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DELIVERABLE REPORT

D4.1 CHARACTERISATION METHOD FOR IONOMER-SUPPORT INTERACTION STRENGTH DEVELOPED	
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SUMMARY	
Keywords	Nafion®, carbon supports, ionomer, support, Isothermal Titration Calorimetry, zeta potential, centrifuge, F-NMR.
Abstract	In catalyst inks for PEM fuel cell applications, the interaction of the ionomer with the carbon support starts at the ink making step and can influence many properties of the final catalyst layer, including ionic conductivity and mass transport processes. To improve understanding of the way carbon supports and typical fuel cell ionomers interact, this deliverable report summarises attempts to identify at least one technique capable of quantifying the strength of the interaction. CNRS have validated ITC as being a straightforward method to quantify the strength of the ionomer-carbon interaction. The method is sufficiently sensitive to be able to discriminate between carbon samples with different degrees of surface modification by nitrogen and increasing the nitrogen content of the carbon surface increased the heat of adsorption of Nafion® on the modified carbon. At JMFC, changes in the zeta potential for a range of dispersions gave clear evidence of how the solvent type and concentration govern the charge interactions between the ionomer and carbon support. It was clear that in aqueous dispersions of Nafion®, Vulcan XC72R had a weaker interaction with the ionomer than Ketjen EC300J, due to a lower (less positive) zeta potential. For a straightforward quantification of ionomer-carbon interaction strength, the centrifuge method of measuring the amount of free ionomer was very successful and here it was shown that in mixed aqueous-alcohol dispersions, Vulcan XC72R had a stronger interaction with the ionomer than Ketjen EC300J, in agreement with the zeta potential results for the carbons in the same dispersant, but in contrast to the situation in a purely aqueous system. Fluorine-NMR was found to be less straightforward as a way to measure carbon-ionomer interaction strength in work at TUM. Despite reports in the literature, this work demonstrated that the signal-to-noise ratio was not sufficient to quantify the interaction at the low ionomer concentrations needed. In summary, four different techniques were explored, with three of them showing successful quantification of ionomer-support interactions, and the fourth still holding promise of a successful outcome. The early identification and implementation of these techniques within the GAIA project means that WP4 is in a strong position to deliver modified supports that will enable catalyst layers to be designed with the right properties to meet the challenging 1.8 W/cm^2 target in the project.
Public abstract for confidential deliverables	As above

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D4.1: CHARACTERISATION METHOD FOR IONOMER-SUPPORT INTERACTION

CONTENTS

1. INTRODUCTION

The transport processes that occur in the cathode catalyst layer during fuel cell operation are complex and difficult to isolate, but if the limiting factors can be identified, this can help lead to improved performance under a wide range of conditions. In GAIA, the aim is to significantly reduce the mass transport losses seen at high current densities: the project target is 3.0 A/cm^2 at 0.6 V, 1.8 W/cm^2. The properties of the cathode catalyst layer are critical to meet this ambition and are influenced by many factors arising from the wet ink stage, including the ratio of ionomer to catalyst, the solvent type(s), the ink mixing, the layer drying and of course the physical and chemical properties of the materials themselves (catalyst, catalyst support, ionomer).

The aim of the work reported here was to identify at least one technique that could quantify the interaction strength between the carbon support and the ionomer at the wet ink stage. Subsequent work will then try to correlate interaction strength with the structure and performance of the resultant cathode catalyst layers.

This deliverable report details collaborative work from several of the partners involved in WP4: CNRS, TUM and JMFC. Nafion® 1100EW was selected as the reference ionomer and Vulcan XC72R and Ketjen EC300J as the carbon supports. A wide range of experiments with aqueous and organic solvents were carried out including changes to the solvent concentration.

CNRS investigated Isothermal Titration Calorimetry (ITC), a technique conventionally used for the investigation of the adsorption of low-molecular-weight ligands on nanoparticles[1,2]. Recently, ITC has been used to characterise the thermodynamics of ionomer adsorption on carbon black, as applied to Aquivion© ionomer with a range of equivalent weights and Vulcan XC72R[3]. According to this publication, the response of the heat flow *versus* the PFSA concentration can be fitted to a Langmuir type isotherm model and yields the equilibrium constant and the enthalpy of adsorption.

JMFC used ionomer titration experiments to observe changes in the zeta potential when using different solvents and concentrations. Although this technique is not a direct measure of strength of interaction, this approach can determine the surface charge of the support, which leads to a better understanding of the interaction with the ionomer. As a direct measure of interaction strength, JMFC used centrifuge experiments of carbon/ionomer inks to quantify un-bound ionomer.

Lastly, TUM investigated ^{19}F-NMR, a technique reported in the literature as able to study the adsorption of Nafion® on carbon supports and carbon-supported Pt based catalysts. With this approach, the strength of the interaction between the ionomer and the selected material is inferred from the measured adsorption isotherms.

2. EXPERIMENTAL

2.1 ISOTHERMAL TITRATION CALORIMETRY (ITC)

A TAM III thermostat (TA Instruments) equipped with 3 nanocalorimeters with a detection limit of 10 µJ was used to perform heat flow measurements at 25 °C. Titration and reference vials made of stainless steel with a volume of 1 mL were used. For the measurements, 800 µL of Vulcan XC72R suspension at 1-10 mg/mL was prepared. 25 aliquots of 10 µL for each ionomer dispersion at 0.2-2% wt. were injected. Between the injections, an interval time of 1 hour was set, to allow equilibrium to be reached after every titration step. All the samples were stirred during the measurements to prevent sedimentation of the Vulcan XC72R carbon during the 24 hours' duration of the experiment. The reference vial was filled with a mixture of deionised water and 1-propanol and the 25 aliquots were added as for the titration. Every titration was made simultaneously on the 3 nanocalorimeters to check reproducibility of the results.

5 wt. % Nafion® EW1100 dispersion in alcohol was purchased from Sigma Aldrich and Vulcan XC72R from Cabot. Further chemical functionalisation was performed at CNRS on the Vulcan XC72R, leading to three different samples bearing 0 (pristine Vulcan), 2 and 3 wt% of nitrogen moieties and labelled respectively as V0, V2 and V3. Deionised water (Milli-Q ultrapure water, 18 MΩ.cm) and 1-propanol were used for the preparation of all dispersion solutions.

2.2 ZETA POTENTIAL AND CHARGE TITRATION

Nearly any particle surface carries ionic charge and the Stabino II Charge Titration unit is a streaming potential instrument for analysing and quantifying surface charge. The ionic charge of the particle-solvent interface is measurable as a Particle Interface Potential (PIP). The streaming potential is a voltage that originates from shearing the ionic cloud around the particles in a thin gap between the measurement cylinder and the oscillating piston, which is proportional to the PIP. This represents the degree of electrostatic repulsion between particles and reacts to changes in pH, conductivity and the surrounding polyelectrolyte. The titration result is characteristic for the sample in a certain chemical environment.

For these investigations, aqueous Nafion® solutions were made by diluting the 10-12wt% Aqueous Nafion® solution with demineralised water (18.2 µS/cm) at concentrations of 0.325 and 1 wt%. 22 wt% n-propanol/water (22nP) Nafion® solutions were made by diluting the 10-12 wt% aqueous Nafion® solution with demineralised water and n-propanol (nP or 1-propanol) at concentrations of 0.325, 0.5, 1 and 5 wt%.

2.3 IONOMER-CARBON INTERACTIONS MEASURED BY CENTRIFUGE

This work examined the adsorption strength of Nafion® 1100EW ionomer in water and 22% n-propanol/water on XC72R and EC300J carbons. Aqueous Nafion® 1100EW dispersion at 10-12 wt% solids was used to make aqueous carbon inks and, with the addition of n-propanol to the aqueous Nafion® solution, for making organic carbon inks. The surface areas (SAs) of both the carbons were measured by the N_2-BET method. The total SA for XC72R was 237 m^2/g, with only 38 m^2/g of that area being in pores greater than 6 nm pore diameter. It is believed that ionomer is unlikely to penetrate pores smaller than 6 nm diameter[4] and so a large fraction of the surface area is not available for ionomer adsorption. The total SA for the Ketjen EC300J carbon was 866 m^2/g, with 181 m^2/g of area being in pores greater than 6 nm pore diameter. On this basis, the EC300J carbon has nearly 5 times more available SA for ionomer adsorption than the XC72R carbon.

The effect of the two carbon types was studied with carbon/ionomer inks in partially organic solvent (22:78 n-propanol:water); the effect of the solvent type (water versus 22:78 n-propanol:water) was studied with XC72R carbon-ionomer inks and the effect of ink solids and ink processing was also studied.

2.4 ^{19}F-NMR

All measurements ^{19}F-NMR were taken in a 5 mm glass NMR tube with a 400 MHz spectrometer (BRUKER, Ascend^{TM}) at room temperature. The selected carbon support was suspended in an aqueous solution containing a fixed amount of the ionomer. After a specific mixing time, the suspensions were centrifuged and the supernatant liquid analysed using ^{19}F-NMR. The amount of Nafion® adsorbed on the solid sample was quantified with the help of a calibration curve and an internal standard placed in each of the NMR samples. Trifluoroacetic acid (TFA) was used as an internal reference and 55 µL D_2O used as a deuterium lock for the instrument. The amounts of each component were chosen to give a total volume of 550 µL. The experiment was repeated with different concentrations of the ionomer to obtain adsorption isotherms.

3. RESULTS AND DISCUSSION

3.1 ISOTHERMAL TITRATION CALORIMETRY (ITC)

ITC was used at CNRS to quantify the interaction between the ionomer and the carbon support. Different PFSA ionomers were used such as Nafion®, Aquivion® and ionomer from 3M with the XC72R carbon. The results with the Nafion® ionomer are reported here. In addition, carbon supports were modified with nitrogen, using a N₂-plasma technique, to investigate the effect of the speciation and concentration of this heteroatom on the strength of the ionomer-support interaction. In order to commission this technique, it was decided to use Nafion® EW1000 and Vulcan XC72R.

To examine the effect of nitrogen content, three suspensions of XC72R with different nitrogen contents (0, 2, 3 wt%, labelled C0, C2 and C3, respectively) in water/1-propanol were titrated with a dilute dispersion of Nafion® EW1100. The thermograms corresponding to the heat flow recorded during the injection of Nafion® into the three different carbon black suspensions are shown in Figure 1. The result of the blank (reference) experiment is also shown, consisting of the titration (dilution) of Nafion® in the water/1-propanol solvent without carbon present. This enables a correction to be made for the influence of the enthalpy of mixing on the overall heat flow. In all cases, the results of Figure 1 indicate that the timescale of 1 hour was enough for the decay of the heat flow to the baseline level.
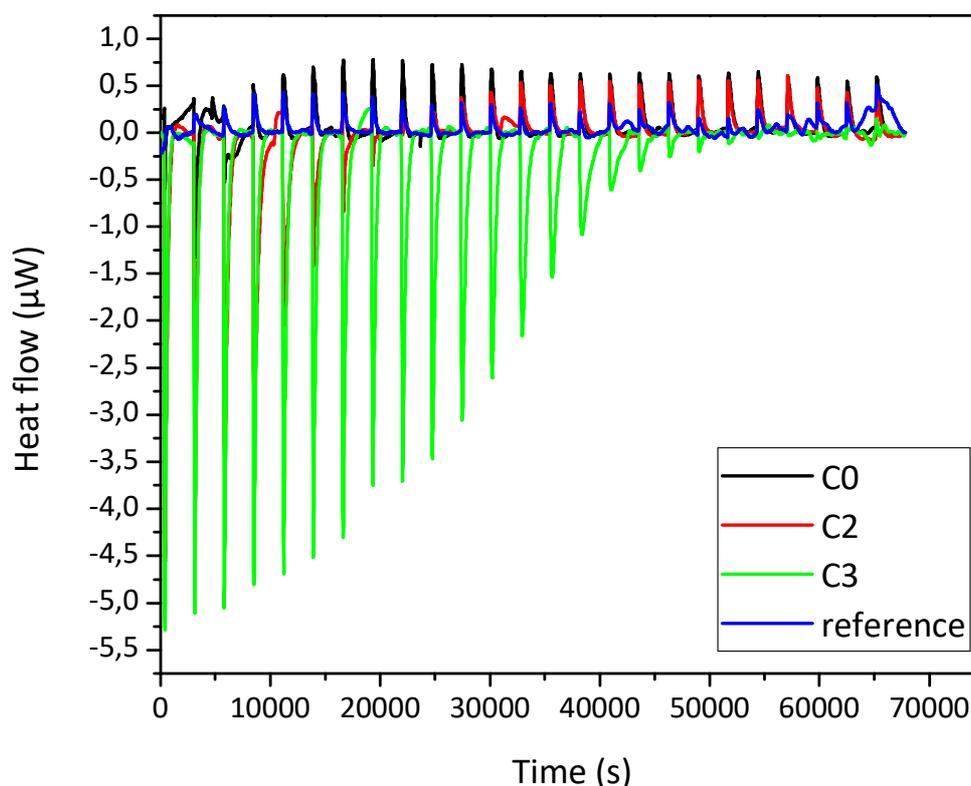

Figure 1: Heat flow during titration of Nafion® with non-modified (C0) and nitrogen-doped (C2, C3) carbon black Vulcan XC72R suspended in water/1-propanol or with the solvent mixture as a reference (dilution).

The experimental conditions used and the method were validated by these results: the injection of the ionomer dispersion into the carbon suspensions resulted in more intense peaks than the dilution peaks (reference, blue line). Furthermore, the carbons having different amounts of nitrogen gave rise to different thermograms with different heat flow intensities and inflections.

To compare clearly the three experiments, the cumulative heat release due to ionomer adsorption measured by ITC is depicted in Figure 2.
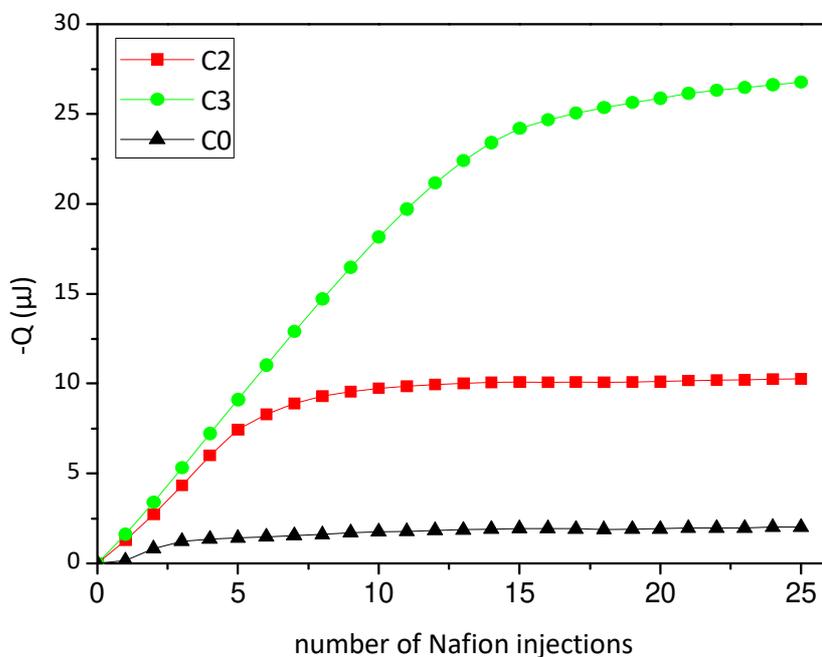

Figure 2: Cumulative heat release during titration of Nafion® with non-modified and nitrogen-doped carbon black Vulcan XC72R suspended in water/1-propanol.

Firstly, it can be observed that for each sample the heat release progressively increases with the ionomer injections up to a critical value, after which a plateau is reached. This number of injections needed to reach the onset of the plateau increases with nitrogen content in the carbon black: the plateau is achieved after about 3 Nafion® additions for C0, about 7 for C2 and about 17 for C3. As already reported[3], the form of the isotherm can be related to ionomer adsorption on different sites on the carbon surface. First, the most energetic sites (defects, kinks, surface roughness) are covered by the ionomer, leading to the strongest heat release during adsorption. Later, a lower increase of heat release is observed when injecting ionomer since the adsorption takes place at lower-energy sites. The plateau might be ascribed to the successive adsorption of Nafion® onto Nafion® that is already adsorbed on the carbon. Further experiments (*e.g.* adsorption isotherms) will be performed to validate this hypothesis and quantify the amount of ionomer effectively adsorbed on carbon particles.

The heat release, and thus the strength of the carbon/Nafion® interaction, is also very different on the three carbon samples and strongly depends on the nitrogen functionalisation of the XC72R. The strongest heat release per added amount of ionomer is found for the Vulcan bearing the highest amount of nitrogen (3 wt%, C3), and the lowest for the pristine Vulcan XC72R. Thus, the following trend of Nafion®/carbon support interaction strength is seen: C3 > C2 > C0 (undoped C).

3.2   ZETA POTENTIAL MEASUREMENTS ON CARBON AND IONOMER DISPERSIONS

Zeta potential (ZP) was selected as a technique to study the interaction of the ionomer with the carbon support and the effect of aqueous and organic solvents (water and 22:78 1-propanol:water) using Nafion® 1100EW ionomer and carbons in the as-received condition (XC72R and Ketjen EC300J). In addition, the concentration (wt% solids) was varied for the carbons and ionomer.

3.2.1 ZP ON IONOMER DISPERSIONS

Weak aqueous Nafion® solutions were made by diluting as-received 10-12 wt% Aqueous Nafion® solution with demineralised water (18.2 µS/cm) and then making zeta potential measurements, using the Stabino instrument, as a function of Nafion® ionomer concentration in water and in 22% 1-propanol/water, as shown in Figure 3.

Figure 3: Zeta potential plot for Nafion® 1100EW in 22% 1-propanol/water (blue line) and in water only (orange dots) at different concentrations. The pH is shown on the secondary Y-axis (grey line).
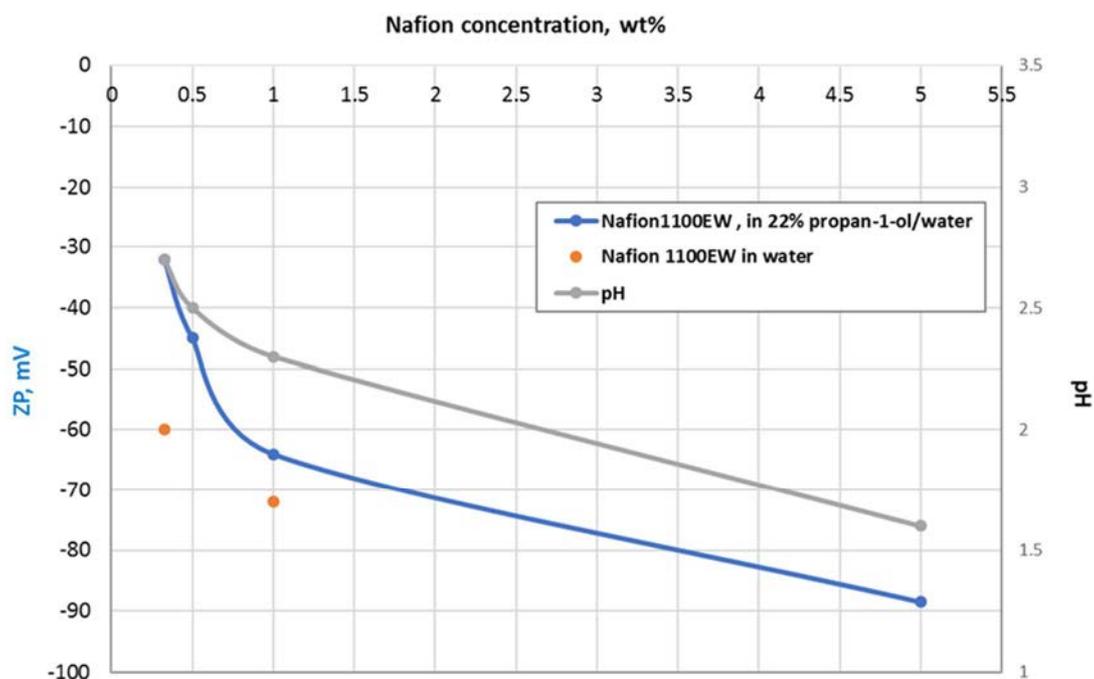
From Figure 3: Zeta potential plot for Nafion® 1100EW in 22% 1-propanol/water (blue line) and in water only (orange dots) at different concentrations. The pH is shown on the secondary Y-axis (grey line). it is clear that the Nafion® ionomer, in both solvents and at all concentrations, carries a negative charge and this is attributed to the SO_3^- ions attached to the side chains of the ionomer. The increasing ZP with increasing concentration can be explained by Nafion® ionomer particle aggregation, which increases the charge density of the aggregates. The concentration also affects the pH of the solutions, as expected, such that the pH is less acidic at low ionomer concentrations. Nafion® ionomer in aqueous solutions seem to have slightly more negative ZPs, compared to those in 22nP solvent at the same ionomer concentration, possibly due to differences in the conformation of the ionomer chains in these solvents. In water, the ionomer chains will be more curled-up and compact in the aggregates, due to poor solvation of the hydrophobic PTFE backbone; the aggregates will therefore have a higher charge density. By contrast, the Nafion® dispersed in 22nP solvent will be more extended and un-furled, due to better solvation of the hydrophobic PTFE backbone, and therefore has a lower charge density.

3.2.2 ZP ON CARBON DISPERSIONS

The Vulcan XC72R and Ketjen EC300J carbons used for this study were dispersed in deionised water and in 22% 1-propanol/water solvent. XC72R dispersions were processed at 8 wt% solids and EC300J dispersions were processed at 5 wt% solids. The dispersions were then diluted to 1 wt% using their respective solvents and stirred for a minimum of 1 hour and a maximum of 24 hours, prior to carrying out ZP measurements. The carbon dispersions were continuously agitated in an up/down direction by the piston during the measurements in the Stabino instrument, to prevent any sedimentation. The ZP values of 1 wt% solutions stirred for 24 hours were

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found to be stable and the ZP and pH values for carbon dispersions in aqueous and organic solvents at 1 wt% solids are presented in Figure 4.

Figure 4: Zeta potentials (top) and pHs (bottom) of the two different carbon dispersions (XC72R and EC300J) in water (Aq) and water/propanol (22nP) solvents.

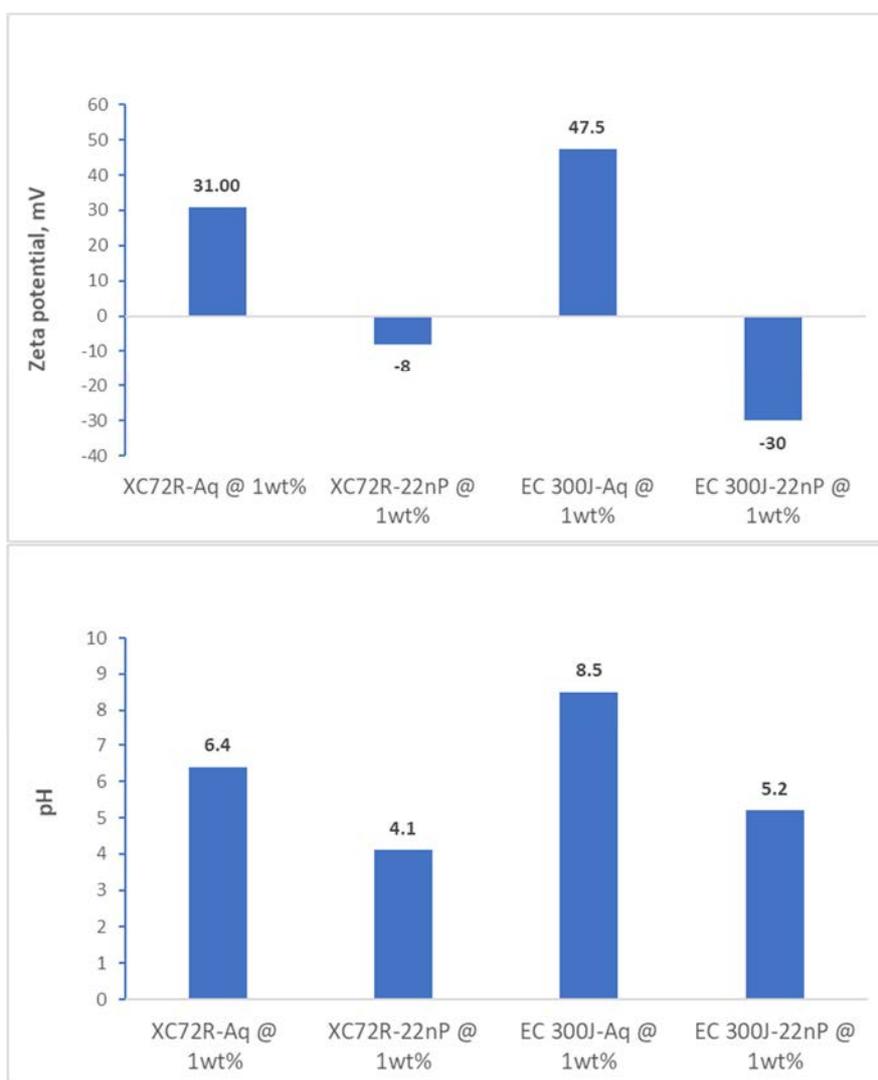The results in Figure 4: Zeta potentials (top) and pHs (bottom) of the two different carbon dispersions (XC72R and EC300J) in water (Aq) and water/propanol (22nP) solvents.(top) show that the zeta potential of XC72R and EC300J carbon dispersions at 1 wt% in an aqueous medium are both positive, +31.0 mV and +47.5 mV respectively. The carbon dispersions at 1 wt% in 22nP both have negative ZPs however, at -8 mV and -30 mV respectively. In both aqueous and organic solvents EC300J has a higher ZP value, indicating that the particles in dispersion are more stable than the XC72R carbon particles.

Figure 4 (bottom) shows the pH of as-made carbon dispersions in the aqueous and organic solvents. The XC72R carbon in water is slightly acidic and the EC300J carbon in water is slightly basic. When both carbons were dispersed in 22nP solvent however, they became acidic. This result highlights that the ZP and pH of different carbon dispersions in aqueous and organic media are significantly different and will therefore be expected to have different interactions with the negatively charged, acidic ionomer.

In summary, the ZP method is very useful in helping to understand carbon-ionomer interactions and, for aqueous ionomer dispersions, a stronger interaction with the ionomer is expected for carbons that show a larger, positive ZP. For the partially organic medium used in this work, the situation is more complex, because the carbons both

show negative ZPs. Nevertheless, a less negative ZP (XC72R) should predict a less-weak carbon-ionomer interaction strength than the more negative ZP seen for the EC300J.

3.2.3 ZP Polyelectrolyte (Ionomer) Titrations

The total charge of an unknown surface can be estimated by measuring the consumption of a polyelectrolyte of known concentration in neutralising the charge on that surface to reach the point of zero charge (PZC). In this study, dispersions of Nafion® 1100EW ionomer in water and in 22nP were used as polyelectrolytes to estimate the amount of ionomer required to neutralise the charge on the carbon particles. Only results using water are reported here as measurements in 22nP were complicated by the fact that the charge on both the carbon and the ionomer is negative in 22nP, which considerably reduces the strength of the ionomer-carbon interaction and makes this type of titration impossible without changes to the system.

Since both aqueous carbon dispersions at 1 wt% solids carried positive charges (see Figure 4, top) and aqueous Nafion® ionomer at 0.325 wt% solids had negatively charged particles, a neutralisation by titration study could be performed using the aqueous solutions, as shown in Figure 5: Ionomer titrations of aqueous dispersions of XC72R and EC300J
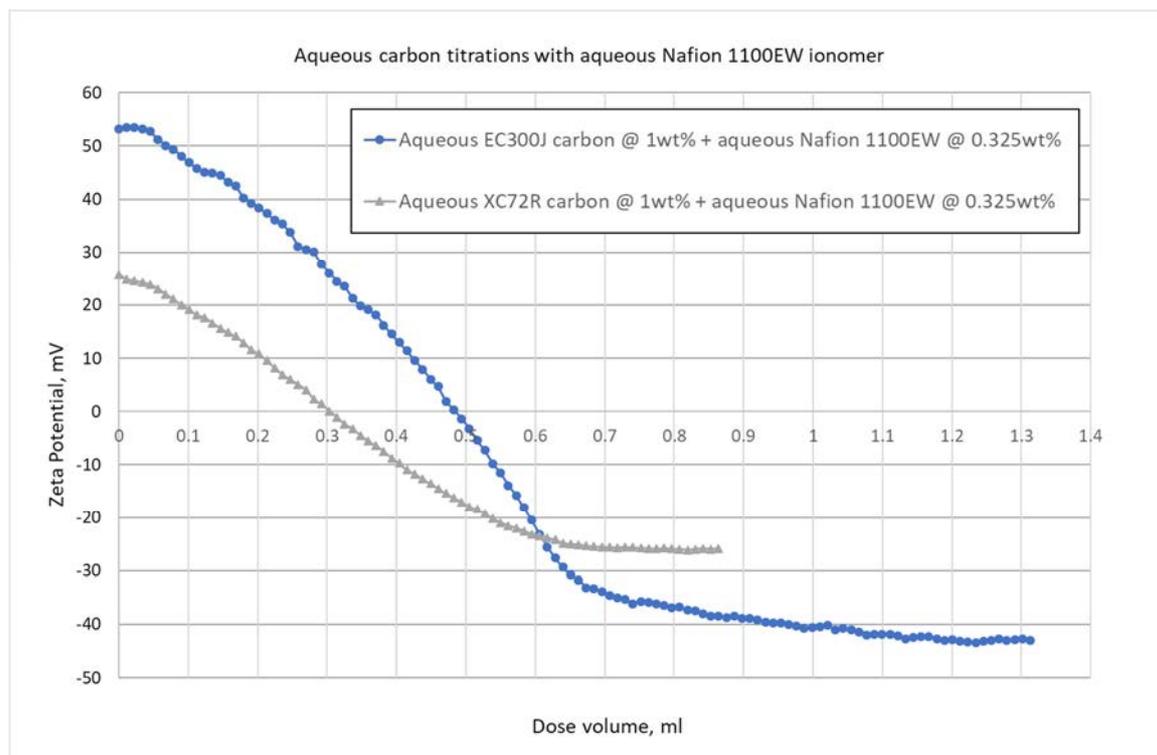

Figure 5: Ionomer titrations of aqueous dispersions of XC72R and EC300J carbons.

The consumption of ionomer needed to reach a ZP of 0 mV and the corresponding ZPs and pHs before and after titration are tabulated in Table 1. It was clear that the higher surface area EC300J carbon consumed about 1.6 times more ionomer to reach the PZC than the lower surface area XC72R carbon.

Table 1: Comparison of the ZPs and pHs of XC72R and EC300J carbons in the as-received condition (0 mL) and after titration with ionomer to reach the potential of zero charge (0 mV).

	ZP with no ionomer added (0 mL) [mV]	pH with no ionomer added (0 mL)	Ionomer added at PZC (0 mV) [mL]	pH at PZC after ionomer added(0 mV)
Aq XC72R + Aq Nafion	25.8	5.7	0.304	4.6
Aq EC300J + Aq Nafion	53.2	8.1	0.484	7.2

Knowing the amount of ionomer needed to reach the PZC (0 mV), the amount of carbon in the dispersion (10 ml @ 1 wt% solids) and the surface area (SA) of the carbon in pores larger than 6nm, the ionomer coverage on the surface of the carbon can be calculated in g/m². It is an implicit assumption of the calculation that the ionomer adsorbed in a uniform way onto the carbon and this may not be the case. It was also assumed that, as mentioned previously, the ionomer did not penetrate pores below 6 nm in diameter. The results are tabulated in Table 2 below.

Table 2: Calculations derived from ionomer titrations with carbon to show ionomer coverage of carbon.

Solution Type (1 wt%)	Ionomer added at PZC (0 mV) [mL]	wt of ionomer @ 0.325 wt% [g]	wt of carbon in 10ml (@ 1wt%) [g]	Ionomer:Carbon mass ratio [g/g]	SA of C >6nm pores [m²/g]	Ionomer mass per carbon area (>6nm) [g/m²]
Aq XC72R + Aq Nafion	0.304	9.88E-04	0.105	9.73E-03	3.97	2.57E-04
Aq EC300J + Aq Nafion	0.484	1.57E-03	0.105	1.55E-02	19.01	8.56E-05

In summary, on the basis of simple charge attraction, the ZP method predicts a stronger interaction between EC300J and aqueous Nafion® than XC72R and aqueous Nafion® (Figure 4). For Nafion® dispersed in the 22nP solvent, the situation is reversed with charge repulsion being stronger for the EC300J than the XC72R, predicting a weaker ionomer-carbon interaction strength for the EC300J.

The results further show that although the EC300J carbon consumed more ionomer per gram of carbon in the aqueous dispersion, the ionomer coverage per unit area is lower than for the XC72R due to the large difference in available surface area for the two carbons. Thus, at the PZC, a thinner ionomer film is formed on the EC300J than on the XC72R.

3.3 IONOMER-CARBON INTERACTION STRENGTH USING CENTRIFUGATION

As mentioned above, ZP measurements are not straightforward to use to study carbon-ionomer interactions in organic dispersions. As an alternative approach, centrifuge experiments were undertaken, to determine the amount of ionomer strongly adsorbed onto the carbon surface by measuring the amount of non-adsorbed or 'free' ionomer in the supernatant.

Aqueous carbon-ionomer inks were prepared by weighing carbon powder and adding aqueous Nafion® 1100EW ionomer solution and mixing well. Organic inks were made in a similar way to the aqueous inks, except that n-propanol was added to the carbon/ionomer mix and extra water as needed to achieve a 22:78 n-propanol: water ratio (22nP) in the solvent mix and the target ink solids prior to ink processing. After mixing, the high solids inks were diluted to low solids (12.7 wt%, suitable for layer deposition) using demineralised water for aqueous inks and 22% n-propanol/water for organic inks. The diluted inks were left to rest for a minimum of 1 day before using for centrifuge experiments.

The process described above used a high shear process to make inks at high solids initially, followed by dilution. By way of contrast, a low solids ink was made directly using a low shear process to mix the ionomer with the carbon. This ink was prepared from carbon powder by adding 22:78 n-propanol:water.

For free ionomer quantification, 7-8 g of diluted carbon/ionomer inks were added into centrifuge tubes and centrifuged for 10-20 hours at maximum speed at 20 °C. In general, aqueous inks required 8-10 hours, whilst organic inks took 2-3 days, to yield a clear supernatant liquid, because of the presence of more fine particles in the organic inks. The clear supernatant liquids were carefully decanted, and the weight of the liquid from each experiment measured.

A moisture balance was used to quantify the ionomer present in the supernatant liquid; that is, the ionomer that had not adsorbed onto the carbon. The amount of free ionomer is expressed as a percentage of the total weight of ionomer in the ink. The adsorbed ionomer can be expressed as (i) mass of ionomer per mass of carbon ($mass_i/mass_c$ in g/g), or (ii) as mass of ionomer with respect to the carbon surface area in pores >6 nm ($mass_i/SA$>6 nm_c in g/m^2). The experimental results expressed in both these ways are shown in Table 3.

Table 3. Quantification of free and adsorbed ionomer obtained from centrifuge experiments with ionomer/carbon inks.

Ink type	% ionomer in supernatent liquid	$mass_i/mass_c$, g/g	$mass_i/SA_c(>6nm)$, g/m^2
Effect of carbon type on 22nP solvent			
XC72R/80N-22nP @ 12.7% (HS processed & diluted)	59	3.24E-01	8.72E-03
Ketjen/80N-22nP @ 12.7% (HS processed & diluted)	20	6.41E-01	3.33E-03
Effect of solvent type on XC72R			
XC72R/80N-22nP @ 12.7% (HS processed & diluted)	59	3.24E-01	8.72E-03
XC72R/80N-Aqueous @ 12.7% (HS processed & diluted)	22	6.28E-01	1.69E-02
Effect of ink solids & processing type on XC72R			
XC72R/80N-22nP @ 12.7% (HS processed & diluted)	59	3.24E-01	8.72E-03
XC72R/80N-22nP @ 1.66% (LS processed, 48hr stirring)	75.5	1.95E-01	5.26E-03

The centrifugation experimental results listed in Table 3 show that the higher surface area EC300J carbon ink released significantly less free ionomer than the lower surface area XC72R carbon ink and therefore had more ionomer adsorbed per mass of carbon. When the adsorbed ionomer loading onto carbon was normalised by the surface area in pores greater than 6 nm however, the EC300J had significantly lower ionomer coverage compared to XC72R and would be expected to have a thinner ionomer film thickness, assuming uniform coverage, consistent with the ZP titration results in Table 2.

The effect of solvent type examined for the XC72R carbon at the same ionomer loading and ink solids showed that the aqueous ink had far less free ionomer compared to the organic ink (22% versus 59%). This is in qualitative agreement with the ZP measurements where it was found that the aqueous inks had a much stronger ionomer-carbon interaction than the organic ones.

The effect of the low ink solids, low shear processing route on the XC72R carbon/ionomer organic ink at the same ionomer:carbon loading, was to give a larger amount of free ionomer, compared to the equivalent high solids ink (Table 3). Thus, the ionomer coverage on the carbon was lower for the low solids XC72R ink. This study was conducted to show that although both carbon and ionomer would have been negatively charged (see Section 3.2 on ZP measurements), charge attraction is not the only factor controlling the carbon-ionomer interaction and other factors such as the ionomer concentration, ink solids and processing are all influential.

The data from Table 3 are also summarised in Figure 6, for the different inks described above.
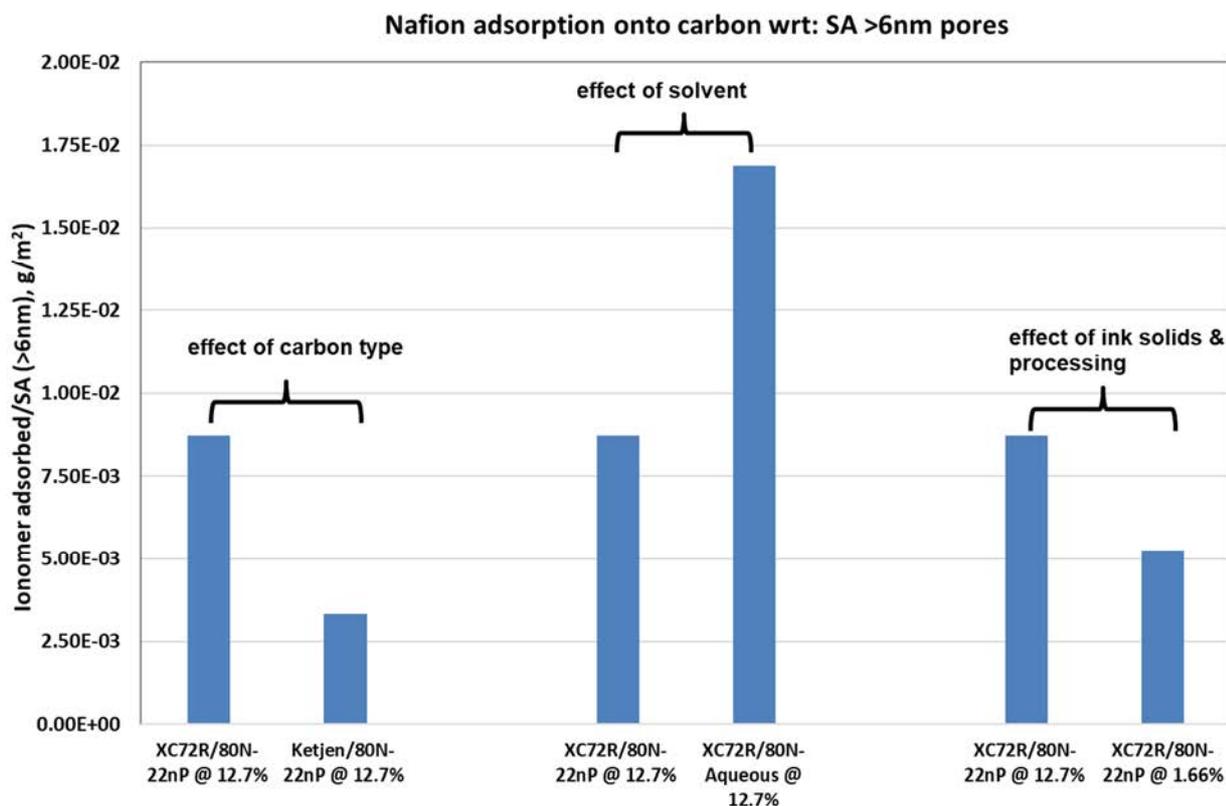
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Figure 6: Nafion® 1100EW adsorption with respect to carbon surface area >6 nm micropores (surface coverage) on different inks.

As the results in Figure 6 show, the centrifuge technique is a very useful way to quantify the strength of carbon-ionomer interaction for a wide range of systems and could be used to further study functionalised carbon, ionomer loading with respect to carbon, ionomer type and ionomer equivalent weight.

3.4 ^{19}F-NMR

^{19}F-NMR has been reported in the literature as a tool to study the adsorption of Nafion® on carbon supports and on carbon-supported Pt-based catalysts commonly used in PEMFCs. With this approach, the strength of the interaction between the ionomer and the carbon or catalyst is inferred from the measured adsorption isotherms; for example, stronger ionomer interactions have been shown with the carbon supports when compared to the noble metal alone[5]. Based on this study, TUM is developing the ^{19}F-NMR technique as a method to measure the interaction strength between ionomers and different modified carbon supports (with Nafion® as a reference case and then ionomers from Dyneon®. During the experiments, the selected support was suspended in an aqueous solution containing a fixed amount of the ionomer. After a specific mixing time, the suspensions were centrifuged and the supernatant analysed using ^{19}F-NMR. The amount of Nafion® adsorbed on the solid sample was quantified with the help of a calibration curve and an internal standard placed in each of the NMR samples. The experiment was repeated with several different ionomer concentrations to obtain adsorption isotherms. In the past months, TUM has been focusing on evaluating the sensitivity of the technique towards ionomer concentration. Once this phase is concluded, a calibration curve for the ionomer will be obtained and further experiments performed.

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Following the literature route,[Erreur ! Signet non défini.] aqueous Nafion® dispersions with different concentrations up to 20 g/L were prepared using a commercial 10 wt% Nafion® dispersion in water (1100 EW). An appropriate amount of trifluoroacetic acid (TFA) was used as an internal reference and 55 µL of D_2O as a deuterium lock for the instrument. The amounts of each component were chosen to give a total volume of 550 µL. All measurements were made in a 5 mm glass NMR tube with a 400 MHz spectrometer (BRUKER, Ascend™) at room temperature. Figure 1Figure 7 shows a typical ^{19}F-NMR spectrum at a Nafion® concentration of 20 g/L.
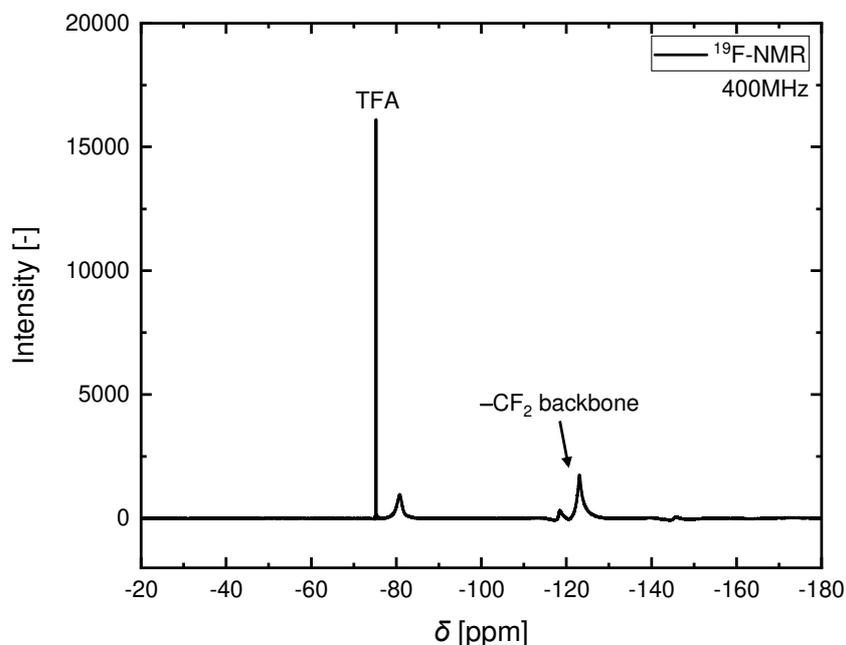

Figure 7: ^{19}F-NMR spectrum of a solution of 20 g/L Nafion® and 0.57 g/L TFA as an internal reference in water. The spectrum is measured at 400 MHz and room temperature.

The NMR spectra are referenced to the chemical shift of TFA at -75.25 ppm[6]. The signals arising from the ^{19}F nuclei within the ionomer appear at chemical shifts of -81, -120 and -146 ppm. The strongest intensity is referred to the nuclei of the $-CF_2$ backbone and is useful for further quantitative analysis. All chemical shifts are in agreement with the literature, except that the signal at -139 ppm, which is expected to arise from the $-CF_2CF_2SO_3^-$ nuclei and which was reported in the literature[7] is absent in our measurements, presumably due to insufficient resolution of the spectrometer.

So far in this work, NMR spectra with acceptable signal-to-noise ratios have only been obtained with concentrated aqueous Nafion® dispersions (20 g/L). At lower ionomer concentrations, quantifiable data could not be obtained, which are required for the planned study (down to ca. 0.2 g/L) and which had been reported as feasible concentration ranges in the literature. Experimental optimisations to enhance the signal/noise ratio of the ^{19}F NMR measurements, for example by switching to a 500 MHz spectrometer with a CryoProbe™ probe head (BRUKER), are, therefore, ongoing. If these modifications are successful, a complete quantitative analysis of the adsorption behaviour of the various ionomers on different carbon supports will be continued.

4. SUMMARY, CONCLUSIONS AND FUTURE WORK

Several different techniques have been identified and implemented to study ionomer-carbon support interactions. Results at CNRS have validated ITC as being a straightforward method to quantify the strength of the ionomer-carbon interaction. This methodology will be applied to other carbon blacks and PFSA ionomers being developed in the GAIA project. Furthermore, ITC is sufficiently sensitive to be able to discriminate between carbon samples with different degrees of surface modification by nitrogen. Increasing the nitrogen content of the carbon surface increased the heat of adsorption of Nafion® on the modified carbon, indicating a difference in ionomer-support interaction. In addition to its use to investigate how the ionomer-support interaction varies with different ionomers and ionomer equivalent weights, and with different types of carbon, this sensitivity opens up the possibility of the use of ITC as a routine method to characterise functionalised carbon materials. Further ITC experiments and adsorption isotherms will allow the extraction of thermodynamic parameters, including Gibbs free energy, adsorption enthalpy and entropy of the adsorption process. Thus, a fuller interpretation of the results obtained so far should be forthcoming (e.g. ionomer:carbon ratio, thermal plateau, adsorption mode).

The work at JMFC with the use of ionomer titration and centrifuge techniques has also produced extremely useful results. The changes in the zeta potential for the different dispersions used gave clear evidence of how the solvent type and concentration govern the charge interactions between the ionomer and carbon support. The results show how complex and sensitive to many variables these interactions can be, but also that the strength of interaction can be predicted for individual systems. It was clear that in aqueous dispersions of Nafion®, Vulcan XC72R had a weaker interaction with the ionomer than Ketjen EC300J, due to a lower (less positive) zeta potential. For a straightforward quantification of ionomer-carbon interaction strength, the centrifuge method of measuring the amount of free ionomer was very successful and here it was shown that in mixed aqueous-alcohol dispersions, Vulcan XC72R had a stronger interaction with the ionomer than Ketjen EC300J, in agreement with the zeta potential results for the carbons in the same dispersant, but in contrast to the situation in a purely aqueous system. Both the centrifuge and zeta potential techniques will be used through the rest of the project to help develop modified supports with beneficial carbon-ionomer interactions. The effect of Pt and Pt alloys on the interactions described in this report will also be investigated.

Fluorine-NMR was found to be less straightforward as a way to measure carbon-ionomer interaction strength in work at TUM. Despite reports in the literature, this work demonstrated that the signal-to-noise ratio was not sufficient to quantify the interaction at the low ionomer concentrations needed. Further work is in progress however, and following very recent work at CNRS (not yet reported) a promising experimental protocol has been found that may lead to improved quantification.

In summary, four different techniques were explored, with three of them showing successful quantification of ionomer-support interactions, and the fourth still holding promise of a successful outcome. The early identification and implementation of these techniques within the GAIA project means that WP4 is in a strong position to deliver modified supports that will enable catalyst layers to be designed with the right properties to meet the challenging 1.8 W/cm^2 target in the project.

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