Pt | 8.4(2) | 2.751‍(1) | 0.55‍(2) | 25 | 1.2 |
| Pt<C->Rh | 1.2(2) | 2.73 e | 0.48‍(8) e |
| Rh<C->Rh | 3(3) | 2.71‍(3) | 0.5(7) | 133 |
| Rh<C->Pt | 6(3) | 2.73[e] | 0.48‍(8)[e] |

[a]The Pt<C->Pt and Rh<C->Rh scattering paths were calculated using the crystal structure of Pt (ICSD 52250) and Rh (ICSD 52252), respectively. The heteroatomic scattering paths, Pt<C->Rh and Rh<C->Pt, were modelled by replacing all the scattered atoms in Pt with Rh or the scattered atoms in Rh with Pt, and the unit cells of these two models were set as the same lattice parameter of 3.875^^Å, which is between those of Pt and Rh. [b] N, the coordination number of absorber-backscatter scattering pairs. [c] R, the average distance of the pair. [d] σ2, mean square relative replacement of the R. [e] The R and the σ2 of Rh<C->Pt are set as the same as those of Pt<C->Rh, respectively.

Table^^2 CO and ethanol oxidation onset potential, specific activity, and Tafel slopes for all catalysts synthesised in this study.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Catalyst | ECSA [cm2] | CO oxidation onset potential [V] | Ethanol oxidation onset potential [V][a] | Specific activity [mA cm<M->2][b] |
| Pt/C JM | 2.61 | 0.77 | 0.56 | 0.24 |
| Pt/C | 2.97 | 0.68 | 0.55 | 0.34 |
| <?IMA tbcolhmode=0?>Pt<C->Rh/C | 4.07 | 0.61 | 0.50 | 0.40 |

[a] Values obtained at the anodic scan peak. [b] Values obtained from cyclic voltammetry.