IMPROVED LIFETIME STACKS FOR HEAVY DUTY TRUCKS THROUGH ULTRA-DURABLE COMPONENTS

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DELIVERABLE REPORT

D3.2: MODIFIED SUPPORT DEVELOPED WITH IMPROVED IONOMER INTERACTION THAT LEADS TO IMPROVED IONOMER STABILITY WITHIN THE CATHODE CATALYST LAYER	
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NATURE OF THE DELIVERABLE		
R	*Report*	*x*
P	*Prototype*	
D	*Demonstrator*	
O	*Other*	

SUMMARY	
Keywords	*Nitrogen functionalised carbon, surface functionalisation, reactive plasma, isothermal titration calorimetry, support-ionomer interaction*
Abstract	*Carbon (Vulcan XC72) was functionalised with nitrogen using a N_2-plasma treatment with the aim of strengthening its interaction with the PFSA ionomer, and thereby to improve the stability of the catalyst layer. By changing the reaction parameters, this approach allows introduction of up to 5% wt. nitrogen into the carbon surface in a reproducible and controlled way. XPS analysis revealed the presence of pyridinic, pyrrolic and graphitic nitrogen whatever the degree of functionalisation of the supports. Nitrogen physisorption and pore size distribution calculations confirmed that the bulk properties of carbon are not affected by the plasma treatment, which only induces surface functionalisation. Isothermal titration calorimetry allowed the quantification of the strength of the carbon/ionomer interaction, demonstrating the role of nitrogen in promoting the adsorption of the ionomer on the carbon surface. Increasing the amount of nitrogen on the carbon black strengthens the interaction with the ionomer, with potential impact on catalyst and fuel cell performance and durability.*
Public abstract for confidential deliverables	*N/A*

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D3.2 Modified support developed with improved ionomer interaction that leads to improved ionomer stability within the cathode catalyst layer

CONTENTS

1 INTRODUCTION

To achieve the objectives of IMMORTAL and meet heavy duty MEA application durability requirements, the properties of the cathode catalyst layer (CL), and in particular ionomer stability, are pivotal. One of the aims of Work Package 3 is therefore the development of carbon-based supports that are both stable to corrosion, and that can exert a strong stabilisation effect by interaction with the metal catalyst particles and the CL ionomer. The expected benefit of the latter is the formation of a thin, conformal film of ionomer distributed over the surface of the support that will be less susceptible to displacement from the carbon surface at high current density.[1,2]

With this aim, CNRS developed carbon supports specifically modified to improve their interaction with a perfluorosulfonic acid (PFSA) ionomer. Nafion® 1100EW was selected as the reference ionomer and Vulcan XC72R (VC) as the carbon support. Due to the hydrophilicity of the carbon surface, Nafion® is probably adsorbed on VC *via* polar sulfonic groups, while it interacts *via* the polytetrafluoroethylene (PTFE) main chain with more hydrophobic carbonaceous materials.[3] The interaction of the terminal sulfonic acid groups (SO_3H) of Nafion® PFSA with the carbon support depends on the surface properties of the latter as well as its structure, porosity and degree of graphitisation.

The selected approach consists of the introduction of nitrogen atoms at the carbon surface by using a nitrogen plasma treatment. The physico-chemical characterisation of pristine and N-doped materials are described in this report. In particular, Isothermal Titration Calorimetry (ITC), conventionally used for the investigation of the adsorption of ligands on nanoparticles, was used to quantify the interaction strength between the carbon supports and the ionomer. This technique was recently demonstrated to be a useful tool for the investigation of the adsorption of PFSA on carbon black with the determination of thermodynamic parameters.[4] Further work will attempt to correlate the interaction strength with the stability of the resultant cathode catalyst layers.

2 EXPERIMENTAL

2.1 N-doping of Vulcan XC72R carbon black

Carbon black Vulcan XC72R (VC) (Cabot) was treated by nitrogen plasma with a plasma generator from Europlasma including a 13.56 MHz RF generator and a primary pump. Mass flow controllers metered a 100 sccm flow of nitrogen gas (Air Liquide 99.9999 %) in the chamber. The applied power was modulated up to 300 W for a duration between 1 h and 8 h of plasma treatment.

2.2 Physico-chemical characterisation

Elemental analysis

The composition of the pristine and modified carbon blacks was determined by elemental analysis performed with a Vario Micro Cube Element Analyser.

X-ray photoelectron spectroscopy (XPS)

XPS was performed on an ESCALAB 250 spectroscope from Thermo Electron with a monochromatic Al K_α ray (1486.6 eV) excitation source, and data were analysed using the Avantage software. Binding energies (BEs) of all core levels are referenced to the C−C bond of C 1s component at 284.4 eV.

Nitrogen physisorption

Nitrogen adsorption/desorption isotherms were recorded at -196 °C by means of a Micromeritics 3Flex apparatus after outgassing samples overnight at 200 °C under vacuum (10^{-5} Torr). The specific surface area (S_{BET}) was calculated using the Brunauer Emmett Teller (BET) equation[5] and taking 0.162 nm^2 as the cross-sectional area of one N_2 molecule. The pore size distributions (PSD) were calculated by using the SAEIUS software for the 2D non-local density functional theory (2D-NLDFT).[6]

Isothermal Titration Calorimetry (ITC)

A TAM III thermostat (TA Instruments) equipped with 3 nanocalorimeters (used simultaneously) with a detection limit of 10 µJ was used to perform heat flow measurements at 25 °C. For the measurements, 800 µL of carbon suspensions in a mixture of deionised water and 1-propanol (16/84) at 1-10 mg mL^{-1} were prepared. 25 aliquots of 10 µL for each ionomer dispersion in the same solvent mixture at 0.2-2 wt. % were injected. The reference vial was filled with the solvent and the 25 aliquots were added as for the titration.

3 EXPERIMENTAL RESULTS AND DISCUSSION

3.1 Characterisation of pristine and N-functionalised carbon blacks

Vulcan XC72R carbon was held under nitrogen plasma using a range of plasma powers (0- 300 W) and exposure times (0-8 hours) to modulate the amount of nitrogen introduced.

Elemental analysis (EA) confirmed the N-functionalisation with a maximum of 5 % of nitrogen after 8 h treatment under 300 W plasma. The nitrogen content linearly increases with the exposure time and power. In this report the focus is on samples containing 0 to 3 %N (VC-0, VC-1, VC-2, VC-3). Their chemical compositions evaluated by EA are listed in Table 1.

Table 1. Chemical compositions of Vulcan XC72 before and after N_2-plasma treatment.

Sample	Plasma treatment duration (h)	Plasma treatment power (W)	C (wt.%)	N (wt.%)	S (wt.%)	O (wt.%)
VC-0	-	-	96.57 ± 2.34	0.10 ± 0.06	0.88 ± 0.20	2.48 ± 1.90
VC-1	1	300	94.65 ± 0.04	1.46 ± 0.15	1.02 ± 0.16	3.31 ± 0.40
VC-2	2	300	92.05 ± 1.87	2.50 ± 0.14	1.09 ± 0.19	4.63 ± 1.66
VC-3	4	300	92.95 ± 1.15	3.40 ± 0.08	0.40 ± 0.47	3.02 ± 1.15

X-ray photoelectron spectroscopy (XPS) allowed identification of the nitrogen speciation in the modified carbons as well as the quantification of surface nitrogen.

The XPS spectrum of VC-0 presented no peak in the N 1s region, while the sample bearing 3 wt.% N presented three peaks centred at 399.0 eV, 400.2 eV and 401.5 eV (Figure 1), which correspond to pyridinic, pyrrolic and graphitic nitrogen[7] respectively (represented schematically in Figure 1 b).

The nitrogen content obtained from XPS was higher than that measured by EA (Table 2). This indicates that the plasma treatment introduces nitrogen preferentially on the surface of the carbon, without significantly affecting its bulk composition. Independently from the duration of the plasma treatment and of the resulting total amount of nitrogen introduced, the relative percentage of the different types of nitrogen determined by XPS was very similar: 31-32 % pyridinic-N, 30-31 % amine, 23-24 % pyrrolic-N, 11 % graphitic-N and 4-5 % N-oxides (Table 2).

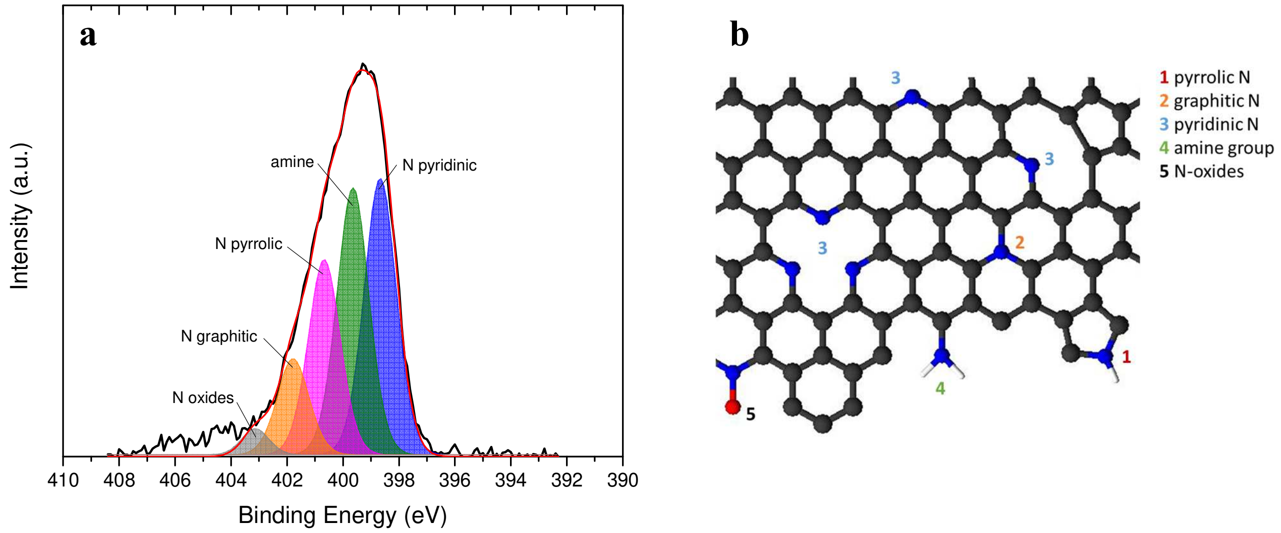

Figure 1. High-resolution XPS spectrum of the N 1s region of VC-3 (a) and type of nitrogen-containing groups introduced in the carbon structure by nitrogen plasma treatment (b).

Table 2. Comparison between nitrogen content values obtained by elemental analysis (EA) and from XPS for samples VC-1, VC-2 and VC-3.

Sample	EA		XPS						
	N (wt.%)	N/C	Pyridinic-N (wt.%)	Amine (wt.%)	Pyrrolic-N (wt.%)	Graphitic-N (wt.%)	N-oxides (wt.%)	N total (wt.%)	N/C
VC-1	1.46 ± 0.15	0.015	0.96	0.94	0.75	0.35	0.14	3.14	0.034
VC-2	2.50 ± 0.14	0.027	1.16	1.00	0.64	0.31	0.25	3.36	0.037
VC-3	3.42 ± 0.11	0.037	2.28	2.21	1.62	0.8	0.19	7.1	0.081

Nitrogen adsorption-desorption measurements and pore size distribution calculations showed that, in general, the total S_{BET} slightly decreased in agreement with micropore surface area upon the N_2 plasma treatment, but that the proportion of the surface area in mesopores was unchanged (see Table 3). Unmodified carbon VC-0 possesses specific surface area (S_{BET}) of 230 $m^2\ g^{-1}$ and contains mesopores and micropores.[2] Analysis of the micropore surface area by SAEIUS (2D-NLDFT)[6] leads to the determination of the mesopore+macropore (external) surface area by difference with the BET surface area.

Table 3. Specific surface area (S_{BET}) and volume ($V_{\mu pores}$) and surface ($S_{\mu pores}$) of micropores for pristine and N-functionalised carbon blacks.

Sample	S_{BET} ($m^2\ g^{-1}$)	$S_{NL\text{-}DFT}$ ($m^2\ g^{-1}$)	$S_{\mu pores}$ ($m^2\ g^{-1}$)	$S_{mesopores}$ ($m^2\ g^{-1}$)
VC-0	230	239	188	51
VC-1	213	220	173	47
VC-2	167	163	123	40
VC-3	160	160	110	50

3.2 Quantification of support/ionomer interaction

The determination of the strength of the interaction between Nafion® and pristine and N-functionalised Vulcan XC72 was addressed with Isothermal titration calorimetry (ITC).

Suspensions of VC-0, VC-2 and VC-3 were titrated with a dilute dispersion of Nafion® EW1100. A blank (reference) experiment was also performed in the absence of carbon.

On injecting the ionomer into the carbon suspension, a highly exothermic peak appeared, while dilution peaks were endothermic and less intense, providing clear evidence for an interaction between the carbon and the ionomer. Furthermore, the N-functionalised carbon blacks gave rise to different thermograms with different heat flow intensities and inflections. The cumulative heat release due to ionomer adsorption measured by ITC is depicted in Figure 2.

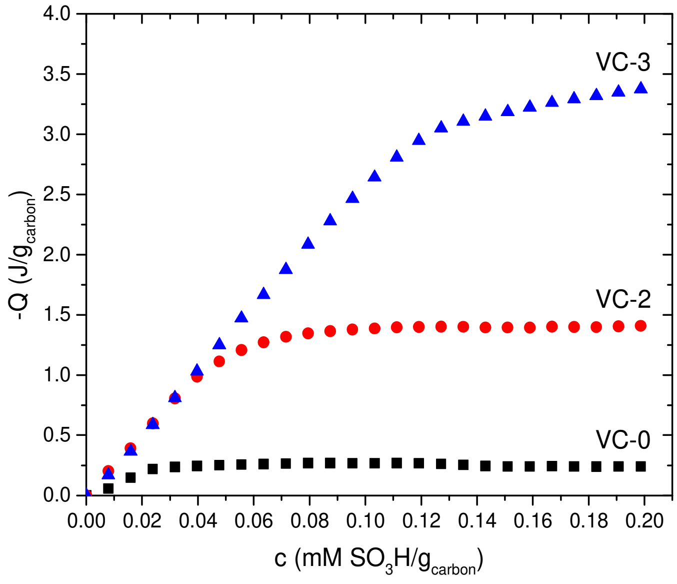

Figure 2. Cumulative heat release during titration of Nafion® with non-modified and nitrogen-doped carbon black Vulcan XC72R suspended in water/1-propanol normalised by carbon mass: VC-0 (black squares), VC-2 (red dots) and VC-3 (blue triangles).

The heat release progressively increases with the ionomer injections up to a plateau (Figure 2). The amount of ionomer needed to reach the onset of the plateau increases with the nitrogen content in the carbon and is not proportional to its specific surface area. Once the plateau is reached, additional injections of ionomer suspension have no influence, indicating that equilibrium is reached. Initially, 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 in the titration meaning adsorption at lower-energy sites. The plateau might be ascribed to the successive adsorption of Nafion® onto Nafion® that is already adsorbed on the carbon and is not detected by ITC, but was reported in a study based on ^{19}F NMR characterisation.[3]

The heat release, and therefore the strength of the Vulcan XC72R / Nafion® interaction, is strongly different between samples VC-0, VC-2 and VC-3. XPS having shown very similar proportions of the different types of nitrogen group between samples of different nitrogen content, it is concluded that the interaction strength depends on the degree of nitrogen functionalisation of the XC72R. The strongest heat release is observed for the carbon functionalised with the highest amount of nitrogen (3 wt.%, VC-3), and the lowest for the pristine Vulcan XC72R. The following trend of carbon/Nafion® interaction strength is the following: VC-3 > VC-2 > VC-0.

The normalised representation of Figure 2 leads to calculation of the adsorption enthalpy -ΔH (in kJ per mol of SO_3H) by the determination of the slope before the plateau (Table 4).

Table 4. Adsorption enthalpy obtained by determination of the slope on ITC experimental data with Nafion® and undoped and N-doped Vulcan carbon.

Sample	N content (wt.%)	$-\Delta H$ (kJ mol SO_3H^{-1}) adsorption enthalpy
VC-0	0.10 ± 0.06	6.7 ± 0.5
VC-2	2.5 ± 0.14	24.3 ± 0.2
VC-3	3.10 ± 0.07	26.0 ± 0.1

ITC experiments allowed the quantification of the strength of the carbon/ionomer interaction, demonstrating the role of nitrogen in promoting the adsorption of the ionomer on the carbon surface. The interaction likely occurs between the SO_3H groups of Nafion® and the nitrogen of the doped support. In conclusion, increasing the amount of nitrogen on the carbon black strengthens the interaction with the ionomer, with potential impact on catalyst and fuel cell performance and durability.

4 CONCLUSIONS AND FUTURE WORK

When Vulcan XC72 is treated by nitrogen-plasma, controlled and reproducible nitrogen functionalisation of its surface occurs. Using isothermal titration calorimetry, the strength of the carbon-Nafion® interaction was quantified by the calculation of enthalpy of adsorption. This study provides evidence that the introduction of nitrogen functionalities strengthens the interaction with the ionomer.

This approach can be further extended to carbons synthesised with tuned morphology, graphitisation and porosity, which can further improve their properties in the fuel cell catalyst layer, with significant impact on PEMFC performance and durability. Further work in the framework of IMMORTAL will attempt to correlate the interaction strength with the stability of the resultant cathode catalyst layers of a membrane electrode assembly in an operating fuel cell.

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