

CATAPULT

NOVEL CATALYST STRUCTURES EMPLOYING Pt AT ULTRA LOW AND ZERO LOADINGS FOR AUTOMOTIVE MEAS

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DELIVERABLE REPORT

D5.4 – IL-DERIVED NON-PGM CATALYSTS SYNTHESIS AND CHARACTERISATION INCLUDING RDE

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NATURE OF THE DELIVERABLE

R	Report	X
P	Prototype	
D	Demonstrator	
O	Other	

SUMMARY

Keywords	<i>Non-PGM catalysts, one pot synthetic approach, ionic liquid (IL), oxygen reduction</i>
Abstract	<p>A one-pot approach through direct pyrolysis of a nitrogen-rich ionic liquid (IL) was used for synthesis of N-doped carbon. Carbonisation of IL in the presence of Fe resulted in a highly graphitised carbonaceous material which was tested for oxygen reduction in acid medium under rotating disk and fuel cell conditions. Accordingly, IL was impregnated with 1 wt% of Fe and pyrolysed under argon at three different temperatures, 500, 900 and 1100 °C. The carbonaceous material showed different activity regarding the pyrolysed temperature. While the IL-500 °C has no activity in acid electrolyte, the samples pyrolysed at 900 and 1100 °C showed much improved activity, comparable to our internal reference Fe-N-C material when measured in pH 1 aqueous electrolyte. However, it has to be noted that the IL-derived samples are more limited by O₂ diffusion in the catalytic layer, as seen from the long transition from the kinetic control to full diffusion control outside the active layer. In order to improve the porous properties of the carbonised IL, the best performing catalyst, pyrolysed at 1100 °C in argon, was post-treated in NH₃ at 950 °C and tested in a fuel cell. However, the performance of the IL-derived catalyst showed very low activity in kinetic and diffusion region, even after NH₃-treatment.</p>

REVISIONS

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0.1	10-03-2016	Nastaran Ranjbar	Initiated
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D5.4 - IL-DERIVED NON-PGM CATALYSTS SYNTHESIS AND CHARACTERISATION INCLUDING RDE

1.0 Introduction

This report investigates ionic liquids (IL) as the source of nitrogen and carbon for synthesis of non-PGM electrocatalysts for the oxygen reduction reaction (ORR) in acid medium. ILs as the precursor of carbonaceous materials doped with heteroatoms have numerous applications due to the versatility of the nature of the cation and anion. ILs can be used either directly as the carbon and heteroatom source or as an additional source for doping pre-existing nano-structured carbons. While there are several successful works on the ORR catalysis by materials where ILs were used as an additional source of heteroatom and carbon, their application for ORR as a single source of N and C atoms has not been much explored. Accordingly, some investigations are necessary to be made in order to see if carbonisation of pure ILs under different pyrolysis conditions (atmospheres and temperature) can result in active and stable doped-carbon catalysts for cathodes of polymer electrolyte membrane fuel cells (PEMFC).

A literature survey was performed looking at the previous investigations on the application of ILs for ORR. Kim and coworkers¹ reported on nitrogen-doped carbon catalysts for the oxygen reduction reaction (ORR) synthesized by the pyrolysis of ionic liquids, precursors of both nitrogen and carbon, using a silica hard template in the presence of a transition metal. From the linear sweep voltammogram recorded in an acidic solution, the ORR activity of the nitrogen-doped carbon catalysts increased significantly after the addition of the transition metal during the pyrolysis of the IL. Additionally, they emphasized that the BET surface area, porous structure and in particular the distribution of pore size are important factors in the catalyst's performance. Overbury and coworkers² elucidated the pore-size-distribution dependence of the ORR kinetics of IL-synthesised catalysts. From these two recently published works, one can conclude that ILs can be successfully applied as the carbon and nitrogen source for synthesis of active ORR catalysts, however the porous structure of these catalysts should be taken into consideration.

2.0 Catalyst Synthesis

A nitrogen-rich IL was used in this work as the starting material. In this case, 1 wt % of Fe(II) acetate (FeAc_2) was dissolved (slow, after agitation) in the IL, Figure 1, yielding a liquid catalyst precursor. In order to investigate the influence of the pyrolysis temperature on the ORR activity of the final material, the precursor was calcined at three different temperatures, 500, 900 and 1100 °C. Interestingly, calcination at all the temperatures resulted in highly graphitised carbonaceous material (Figure 2). To confirm the crystalline structure of the synthesised materials, their XRD patterns are compared. As expected, by increasing the temperature from 500 to 1100 °C, graphitization improved as can be reflected in sharpening of the peak at $2\theta=25^\circ$. Additionally, the XRD fingerprint peaks referring to Fe_3C , iron nitrides and metallic Fe particles are significant in IL-1100°C while they cannot be detected in IL-500°C. In this case, it is necessary to investigate closely the XRD patterns between $2\theta=40^\circ$ to $2\theta=60^\circ$. While the peaks at $2\theta=38^\circ, 43^\circ, 50^\circ$ can refer to different forms of Fe_xN_y . The other fingerprints between $2\theta=43^\circ$ and $2\theta=50^\circ$ can be attributed to different crystalline structure of iron. The peaks higher than $2\theta=50^\circ$ can be interpreted as different iron carbide structures.

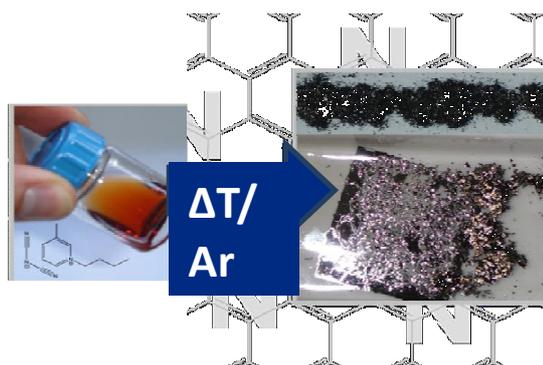


Figure 1: N-rich IL-precursor used for direct carbonization.

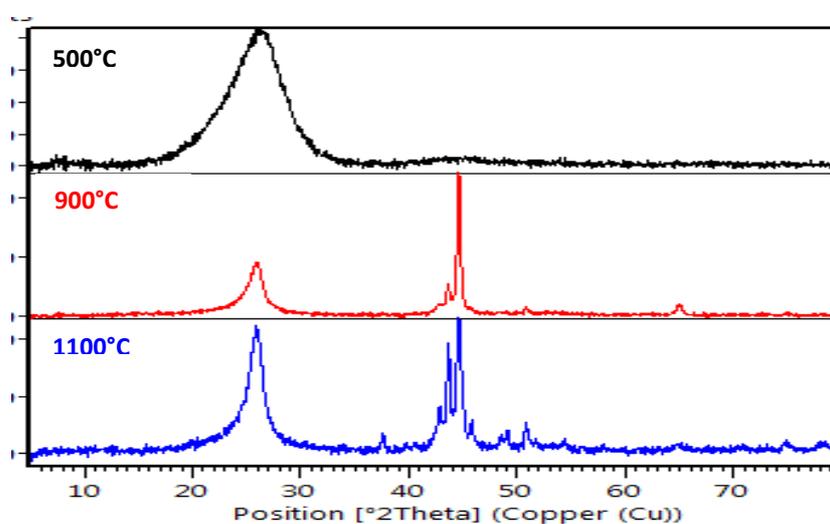


Figure 2: Experimental XRD patterns of IL impregnated with 1 wt% Fe and pyrolysed at 500, 900 or 1100 °C.

3.0 Electrochemical characterization

3.1 Rotating disk electrode measurements

The IL-derived catalysts were first characterised by rotating disk electrode (RDE) technique at pH 1 in O₂ saturated H₂SO₄ (0.1 M). Noteworthy, in order to achieve a fine powder from the highly graphitised synthesized powders, planetary ball-milling was applied for 30 min. The ball-milled powders were used for preparation of the catalytic inks, which resulted in the loading of 0.8 mg_{catalyst} cm⁻² for RDE measurements. Figure 3 shows the RDE results of these catalysts. Apparently, IL-500°C showed no ORR activity (in spite of carbon structure being already formed, as seen from the XRD). A major improvement in activity was observed by increasing the temperature to 900 °C. The onset potential further shifted positively from 900 to 1100 °C. The diffusion inside the catalytic layers remains however relatively low (not the clear S-shape expected from kinetics to diffusion limited plateau), without any significant improvement by elevating the temperature from 900 to 1100 °C. The RDE results however show that these preliminary IL-derived carbonaceous catalysts synthesised in the presence of Fe at temperatures higher than 900 °C show high intrinsic ORR activity (reaching *ca* 1 mA cm⁻² at 0.8 V vs RHE; near the value obtained with benchmark Fe-N-C catalyst made from 1 % Fe, phenanthroline, ZIF-8 and pyrolysed at 1050° C in argon) but its diffusion characteristic seems low, as confirmed by initial PEMFC characterisation.

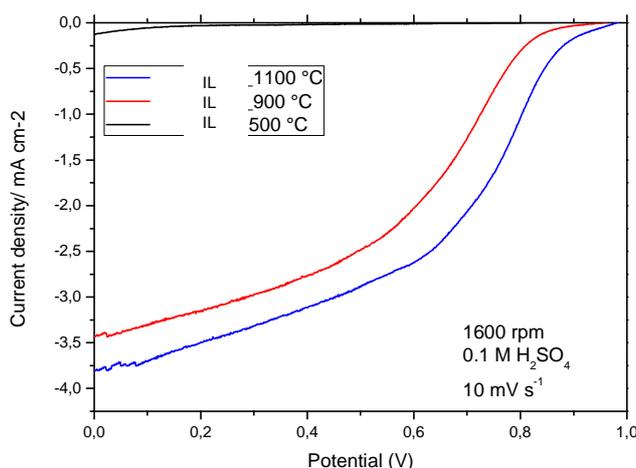


Figure 3. Polarization curves measured with RDE for IL impregnated with Fe and pyrolysed at 500, 900 and 1100 °C. RDE measured at 1600 rpm, in O₂-saturated H₂SO₄, catalyst loading 0.8 mg cm⁻².

3.2 Fuel cell testing

Figure 4 shows the PEMFC polarization curves of the best performing IL-derived catalyst. IL-1100°C refers to the catalyst pyrolysed for 1 hour at 1100 °C under argon atmosphere. The sample IL-1100°C-Ar-NH₃ went through another post-pyrolysis under NH₃ at 900 °C (15 min). We applied post-NH₃-treatment with the hope of increasing the activity and in particular the diffusion characteristics of the catalyst. The cathode loading of 4 mg cm⁻² was used for all fuel cell tests.

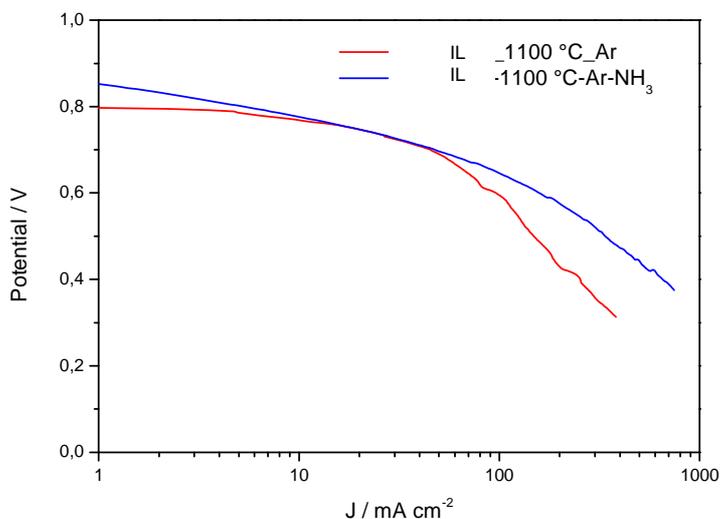


Figure 4. Fuel cell polarisation curves for IL impregnated with Fe and pyrolysed at 1100 °C in Ar, or 1100 °C in Ar + 950 °C in NH₃ Cathode catalyst loading 4 mg cm⁻². 80 °C, H₂, O₂, 100% RH, 1 bar gauge pressure.

Obviously, the activity of the argon-treated catalyst in PEMFC condition is significantly lower than that measured in RDE. Additionally, further treatment in NH₃ did not significantly improve the performance under fuel cell operating condition. We think that one possible reason for low performance in fuel cell condition may be un-optimised Nafion content in the catalyst layer. The recent BET specific area measurements highlight very low surface area (see Figure 5), in strong contrast with BET areas of 400-1000 m²g⁻¹ usually seen for MOF-derived catalysts. Accordingly, the Nafion content used to prepare catalytic layers of such IL-derived catalysts should be considerably lowered. The present content, optimised for other Fe-N-C catalysts, was 1.5 Nafion in mass to 1 catalyst in mass. For Vulcan, a typical carbon black with BET area *ca* 200-250 m²g⁻¹, the optimum mass ratio

Nafion/catalyst (Pt/C) is already only 0.6-0.7. The Nafion content in PEMFC cathode should thus be considerably lowered for such novel Fe-N-C catalysts. This will be investigated in the future.

The nitrogen adsorption/desorption isotherms of samples prepared at 900 °C and 1100 °C are shown in Figure 5 and corresponding BET values are summarised in Table 1. Obviously, pyrolysis temperature has a significant influence on BET surface area of the catalysts. Increasing the temperature from 900 °C to 1100 °C decreases the BET surface area from 253 to 39 m² g⁻¹. Noteworthy, the IL-900 °C sample also shows relatively low BET surface area compared to other non-PGM catalysts. That can confirm that Nafion content used for MEA preparation of these catalysts was relatively high regarding the porous structure. Therefore, it is of high priority to optimise the Nafion content of the IL-derived catalyst.

Additionally, the nitrogen content of the catalysts was characterised by elemental analysis (EA). As expected, increasing the temperature accelerates the decomposition of the IL source and reduces the N-doping degree inside the carbonaceous backbone.

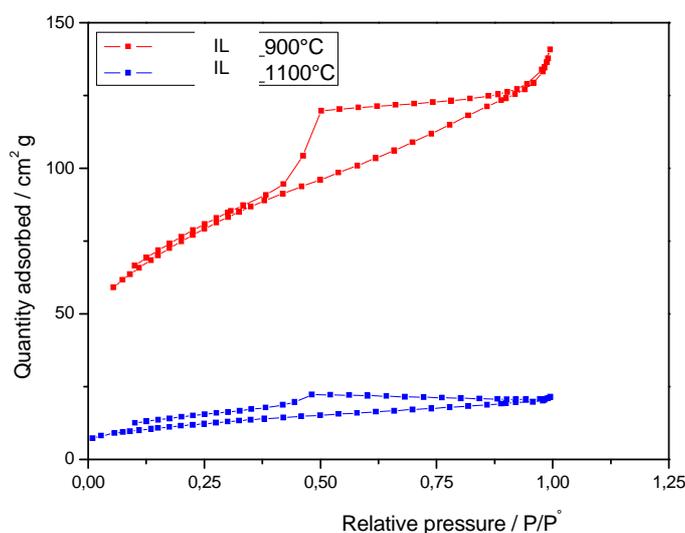


Figure 5. Sorption Isotherms for IL impregnated with Fe and pyrolysed at 900 °C in Ar or 1100 °C in Ar

catalyst	BET surface area m ² g ⁻¹	N content %
IL_900 °C	253	7,6
IL_1100 °C	39	4,5

Table 1. BET area of IL impregnated with Fe and pyrolysed at 900 °C in Ar, or 1100 °C in Ar

Conclusions

The IL-derived catalysts pyrolysed at temperatures above 900 °C showed high ORR activity regarding onset potential in RDE tests, however their poor diffusion performance should be taken into consideration. Apparently the NH₃-treatment does not significantly influence the activity. Optimised synthesis will be investigated, especially with respect to the initial metal content as well as optimisation of fuel cell ink regarding Nafion content. As a literature survey showed, new strategies should be applied in order to increase the porosity and decrease particle size of the final catalysts (foaming agents, spraying the liquid in an oven, etc). The liquid nature of the catalyst precursor may be at the root of such peculiar behaviour. The respectable ORR activity in RDE for such low BET area is however interesting, as well as the improved graphitization at 1100 °C. The synthesis of these composite materials will be investigated further with the aim of optimizing the initial iron content and nature of IL precursor at optimised pyrolysis condition. The stability of optimised catalyst or optimised cathode preparation will then be evaluated in PEMFC.

4.0 References

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2. Zhiyong Zhang, Gabriel M. Veith, Gilbert M. Brown, Pasquale F. Fulvio, Patrick C. Hillesheim, Sheng Daia and Steven H. Overbury, *Chem. Commun.*, 2014, 50, 1469.