



Zirconium(IV)-promoted colloidal stability of carbon black particles and Pt/carbon catalysts

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ARTICLE INFO

Keywords:

Carbon-zirconium interfaces
Solid-state-batteries
Printable inks
Impregnation
ZrO₂/carbon composites

ABSTRACT

The colloidal stability of carbon-based functional materials is a prerequisite in many applications within the energy sector. These applications typically require the preparation of stable suspensions that can be processed over sufficiently long time. While the importance of particle surface functionalization is well recognized, the interaction of oxygen containing functional groups with multivalent metal ions in aqueous solutions remains insufficiently studied. Zirconium (IV) exhibits a complex aqueous chemistry characterized by extensive hydrolysis and the formation of positively charged hydroxo-complexes, making them an attractive model system for probing the relationship between surface functionality and colloidal stability. In this work, the interactions between hydrolyzed Zr(IV) species and three commercially available carbon-based solids, namely carbon black (Vulcan) and two Pt/C samples with different platinum loadings and degree of surface functionalization, are systematically investigated. The addition of Zr(IV) salts significantly modifies the colloidal properties of the carbon-based materials, imparting their water suspensions an excellent long-term stability against sedimentation and aggregation. The interaction between hydrolyzed Zr(IV) species and the carbon surface becomes more pronounced with increasing the pristine surface functionalization, however, its practical benefit is the greatest for the short time stabilization of poorly functionalized Pt/C, where the native surface chemistry alone is not sufficient to ensure the effective dispersion and colloidal stability.

1. Introduction

Carbon materials are widely employed in energy, environmental, and catalytic applications due to their high surface area, electrical conductivity, chemical stability, and tunable surface chemistry. Carbon blacks such as Vulcan-type materials are extensively used in electrochemical applications like CO₂-reduction [1], as ingredients for electrodes in ion batteries [2,3], as catalyst support for the production of hydrogen from various routes [4], including ammonia decomposition [5]. Additionally, Pt/C class of materials are the benchmark electrocatalysts for the reduction and evolution of hydrogen and oxygen [6], and a new avenue for the thermocatalytic hydrogenation and dehydrogenation of liquid organic hydrogen carriers [7]. These applications typically require the preparation of stable suspensions by carrying out

the following steps: a) transfer of the powder in the liquid phase (organic solvent, water or organic solvent-water mixtures); b) wetting of the powder; c) breaking of the agglomerates and aggregates into primary particles and d) stabilization of the resulting dispersion [8]. According to the hierarchical model of Eikerling, primary particles of carbon aggregate and form agglomerates [9,10]. The agglomerates are held together by van der Waals forces, which have to be overcome in the disagglomeration stage [8]. The use of organic solvents and surfactants is often compulsory to aid the early steps of transfer and wetting of the hydrophobic carbon-based powders [11]. In some deposition techniques such as roll-to-roll [12], or spray-coating [13], the resulting suspensions may require long-term colloidal stability for processing which can extend over days. Achieving and maintaining colloidal stability remains a significant challenge, especially for poorly functionalized particle

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<https://doi.org/10.1016/j.cartre.2026.100700>

Received 13 July 2026; Received in revised form 8 September 2026; Accepted 24 September 2026

Available online 24 September 2026

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Open access funding enabled and organized by Projekt DEAL.

surfaces, due to van der Waals interactions and limited electrostatic repulsion [8,14]. Water solutions of metal salts are typically employed to achieve either particle flocculation or colloidal stability, according to the nature, concentration and charge of the ions [14,15].

Zirconium (IV) salts belong to the family of multivalent metal ions and, depending on solution conditions, their hydrolysis generates a variety of positively charged zirconium hydroxo complexes [16,17] that modify the properties of bulk solid surfaces [18–20]. We have recently demonstrated that this ability can be extended as well to the solid-liquid interfaces of various colloidal systems, altering their electrical double layer [21–23]. With a water chemistry similar to zirconium, hafnium salts are also capable of delivering excellent colloidal stability [23].

Recently, the scientific community has shown remarkable interest in the substitution of rare and expensive elements with earth abundant and cheaper counterparts. As an example in the field of energy applications, halide solid electrolytes based on Li_2ZrCl_6 are considered promising materials in all-solid-state Li-ion batteries [24,25] and have been introduced as valid alternative to the less abundant Li_3MCl_6 ($\text{M} = \text{Sc}, \text{Y}, \text{Er}$) species, in light of their superior room-temperature conductivity and outstanding electrochemical stability [26]. The electrodes can be manufactured through both wet (sol-gel, co-precipitation) and dry processing (ball milling followed by cold-press) [26,27] and the presence of carbon additives enables low charge transfer resistance and fast reaction kinetics [28]. Some authors have investigated the use of zirconium and other metal salts to fabricate high stable electrodes for high-temperature polymer electrolyte membrane fuel cells (HT-PEMFC) [29,30]. Finally, other applications of Zr-carbon nanocomposites comprise Zr-doped carbon dots [31], supercapacitors for flexible integrated electronic devices [32] and electromagnetic waves absorbing materials [33].

Considering the widespread use of carbon-based materials in various energy applications, and the increasing interest for composite electrodes containing both carbon-based materials and the earth-abundant element zirconium, it was interesting for us to shed light on the interaction between Zr(IV) salts and this technologically relevant class of materials. Additionally, a complete water-based processing route to effectively disperse and stabilize carbon-based materials appears certainly appealing in comparison with traditional methods employing organic solvents, or their mixtures with water.

Three commercially available carbon-based materials, namely carbon black (Vulcan) and two carbon-supported platinum catalysts with different metal loadings, were first characterized with focus on their surface functionalization, then they were dispersed in water in the presence and in the absence of aqueous solutions of Zr(IV) salts. The results demonstrate that Zr(IV) species significantly enhance the colloidal stability of carbon-based materials, with the strongest effect observed for materials possessing a low density of surface functional groups. As possible application for the results of this work, we foresee the formulation of nanocomposite inks comprising multifunctional materials, using exclusively water as dispersant.

2. Materials and methods

Three commercially available carbon-based materials were investigated: the carbon black Vulcan XC72 (denoted Vulcan, acquired from Sigma Aldrich), a Pt/C solid containing 33 wt.% Pt, and a Pt/C containing 52.6 wt.% Pt, both produced by Tanaka Kikinokogyo (TKK) and acquired from EChem Supplies. All samples were comprehensively characterized prior to use. The designation adopted throughout the manuscript is based on the support type and nominal platinum loading. Zirconium (IV) chloride (ZrCl_4) and zirconium-oxy-dinitrate hydrate ($\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$) both with a purity $\geq 99.5\%$ were purchased from Alfa Aesar. Sigma Aldrich supplied zirconium-oxy-dichloride hydrate ($\text{ZrOCl}_2 \cdot x\text{H}_2\text{O}$) (99.99% trace metals basis). For the adjustment of pH, 1 M and 0.05 M hydrochloric acid from Carl Roth GmbH + Co.KG and Honeywell FlukaTM Fischer Scientific GmbH, respectively, were used. Potassium chloride (KCl) from Carl Roth GmbH + Co.KG was utilized as

background electrolyte for electrophoretic mobility measurements. Ultrapure water was produced with a Purelab Ultra from Elga LabWater or Veolia Water Solutions & Technologies and used in all experiments. All chemicals were used as received without any further purification. **Transmission Electron Microscopy (TEM) analysis** TEM was carried out using a CM30 microscope equipped with a LaB6 cathode, at a voltage of 300 kV. The microscope had a point resolution of 0.23 nm. The samples were prepared by drop casting an aliquot of 8 μl of the particle suspensions in absolute ethanol onto a lacey carbon copper grid from the company Plano GmbH, Germany. The samples were dried overnight at room temperature. Based on the TEM results, the Pt particle size distribution was estimated by measuring manually at least 50 particles from electron microscopy images using the freeware software ImageJ [34]. A cumulative particle size distribution $Q_0(x)$ was obtained for both samples. **Thermogravimetric-mass spectrometry (TG-MS) analysis** A XEMIS gravimetric sorption analyser (Fa. Hiden Isochema Ltd.) was used for high-resolution thermogravimetric analysis coupled with mass spectrometry. The heat treatment took place in 100 mL/min He flow. To remove physisorbed water, a drying step was performed for 240 min at 110°C. After the drying step, the samples were heated to 500°C with a ramp of 1 K/min. The samples were held at 500°C for 720 min. Throughout the experiments, the mass-to-charge ratios with integer values for singly charged ions from 1-50 were analysed using the mass spectrometer. **X-ray diffraction (XRD) analysis** XRD was performed using the D8 Advance diffractometer (Bruker). Measurements were conducted in steps of 0.014° between 20° and 80° 2 θ and an exposure time of 1 s/step. The voltage and current were set to 40 kV and 40 mA, respectively. The powders were pressed into acrylic cups with the aid of microscopy glass to compact and smooth the sample surface. Carbon black particles were slightly grounded in an agate mortar to obtain a fine powder prior analysis. The crystallite size of Pt particles was estimated through the coherence length, using the Scherrer equation [35]:

$$\tau = \frac{K \cdot \lambda}{\beta \cdot \cos\theta} \quad (1)$$

where τ is the mean crystallite size, K is a dimensionless shape factor (0.9 in the present work), λ is the X-ray wavelength ($\text{Cu K}\alpha$, $\lambda = 1.540598 \text{ \AA}$), β is the full width at half maximum (FWHM) of the characteristic reflections and θ is the Bragg angle. The Scherrer equation was also used to estimate the average stack height or the crystalline thickness of the carbon particles using the 002 reflections at around 25° 2 θ . The average length of the crystalline stack can be estimated by using the same reflections and a value of 1.89 for the constant K in Eq. 1 [40]. Finally, the Bragg equation (Eq. 2) can be used to estimate the average distance between the carbon layers d_{002} :

$$d_{002} = \frac{\lambda}{2\sin\theta_{002}} \quad (2)$$

Preparation of the carbon black dispersions For the preparation of the stock dispersions, the initial powders were weighed in a snap cover vial. A glass funnel was used to transfer the carbon black powders into disposable polypropylene (PP) test tubes. After transferring, the powders were dispersed in ultrapure water (1 mL) and subjected to ultrasonication using an UP-200s sonotrode, working at a frequency of 24 kHz and maximum powder of 200 W from the company Dr. Hielscher GmbH. The ultrasonication treatment was applied for 2 minutes at an amplitude of 20%. Three stock dispersions were prepared having concentrations of 11 mg/mL (Pt/C 33 wt.%), 6.3 mg/mL (Pt/C 52.6 wt.%) and 5.3 mg/mL (Vulcan). For better comparability between the samples, the Pt concentration in the stock dispersions was kept constant at 3.3 mg (Pt)/mL, whereas for the stock dispersion containing only carbon, a mean concentration value between the two Pt/C concentrations was considered (5.3 mg/mL). This value results as an average of the carbon content of the two Pt/C solids taking into account the Pt loading. The

detailed calculation is reported in the supporting information (Eq. S1-S3). Aliquots (100 μL) of the carbon or Pt/C stock dispersions were diluted with ultrapure water and suitable volumes of the freshly prepared aqueous solution of Zr(IV) stabilizers (0.28 M, independent of the salt used) were added, so that a final volume of 600 μL was obtained. The Pt concentration for both loadings was constant throughout all samples (0.55 $\text{mg}_{\text{Pt}}/\text{mL}$), the Vulcan concentration was 0.883 mg/mL . A series of nine samples was prepared for each sample, comprising a molar ratio Zr (IV)/Pt ranging from 0 (reference sample) to 83 mol/mol (see Table S1 in ESI for experimental details). In all cases, no incubation time was required to achieve complete dispersion of the solids and stable suspensions. However, for both dispersion of the solids and stabilization the ultrasonication step had to be carried out. For all samples, tip-sonication was performed for two minutes at a cycle of 0.3 seconds and an amplitude of 20% (20 W). In the presence of Zr(IV) stabilizers, the pH of the suspensions dropped to acidic values. To disentangle the effect of pH and Zr(IV) stabilization, samples were prepared where the pH was adjusted with a HCl water solution to match the pH of the Zr(IV) stabilized suspensions. Aliquots of the freshly prepared suspensions were characterized in depth as described in the following sections. Alternatively, the suspensions were left to stand still over two days to observe the colloidal stability against sedimentation at a macroscopic scale. **Zeta potential measurements** Electrophoretic mobility was measured with a Zetasizer Nano ZS (Malvern Instruments GmbH, Germany) using reusable DTS1070 folded capillary cells. Between the measurements, the cell was rinsed with deionized water and absolute ethanol and dried with filtered pressurized air. All measurements were performed at 25°C and an equilibration time of 120 seconds. For each sample, three individual measurements with a delay of 10 sec in between each run were performed. The Smoluchowski model was applied for the calculation of the individual ζ -potential values based on the electrophoretic measurements of mobility, using the Henry equation (Eq. 3):

$$U_E = \frac{2\epsilon\zeta f(\kappa a)}{3\eta} \quad (3)$$

where U_E is the electrophoretic mobility, ζ is the Zeta potential, ϵ the dielectric constant and η is the viscosity of the solvent. $f(\kappa a)$ is the Henry function with κ^{-1} being the Debye length and a referring to the particles size. For experimental conditions investigated in the current work where $\kappa a \gg 1$, the electrophoretic mobility of a particle does not depend on its shape and the particle does not rotate in the applied field [36,37]. Therefore, no corrections were made for particles anisotropy. The electrophoretic mobility increased upon stabilization with aqueous solutions of Zr(IV) salts with respect to non-stabilized samples. By increasing the concentration of the salts, a plateau was reached where the mobility was independent of the Zr(IV) concentration. The contribution of the surface conductivity was not specifically taken into account, therefore the mean apparent ζ -potential is reported throughout the manuscript [38]. The stabilized suspensions were diluted 1:100 (vol : vol) with a water solution of KCl (0.01 M) as background electrolyte prior to measurements. Standard deviation was obtained over at least six independent samples; each sample was measured thrice. **pH measurements** The pH-Electrode InLab Expert Go-ISM from Mettler Toledo was used for measuring the pH. Before the measurements, the pH-sensor was calibrated with buffer solutions at pH = 4 and pH = 7. For the pH measurement in snap flask vials, a minimal volume of 3 mL was required to ensure that the pH-electrode is fully immersed in the suspension. In between each measurement, the pH-electrode was cleaned with ultrapure water and dried with a non-linting cloth. The pH-value of a specific Zr(IV) in 1:100 dilutions was determined by measuring the pH-value of each of the six dilutions per each different Zr(IV) concentration. A mean value out of the six measurements with a standard deviation was calculated and is reported throughout the manuscript. The same procedure was used for the corresponding HCl-stabilized suspensions. **UV-Vis Spectroscopy** Kinetic measurements of the time evolution of

extinction were performed using the CARY 100 Scan Ultraviolet-Visible spectrophotometer (Varian, Inc). The measurements were performed at a fixed wavelength of 800 nm, using samples with a relatively high concentration of 0.0735 M (Vulcan) and 0.00338 M (Pt) obtained through a 1:5 (Vol:Vol) dilution of the corresponding stock dispersions, with ultrapure water. This was the highest ink concentration that could be investigated, as the value of the optical density was around 3.2 at 800 nm, hence slightly below the maximum linearity range of the spectrophotometer (maximum optical density of 3.25 at 800 nm). Kinetic measurements were performed for one hour at 25°C using semi-micro cuvettes with optical path of 1 cm. Normalized extinctions were calculated by dividing the extinction values of each suspension by the value of the extinction at time zero.

3. Results and discussion

3.1. Structural characterization

Considering that commercial carbon-based materials often exhibit substantial differences in surface functionalization arising from their manufacturing processes, thermal histories, and post-treatment procedures, our work started with an in-depth characterization of the pristine samples. In fact, a detailed understanding of these differences is essential to bridge the properties of solids with the stability of the suspensions and hence, to select the suitable stabilization strategy.

According to the literature, Vulcan XC72 consists of primary carbon particles with sizes typically ranging from 20 to 50 nm (Fig. S1), which are covalently connected to form larger aggregates with characteristic sizes of approximately 200–500 nm [39]. Fig. 1 shows the TEM images of the Pt/C 33 wt.% and 52.6 wt.% (Fig. 1a, b), the cumulative number size distribution of Pt nanoparticles (NPs) retrieved from the electron micrographs (Fig. 1c) and the powder XRD patterns of the three samples (Fig. 1d).

The results show that Pt NPs are evenly distributed onto the carbon support, whereas the estimation of their size distribution from the TEM micrographs shows that the Pt NPs in the Pt/C 33 wt.% are smaller (around 2 nm) than the Pt NPs in the 52.6 wt.% (around 4 nm). Additionally, the PSD of the Pt NPs in the 52.6 wt.% sample is broader, compared with the PSD of the Pt NPs in the 33 wt.% sample (Fig. 1c and Table 1). For a more quantitative evaluation, the span between the distribution at 5 and 95 percentiles (Δx_{5-95}) can be considered, which leads to a slightly larger breath of the distribution for the Pt/C 52.6 wt.% (Table 1). The XRD analysis reveals that in both cases, the Pt NPs are highly crystalline (Fig. 1d). The reflections at 39.7°, 46.3° and 67.7° 2 θ correspond to (111), (200) and (220) planes of the face-centered cubic phase, respectively. The crystallite sizes of Pt NPs can be estimated through the coherence length using the Scherrer equation (Eq. 1) and the results show that the Pt NPs in the Pt/C 33 wt.% samples are smaller than in the 52.6 wt.% samples, confirming the estimation of the size from TEM analysis (Table 1). The disagreement between the absolute values of the sizes has to be assigned to the different sensitivity of the two techniques, whereby XRD, being a bulk technique, results in larger average sizes when compared to number-based TEM analysis.

Another important result of the XRD analysis is the difference in the nature of the carbon support of the commercial samples. Vulcan shows a high intensity peak at 24.7°, which is due to (002) reflections and another peak with lower intensity at 43.2°, which is due to an overlapping of (001) and (101) planes [40]. The Pt/C 33 wt.% sample shows the reflection at around 25°, which is negligible in the Pt/C 52.6 wt.% sample, whereas the lowest intensity peak at 43.2° is not visible in both samples [40]. This result suggests differences in the crystallinity of the carbon supports in the Pt/C commercial samples.

Additional parameters about the carbon component of the samples can be retrieved from the XRD pattern using the reflections around 25° that are visible in the patterns of Vulcan and Pt/C 33 wt.%. Using Eq. 1, the average height and length of the crystalline stacks τ_H and τ_L ,

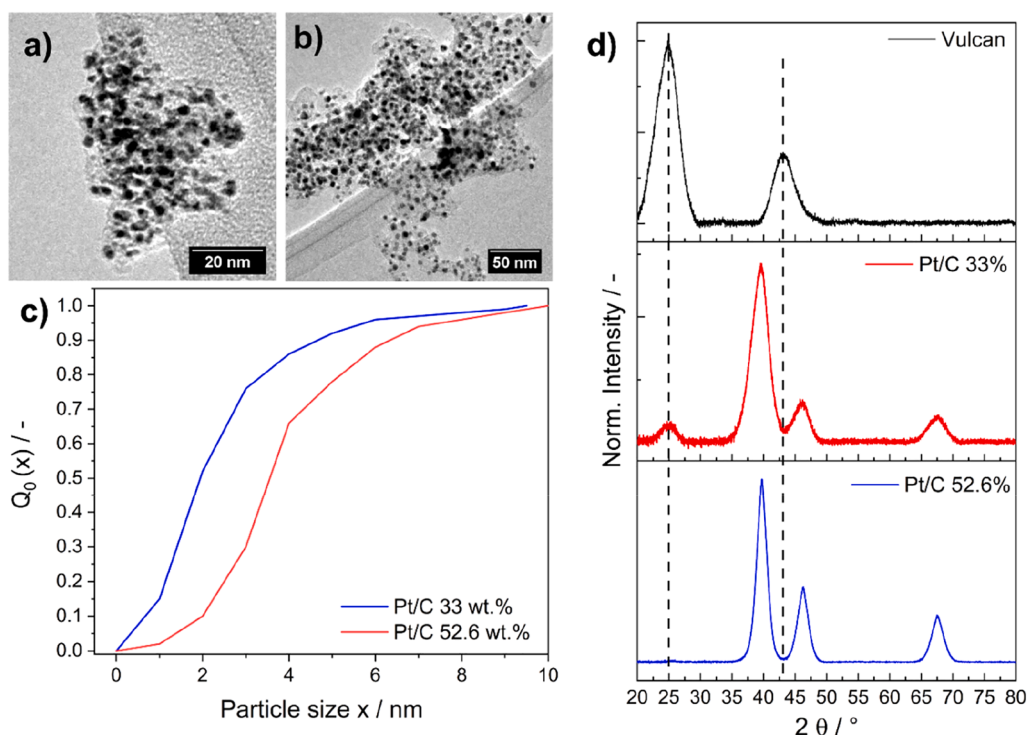


Fig. 1. Microstructure characterization of the pristine materials. a) and b) TEM analysis of the Pt/C 33 wt.% and Pt/C 52.6 wt.% samples, respectively. c) Corresponding cumulative number size distribution $Q_0(x)$ of the Pt nanoparticles dispersed onto the carbon support. The estimation of the PSD is based on a minimum number of 50 particles. d) Powder XRD analysis of the materials used in the current work. The patterns were normalized to the maximum intensity.

Table 1

Comparison of the distribution parameters $x_{5,0}$, $x_{50,0}$ and $x_{95,0}$ of the cumulative particle size distribution of the Pt nanoparticles deposited on carbon support based on TEM image analysis and coherence length estimated from the XRD pattern using the Scherrer equation[§].

Sample	$x_{5,0}$ / nm	$x_{50,0}$ / nm	$x_{95,0}$ / nm	Δx_{5-95} / nm	τ (Pt) / nm	τ_H (d_{002}) / nm	τ_L (d_{002}) / nm	d_{002} / nm
Vulcan	-	-	-	-	-	1.6	3.4	0.359
33 wt.% Pt/C	1.1	2.0	5.8	4.7	2.4	2.7	5.7	0.357
52.6 wt.% Pt/C	2.2	3.6	7.6	5.4	4.4	-	-	-

[§] Cu K_{α} , $\lambda = 1.540598$ Å; $K = 0.9$ for τ (Pt) and τ_H ; $K = 1.89$ for τ_L [40].

respectively, can be estimated. Additionally, the interlayer stacking of carbon sheets can be determined using the Bragg equation (Eq. 2). Lower values of the interlayer stacking d_{002} and higher values of the average height of the crystalline stacking τ_H corresponds to higher degree of graphitization [40]. The data reported in Table 1 show that Vulcan and Pt/C 33 wt.% have very similar values of the interlayer stacking of carbon sheets, indicating in both cases a high degree of graphitization [40]. However, a certain degree of disorder is present, considering that the 0.36 nm value is larger than the 0.34 nm observed for graphite [40]. The Vulcan and Pt/C 33 wt. % differ for the height and length of the crystalline stacks, which are larger for the carbon particles in the Pt/C 33 wt.%. Concerning the sample Pt/C 52.6 wt.%, the d_{002} reflection at around $2\theta = 20$ are barely visible in the experimental pattern, indicating the low degree of graphitization of this sample (Fig. 1d).

3.2. Surface characterization of the solid samples

The structural characterization shows that the two Pt/C samples are quite different in terms of Pt loading, primary nanoparticle size and microstructure of the carbon support, which have important impact on the material performance in functional devices. Herein, the three pristine materials were analysed via thermogravimetric analysis to identify the amount and nature of the functional groups on the surface. Fig. 2a

shows the relative mass loss of the materials during the heating ramp under helium atmosphere. All samples display a weight loss during the first heating ramp from 25 to 110°C, which may be assigned to physisorbed water. The smallest overall weight loss of 0.16 wt.% during the first heating ramp is observed for Vulcan (Fig. 2a). The weight loss in this temperature range is 4.23 wt.% for the Pt/C 33 wt.% and 2.02 wt.% for the Pt/C 52.6 wt.% samples.

The second temperature range with detected weight loss is observed between 110 and 500°C (Fig. 2a). The additional weight loss in this interval amounts to 0.29 wt.% for carbon, 1.87 wt.% for the Pt/C sample with the highest Pt loading, and 5.4 wt.% for the 33 wt.% Pt/C sample, respectively. Consequently, some conclusions can already be drawn based on the overall weight loss and materials, namely that the carbon sample has almost no functional groups on the surface (total weight loss 0.45 wt.%), whereas the Pt/C 33 wt.%, with a total weight loss of 10.15 wt.%, shows a higher surface functionalization compared with the Pt/C 52.6 wt.% sample, which showed a total weight loss of 3.89 wt.%.

However, not only the amount, but also the nature of surface functional groups is important to rationalize and predict the dispersibility of materials in liquid phase in the presence of Zr(IV) hydroxo-complexes. In fact, our previous studies demonstrate the relevance of carboxylic acid functional groups for the synthesis of sub-100 nm particles of ibuprofen and naproxen via antisolvent crystallization [21], as well as

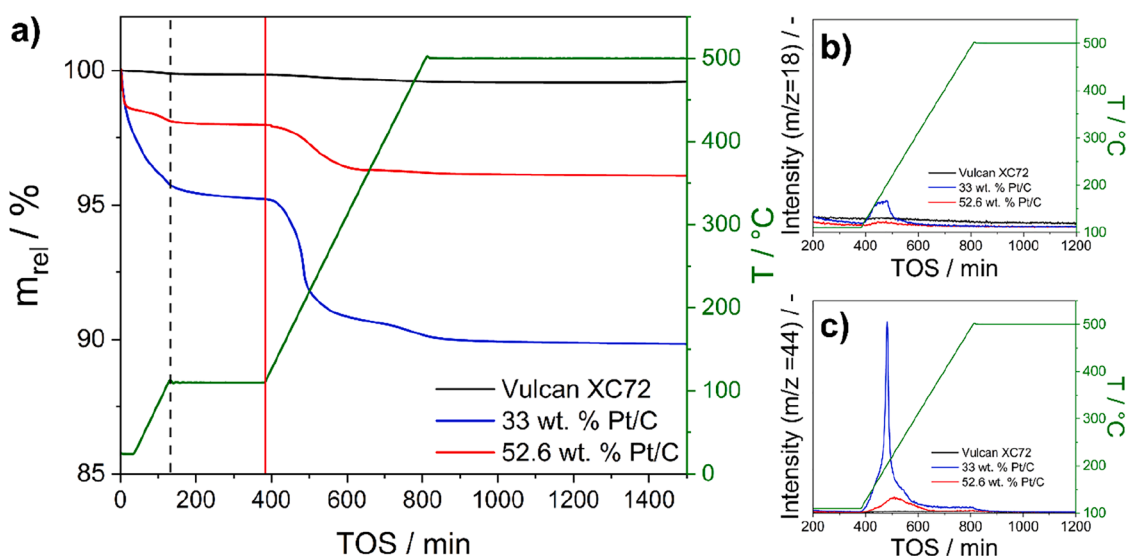


Fig. 2. Thermogravimetric analysis of the carbon, Pt/C 33 wt.% and 52.6 wt.% samples under inert atmosphere (100 mL/min He flow). a) Measured relative weight loss during the thermal treatment (TOS = Time on stream) with temperature profile (green). b) and c) Detected signals from the mass spectrometer which can be linked to the formation of CO_2 and H_2O . The drying step at 110°C for 240 min to remove physisorbed water was followed by a heating ramp of 1 K/min up to 500°C where TOS was 400 minutes.

the role of stoichiometric surface -OH groups for the stabilization [22] and post-processing [23] of goethite ($\alpha\text{-FeOOH}$) particles. Therefore, thermogravimetric analysis coupled with mass spectrometry was employed in the present study to monitor the evolution of two signals with $m/z = 18$ and 44 , related to water formation from -OH and CO_2 formation from carboxylic groups on the surface, respectively, during the heating ramp from 110 to 500°C (Fig. 2b and c). The intensity profiles are characteristic for each sample. The Pt/C 33 wt.% sample shows the highest intensity in terms of -OH groups, whereas the Pt/C 52.6 wt.% sample only has a small amount of hydroxylic groups. Almost no -OH groups are present on the surface of Vulcan (Fig. 2b). The same trend is observed for the $m/z = 44$, with the highest intensity of CO_2 formation observed for the Pt/C 33 wt.%, followed by the Pt/C 52.6 wt.%, and finally Vulcan. For the sample with the highest Pt loading, the intensity of the $m/z = 44$ peak is slightly higher compared with the $m/z = 18$, indicating the presence of more carboxylic functional groups with respect to -OH groups (Fig. 2b and c). The intensity profiles in Fig. 2b and c are in line with the weight loss observed during the heating ramp from 110 to 500°C in Fig. 2a.

Knowing the specific surface area of the materials [22] (Table 2) and the weight loss observed throughout the TG-MS study, the density of surface functionalization can be estimated for each functional group based on their relative area (Fig. 2b and c) and is reported in Table 2. For carbon, this estimation could not be carried out in a reliable way, due to its poor surface functionalization.

3.3. Dispersion of the powders in water

The low surface functionalization of Vulcan translates into a pronounced hydrophobic behavior rendering its dispersion in water

Table 2
Surface area of the three samples and number density of the surface functional groups derived from TG-MS analysis.

Sample	S_{BET} , m^2/g	Number(OH groups)/ nm^2	Number($-\text{CO}_2\text{H}$ groups)/ nm^2
Vulcan	273	-	-
Pt/C 33 wt. %	151	3	4
Pt/C 52.6 wt. %	395	0.3	0.5

challenging. Consequently, organic solvents are often used to aid the dispersion of carbon-black based materials and enable the subsequent processing. Herein, the dispersion of carbon-based materials was carried out in water using two different dispersions, obtained through a 1:5 (Vol:Vol) and 1:100 (Vol:Vol) dilutions of the stock dispersion. These dilution factors correspond to molar concentrations of Vulcan of 0.0735 M and $0.441 \times 10^{-3}\text{ M}$, respectively and were selected to enable the characterizations of the suspensions by UV-Vis spectroscopy and electrophoretic mobility, respectively.

The addition of a background electrolyte is essential for measurements of the ζ -potential, as it controls the properties of the electric double layer (EDL) and ensures both reproducibility of the measurements and comparisons between different samples. In this work, an aqueous solution of KCl with a concentration of 0.01 M was used and the results were compared with an analogous sample dispersed in water (Experimental part). The results show that when Vulcan is dispersed in water a pH around 6 is attained, independent of the particle concentration. The mean apparent ζ -potential of these dispersions show values of $23.7 \pm 1.6\text{ mV}$ and $-8.8 \pm 0.9\text{ mV}$ for the 0.0735 M and $0.441 \times 10^{-3}\text{ M}$ concentrations, respectively. In contrast, when the stock dispersion is diluted using an aqueous solution of KCl, the standard deviation of the ζ -potential measurements increases. More specifically, the dispersion of Vulcan with a concentration of 0.0735 M shows a ζ -potential of $21.1 \pm 8.4\text{ mV}$, whereas the dispersion with lower concentration of $0.441 \times 10^{-3}\text{ M}$ showed a ζ -potential of $-16.1 \pm 12\text{ mV}$ (Fig. 3a). This result reflects the compression of the EDL upon addition of the electrolyte and is confirmed by the large aggregates that were observed macroscopically (insert in Fig. 3a). Finally, note that the dilution of the carbon-black dispersions leads to a sign reversal of the ζ -potential, independent of the presence of the background electrolyte (Fig. 3a).

Under diluting conditions analogous to those employed for Vulcan (1:100 Vol:Vol), the mean apparent ζ -potential of the Pt/C particles shows negative values, independent of the presence of the electrolyte or the Pt loading (Fig. 3b). This dilution factor corresponds to a concentration of $0.169 \times 10^{-3}\text{ M}$. However, in this case standard deviations of 6 and 7.5 mV were observed, indicating that the measured electrophoretic mobility of the particles for both samples comprising Pt is highly variable under these experimental conditions. The Pt/C 33 wt.% is an exception, as the ζ -potential in the presence of KCl has comparatively more reliable values of $-16.5 \pm 3\text{ mV}$, reflecting the higher surface

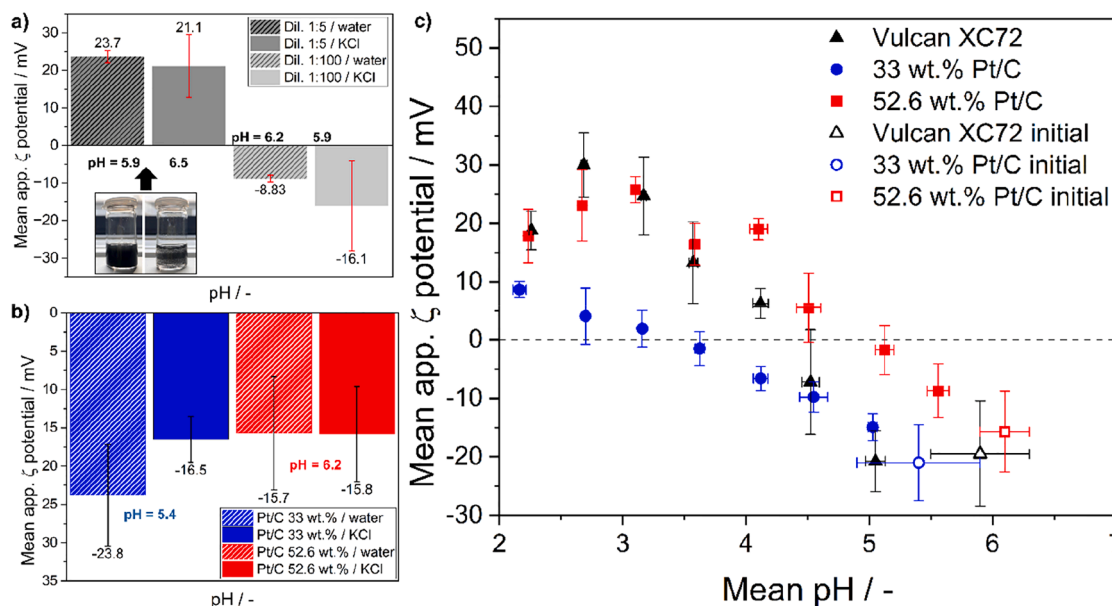


Fig. 3. Mean apparent - potential and corresponding pH values of: a) carbon Vulcan XC72 dispersed in deionized water or aqueous solution of KCl (0.01 M) at 1:5 (0.0735 M) and 1:100 (0.7×10^{-3} M) Vol:Vol dilutions of the initial dispersion. b) Pt/C particles with 33 wt.% and 52.6 wt.% dispersed in deionized water or aqueous solution of KCl (0.01 M) at 1:100 Vol:Vol dilution of the initial dispersion. The values of pH in a) and b) have standard deviations of ± 0.2 . c) Vulcan and Pt/C loaded materials as a function of pH using aqueous solution of HCl as stabilizer. Pt concentration in all cases was 0.033×10^{-3} M. The dilution of the stock dispersions was 1:100 for all samples. Insert in a: photograph of the dispersion of the Vulcan in deionized water (left) and 0.01 M KCl (right).

functionalization (Fig. 2). For the same reason, this sample shows also a more acidic pH upon dispersion in water with respect to the Pt/C 52.6 wt.%, namely a pH value of 5.4 against 6.2 (Fig. 3b).

In light of the significant changes in the mean apparent ζ -potential observed upon small changes of the pH of the dispersant, the surface properties of the three samples were evaluated as function of a wider pH range, which was achieved using water solutions of HCl. Fig. 3c shows that for all three materials an inverse sigmoidal curve as a function of pH was obtained, showing a material dependent point of zero charge (PZC). At the PZC, there are as many negative charges as positive charges so that the mean surface charge density is zero [14] and consequently a ζ -potential value of zero is measured. However, materials can still comprise regions where the surface charge is high negative or positive, leading to short range forces [14]. In fact, near the PZC, the suspensions became highly unstable, due to minimal electrostatic repulsion between particles, which led to progressive aggregation. Nevertheless, the PZC could be determined with sufficient accuracy to identify a significant trend between the three samples. In particular, the carbon sample reaches its PZC at pH values between 4 and 4.5, whereas the PZC of the Pt/C 33 wt.% and Pt/C 52.6 wt.% are found at pH = 3.5–2.5 and pH = 5, respectively. A lower PZC for the Pt/C 33 wt.% was expected based on its higher surface functionalization [41] with respect to the carbon and Pt/C 52.6 wt.% samples, in light of the TG-MS results. The PZC are in agreement with values reported in the literature for carbon-based materials [42]. However, considering the poor surface functionalization of Vulcan assessed through the TG-MS measurements, its PZC should be higher than the Pt/C 52.6 wt.%. This apparent contradiction can be explained by considering an additional mechanism for the generation of surface charges that is not involving oxygen-containing functional groups, but rather oxygen-free Lewis base sites that are protonated in the presence of HCl [43]. Additionally, it is worth mentioning here that already the dispersion of a solid in liquid phase is a crucial step that can potentially influence the surface properties of materials, especially considering that in this work, and in the common praxis, a tip-sonication treatment is employed to reduce the occurrence of aggregates and facilitate the dispersion step in the liquid phase [44,45]. In turn, the ultrasonication has been demonstrated a powerful tool to reduce the size

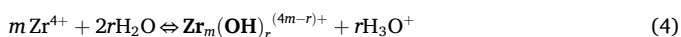
of graphene oxide and nano-diamonds and induce defects in their microstructure [46–48]. Recently, Caidi et al. have demonstrated that ultrasound treatment impacts the physicochemical properties of carbon black and Pt/C catalysts differently, according to the energy input used and the properties of the pristine materials [49]. More precisely, Vulcan underwent an increased surface oxidation upon ultrasonication, which was reflected in a shift of the isoelectric point towards acidic pH and an increased surface functionalization, demonstrated through Bohm titration [49]. In line with our observations, the study shows as well that both Pt/Vulcan and a Pt/C catalysts with a high surface area displayed no significant changes in the surface functionalization upon ultrasonication [49]. For this reason, the tip-sonication (power, time) was kept constant throughout our study, independent of the sample investigated.

In summary, the results of this study up to now show that the correct assessment of the mean apparent ζ -potential of the water dispersions of carbon-based materials is challenging, because: a) it varies with the absolute concentration of particles (Fig. 3a and Fig. S2); b) it is affected not only by the surface functional groups of the pristine materials, but it is also the result of their processing step to transfer the powder in the liquid phase (Fig. 3a and c); c) considering the common accepted boundaries for stable colloidal dispersions having ζ -potential $> |25 \text{ mV}|$, these dispersions are not sufficiently stable and are expected to undergo reaggregation over time [11], as it will be demonstrated later.

Therefore, it is of fundamental importance to develop a method for the assessment of the colloidal properties of carbon-based materials upon dispersion in water considering their limited surface functionalization.

3.4. Dispersion and stabilization using aqueous solution of Zr(IV) complexes

Before moving to the dispersion and stabilization of carbon-based materials in water solutions of Zr(IV) salts, it is worth mentioning that Zr(IV) salts are Lewis acids and readily undergo hydrolysis leading to water solutions with acidic pH, according to Eq. 4:



Various degrees of hydrolysis have been reported in the literature, mononuclear ($m = 1$) or polynuclear ($m \geq 2$) Zr(IV) hydroxo-complexes form according to the pH and the initial Zr(IV) concentration [16]. Species like $\text{Zr}(\text{OH})_4$, $\text{Zr}(\text{OH})_3^+$, and $\text{Zr}(\text{OH})_2^{2+}$ are abundant in pH intervals between 3 and 2.75, between 2.75 and 2.0, and between 2.0 and 1.0, respectively, i.e. under the experimental conditions employed in the current work [17]. Table 3 summarizes for few values of the zirconium tetrachloride concentrations, the pH values attained by the corresponding aqueous solutions and the relative abundance of the hydroxo-complexes arising upon hydrolysis according to Ekberg et al. [17].

Fig. 4 shows the impact of Zr(IV) stabilization on the dispersion and colloidal stabilization of carbon-based powders in water. Fig. 4a shows that by increasing the Zr(IV) concentration the pH of the suspensions decreases progressively from slightly acidic pH ≈ 6 to pH around 2.5 for ZrCl_4 concentration of 2.34×10^{-3} M.

This decrease in pH is independent of the material used, however, it has a strong impact on the mean apparent ζ -potential of particles, as shown in Fig. 4b-d. High values of the mean apparent ζ -potential were observed throughout the entire range of Zr(IV) concentrations investigated. Additionally, a comparison between the pH- and the Zr(IV)-stabilized dispersions and suspensions, respectively, shows that the latter attained consistently a more positive ζ -potential, indicating the importance of the contribution of aqueous solutions of ZrCl_4 to achieve highly stable suspensions of carbon-based materials. In the case of Vulcan, the mean apparent ζ -potential already becomes approximately 30 mV in the pH range of 5 to 4.5, when ZrCl_4 is used as stabilizer. The same value of the mean apparent ζ -potential is obtained at a significantly more acidic pH ≈ 2.5 when using HCl as stabilizer, where in the presence of Zr(IV) species a ζ -potential of 41 mV is observed. Consequently, the ZrCl_4 stabilized Vulcan suspension shows higher colloidal stability, which is already evident at higher pH (Fig. 4b).

Similarly, Fig. 4c and d show that also for Pt/C 33 wt.% and 52.6 wt.%, the Zr(IV)-stabilized suspensions are more stable than the pH-stabilized suspensions, with values consistently above 30 mV below pH 5. Yet higher values of the ζ -potential between 40 and 50 mV are observed at more acidic pH. This degree of stability is never reached through the pH-stabilization for any of the materials considered. Additionally, the differences in the mean apparent ζ -potential values between the ZrCl_4 - and HCl-stabilized systems are the highest for Pt/C with 33 wt.% (Fig. 4d), which indicates that a higher surface functionalization leads to a better interaction with Zr(IV) complexes, and therefore to a better colloidal stability of the suspensions. The consistently higher mean apparent ζ -potentials observed for the Zr(IV)-stabilized samples with respect to pH-stabilization is clear evidence that Zr(IV) hydrolysis species act as stabilizers and that the contribution of the pH-stabilization is comparably negligible. However, the hydrolysis of ZrCl_4 in water, creates not only hydroxo-complexes but also Cl^- ions which are also known as strong surface adsorbing species [50]. Therefore, the stabilization effect of aqueous solutions of Zr(IV) species was investigated using zirconium salts different from ZrCl_4 . The study focused on the Pt/C 52.6 wt.% sample, for which a higher concentration of Zr(IV) of

2.4×10^{-3} M was necessary to obtain high colloidal stability (ζ -potential > 40 mV), in comparison to the Pt/C 33 wt.%, for which a concentration of ZrCl_4 as low as 0.03×10^{-3} M was sufficient (Fig. 4c and d).

3.5. Effect of anion on the Zr(IV)-stabilization of carbon black dispersions

The potential role of chloride in the stabilization mechanism of carbon-based materials, was investigated by considering two additional Zr(IV) salts, namely the ZrOCl_2 and $\text{ZrO}(\text{NO}_3)_2$, and comparing them with the benchmark ZrCl_4 . The former salt was selected for the lower chloride content, whereas the latter offered an independent evaluation of the effect of the anion on the stabilization of carbon-based materials. In all cases, the pH progressively reaches more acidic values by increasing the salt concentration (Fig. 5a). The aqueous solutions of ZrCl_4 reaches slightly lower pH with respect to the ZrOCl_2 and $\text{ZrO}(\text{NO}_3)_2$. The stabilizing effect of all three Zr(IV) salts have in common that almost a plateau with no significant increase of the mean apparent ζ -potential is reached at $[\text{Zr(IV)}] \geq 0.14 \times 10^{-3}$ M.

However, the mean apparent ζ -potential values at the corresponding Zr(IV) concentrations are slightly smaller when using ZrOCl_2 and $\text{ZrO}(\text{NO}_3)_2$ as stabilizing salts, compared with the values reached when ZrCl_4 is used. More precisely, at slightly acidic pH obtained at very low Zr(IV) concentrations a significant destabilizing effect of the Pt/C 52.6 wt.% suspensions is observed for all three Zr(IV) salts (Figure 5b). The dispersion remains unstable with ζ -potential values around 0 mV for $[\text{ZrOCl}_2]$ and $[\text{ZrCl}_4] < 0.014 \times 10^{-3}$ M (Figure 5b). This allows estimating the PZC for the Pt/C 52.6 wt.% at around 5.8 ± 0.5 , hence with a shift towards higher pH values upon Zr(IV) stabilization. By further increasing the concentration of ZrOCl_2 , first higher ζ -potential of 23.2 ± 3.2 mV clearly above the PZC are obtained at $[\text{Zr}] = 0.03 \times 10^{-3}$ M, then exceeds 30 mV by using the salts ZrOCl_2 and $\text{ZrO}(\text{NO}_3)_2$ at a Zr(IV) concentration of 0.06×10^{-3} M. When using ZrCl_4 instead, $\zeta > 30$ mV is reached at a 4.3 times lower concentration of 0.014×10^{-3} M. Therefore, from the comparison of the three Zr(IV) salts, it can be concluded that the main stabilizing effect does not result from the Cl^- ions. The chloride-containing Zr(IV) salts, as well as $\text{ZrO}(\text{NO}_3)_2$, are leading to a notable increase of the mean apparent ζ -potential above 30 mV. Though ZrCl_4 leads to higher mean apparent ζ -potential at the same Zr(IV) concentrations. As shown in Figure 5a, the pH-value decreases slower if ZrOCl_2 and $\text{ZrO}(\text{NO}_3)_2$ are used as stabilizing Zr(IV) salts. The differences are small, but as described in section 3.3, small shifts in the pH-values affect the colloidal stability of the particles and the measured electrophoretic mobility.

These results reveal that the interaction between hydrolyzed Zr(IV) species and the carbon surface strongly depends on the degree of surface functionalization, making possible the assessment of the PZC only for the least functionalized Pt/C material. Accordingly, the PZC of the Pt/C 52.6 wt.% shifted from $\text{pH } 5.0 \pm 0.2$ under pH-stabilized conditions to $\text{pH } 5.8 \pm 0.5$ after the addition of Zr(IV). Similarly, also for Vulcan a shift of the PZC can be estimated from around pH 4.3 to around pH 5.8 (Figure 4b). In contrast, the more functionalized Pt/C 33 wt.% sample exhibited very positive ζ -potentials throughout the investigated acidic pH range, preventing the experimental determination of a PZC (Figure 4b and c). This behavior suggests a more extensive interaction of hydrolyzed Zr(IV) species with the more functionalized carbon surfaces. The TG-MS analysis identifies -OH and -CO₂H groups as the predominant surface functionalities, the interaction with Zr(IV) species might be attributed primarily to these oxygen-containing groups, in agreement with our previous studies [21,22]. However, the exact molecular nature and coordination mode of this interaction cannot be established from the present data.

3.6. Sedimentation behavior monitored by UV-Vis spectroscopy

An important parameter to evaluate the colloidal stability of an ink is

Table 3

Zirconium hydroxide species arising from the hydrolysis of Zr(IV) salts in the pH range between 3.5 to 2.0 encountered in this study, according to Ekberg et al. [17].

$[\text{ZrCl}_4] / \text{mM}^*$	pH interval / - ^(*)	Hydrolytic species ^(*)
0.9	> 3.5	$\text{Zr}(\text{OH})_4$
0.14	$3.5 \div 3$	$\text{Zr}(\text{OH})_4$; $\text{Zr}(\text{OH})_3^+$
0.47	$3 \div 2.5$	$\text{Zr}(\text{OH})_4$; $\text{Zr}(\text{OH})_3^+$
2.34	$2.5 \div 2$	$\text{Zr}(\text{OH})_3^+$; $\text{Zr}(\text{OH})_2^{2+}$

* from our experiments;

^(*) suggested in the literature [17].

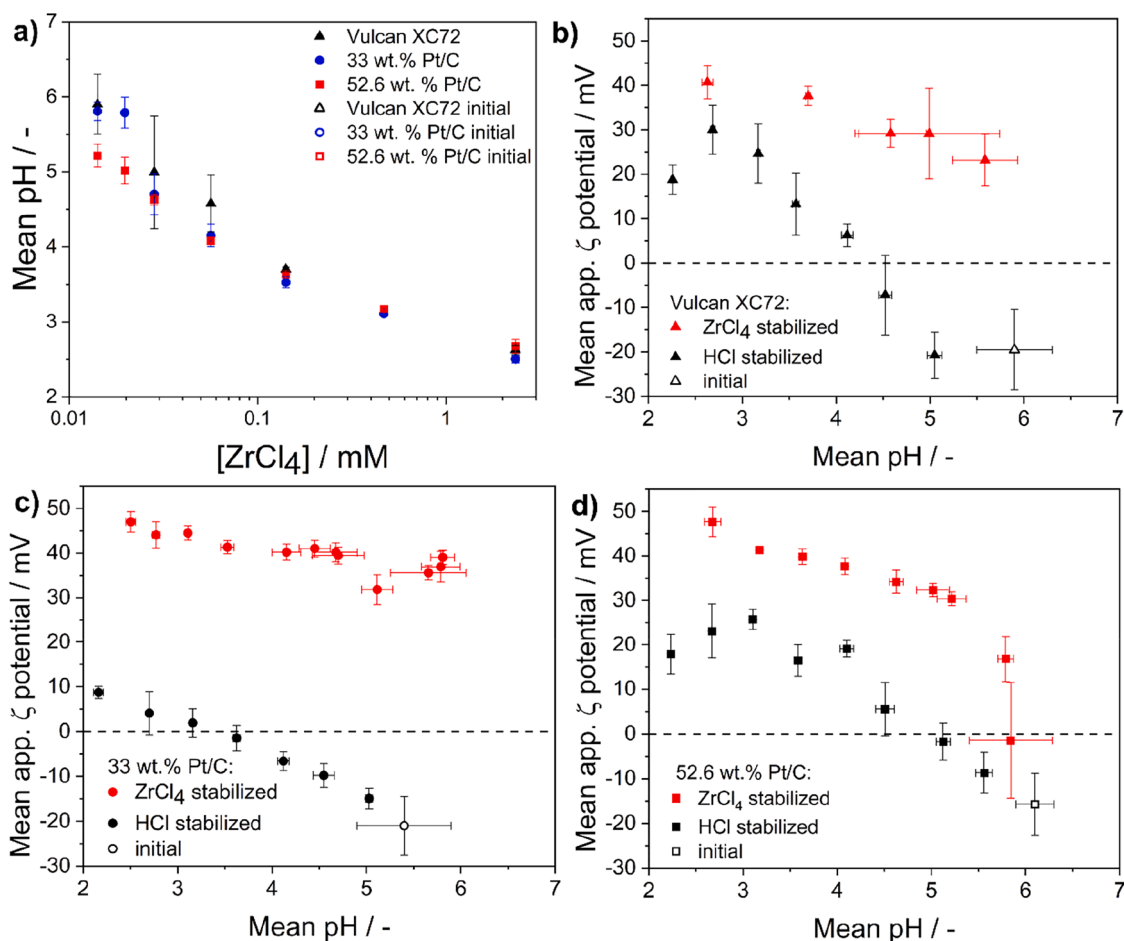


Fig. 4. a) Evolution of the pH for the carbon- and Pt/C-based dispersions using a 1:100 dilution as function of the Zr(IV) concentration. The x-axis uses a logarithmic scale (base 10) for better comparison. b), c) and d) Comparison of the mean apparent ζ -potential of the carbon- and Pt/C-based dispersions stabilized with aqueous solutions of HCl or ZrCl₄. a) Vulcan; b) Pt/C 33 wt.% and c) Pt/C 52.6 wt.%.

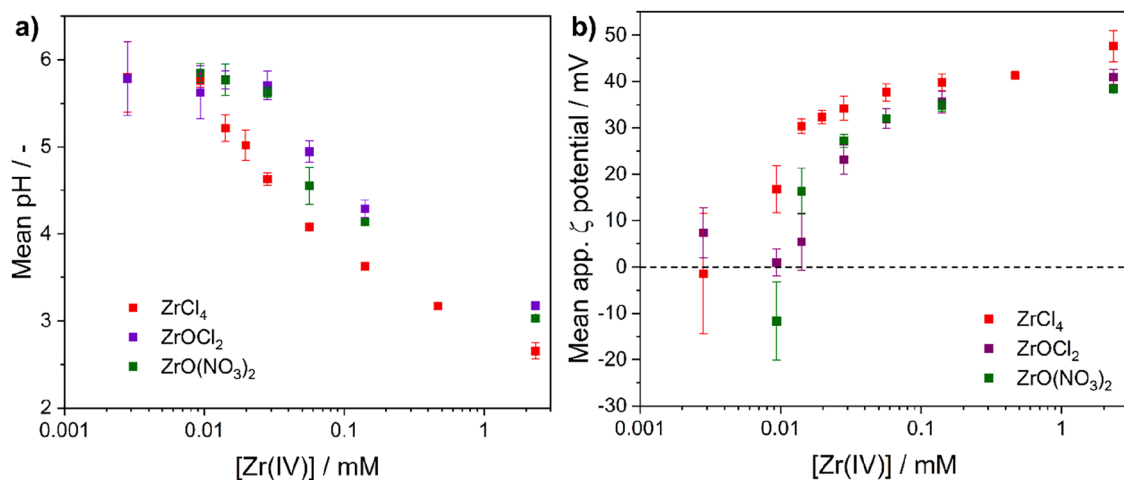


Fig. 5. Colloidal stabilization of Pt/C 52.6 wt.% particles using aqueous solutions of ZrCl₄, ZrOCl₂ and ZrO(NO₃)₂ as stabilizers. a) Mean pH of the suspensions as function of the Zr(IV) concentration. b) Mean apparent ζ -potential of the corresponding suspensions. The dilution factor was 1:100 (Vol:Vol). The x-axes uses logarithmic scale (base 10) for better comparison.

the time-dependent sedimentation that can be monitored via UV-Vis spectroscopy through kinetic extinction measurements. If sedimentation or agglomeration of the particles occur, the extinction decreases or increases, respectively, whereas in the absence of any agglomeration, aggregation or sedimentation the values of the extinction over time

remain constant to the initial value. Therefore, extinction measurements were performed to monitor the short-time stability of the Zr-stabilized suspensions over 60 min and compare them with non-stabilized samples. The data were additionally corroborated by macroscopic observations of the samples left standing over longer time (2880 min). The

results of the kinetic extinction measurements are shown in Fig. 6a-c for each material using $[\text{ZrCl}_4] = 1.41 \times 10^{-3} \text{ M}$, corresponding to a Pt/Zr molar ratio of 0.5 mol/mol (Table S1, ESI).

Only small differences between the reference and stabilized samples are visible after 60 min for Vulcan and Pt/C 33 wt.% (Fig. 6a and b). For the reference samples of these two materials, phase separation becomes notable only after 2882 min (48 h), while the Zr(IV)-stabilized particles remain still homogeneously suspended in water (Fig. 6d and e). Concerning the Pt/C 52.6 wt.% particles, the extinction of the Zr(IV)-stabilized suspension remains constant for 60 min, indicating high short-term colloidal stability (Fig. 6c). For the same time, the reference sample without Zr(IV) shows rapid sedimentation after 60 min with progressively significant phase separation (Fig. 6c). Instead, after two days the ZrCl_4 -stabilized Pt/C 52.6 wt.% particles are still homogeneously dispersed in water, while the reference sample is completely sedimented (Fig. 6f). Therefore, hydrolyzed Zr(IV) species induce a pronounced positive response for both short and long-term colloidal stability of carbon-based materials. For short time of 1 h, the highly functionalized Pt/C 33 wt.% material is already more stable in water in comparison with the Pt/C 52.6 wt.%, and therefore the addition of Zr(IV), despite producing high positive ζ -potentials, did not lead to an obvious macroscopic improvement in the sedimentation behavior. However, the stabilization effect is evident for long-time stability observations, where the Pt/C 33 wt.% sample dispersed in water is almost completely sedimented, whereas the Zr(IV)-stabilized sample remains stable (Fig. 6e). In contrast, the poorly functionalized Pt/C 52.6 wt.% material was intrinsically unstable in water and sedimented within less than one hour. For this material, the addition of Zr(IV) had a marked stabilizing effect, suppressing sedimentation and yielding suspensions that remained stable for at least two days. Thus, the relevance of Zr(IV)-induced stabilization is most evident for poorly functionalized carbon materials, where the native surface chemistry is insufficient to ensure colloidal stability in water. Finally, Dynamic Light Scattering (DLS) measurements were additionally performed to assess the hydrodynamic size of the Pt/C materials in the liquid phase (Table S3). The addition of Zr(IV) resulted in a decrease in both the Z-average and PDI for both Pt/C

samples, consistent with a reduced degree of agglomeration and a more homogeneous dispersion state.

4. Conclusions

This work demonstrates that the colloidal stabilization of carbon-based materials in aqueous media is strongly governed by their surface functionalization and can be effectively tailored through the addition of aqueous solutions of Zr(IV) salts. A systematic comparison of Vulcan and two Pt/C samples with different Pt loadings revealed substantial differences in their degree and nature of surface functionalization, as evidenced by thermogravimetric analysis coupled with mass spectrometry and pH-dependent zeta potential measurements of the corresponding water dispersion.

The addition of Zr(IV) salts significantly altered the colloidal properties of all investigated materials. Because zirconium hydrolysis simultaneously affects both the chemical composition and the pH of the suspensions, the evolution of the mean apparent ζ -potential of the suspensions was evaluated in relation to both parameters. The results show that the excellent colloidal stability cannot be explained solely by pH variations or by the presence of chloride ions, indicating a direct influence of the hydrolyzed Zr(IV) species on the stabilization mechanism.

The extent of the stabilization effect was found to depend as well on the degree of surface functionalization. For the least functionalized Vulcan and Pt/C material, a shift of the point of zero charge upon addition of aqueous solutions of Zr(IV) salts was observed, whereas the more functionalized Pt/C 33 wt.% sample exhibited very positive ζ -potential throughout the investigated acidic pH range, preventing the experimental determination of the point of zero charge. This behavior suggests a more extensive interaction of hydrolyzed Zr(IV) species with carbon surfaces possessing a higher density of oxygen-containing functional groups. Although the strongest effect of Zr-stabilization was observed for the more functionalized material, the short time stability of suspensions upon addition of aqueous solution of Zr(IV) species was more evident for poorly functionalized solids. The highly functionalized Pt/C suspension was already stable in water, and therefore the addition

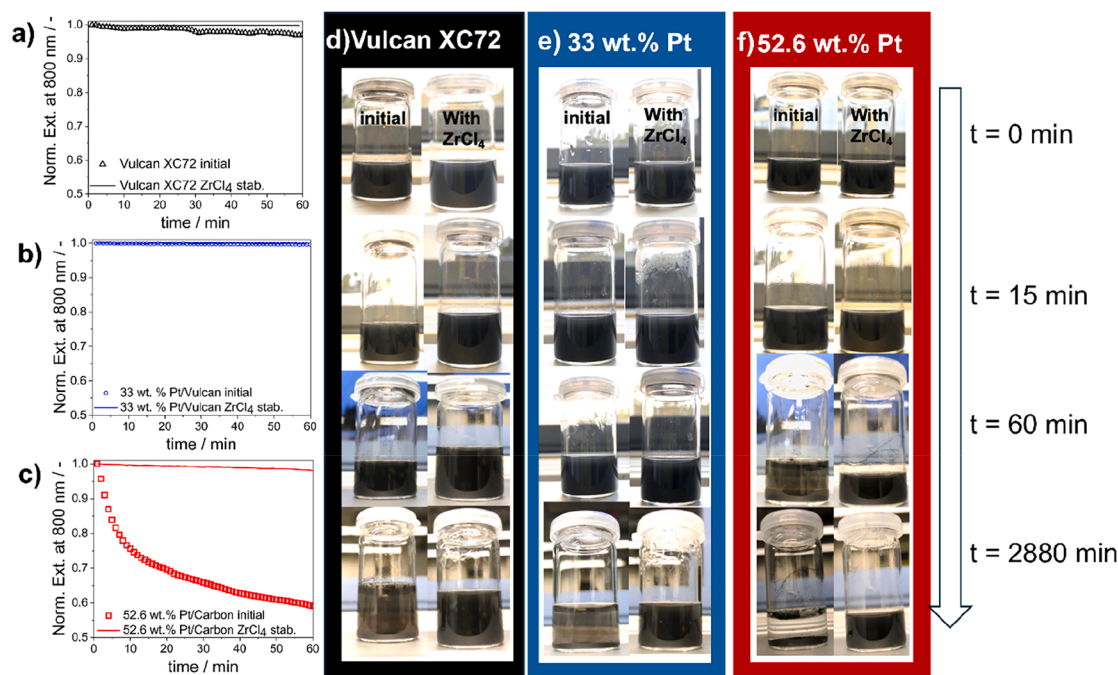


Fig. 6. Sedimentation behavior of the dispersions and suspensions of carbon-based materials as function of time with and without ZrCl_4 stabilization, respectively. a), b) and c) Kinetic extinction measurements at a wavelength of 800 nm over 60 min of: a) Vulcan; b) Pt/C 33 wt.%; c) Pt/C 52.6 wt.%, dispersed in water or stabilized using a water solution of ZrCl_4 with a concentration of 0.1 mM. The extinction values are normalized with the measured maximum extinction at $t = 0 \text{ min}$. d), e) and f) Optical micrograph of the dispersions and suspensions left still for 2880 min (48 h). The dilution factor was 1:5 (Vol:Vol).

of Zr(IV) produced only a limited macroscopic improvement despite the pronounced increase in positive zeta potential. In contrast, the poorly functionalized Pt/C material sedimented rapidly in the absence of Zr (IV), whereas the addition of hydrolyzed zirconium species effectively suppressed sedimentation and produced stable suspensions for prolonged periods.

Overall, the results establish a direct relationship between carbon surface functionalization, colloidal behavior, and stability in the presence of aqueous solutions of Zr(IV) salts. Beyond the specific case of zirconium, the findings provide new insight into how multivalent metal ions interact with carbon surfaces and influence suspension behavior. This understanding may support the rational formulation of stable aqueous dispersions of carbon-based materials, including multifunctional nanocomposite systems, coatings, and other advanced material processing routes. In particular, the application of the Zr(IV) stabilization method to other kinds of carbon, such as nano-onions [51] and carbon nanotubes [52,53] might offer additional tools for the effective exploitation of this important class of materials.

CRedit authorship contribution statement

Devin Brigl: Writing – review & editing, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation. **Moritz Wolf:** Writing – review & editing, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation. **Monica Distaso:** Writing – review & editing, Writing – original draft, Visualization, Supervision, Resources, Methodology, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors acknowledge funding from the Deutsche Forschungsgemeinschaft (DFG) through the Cluster of Excellence Engineering of Advanced Materials. The authors acknowledge the financial support by the Bavarian Ministry of Economic Affairs, Regional Development and Energy through the project “Oxo – LOHC - Autotherme und ultratiefe Wasserstoff-Freisetzung aus LOHC-Systemen”.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.cartre.2026.100700](https://doi.org/10.1016/j.cartre.2026.100700).

Data availability

Data will be made available on request.

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