Highly Conductive Colloidal Carbon Based Suspension for Flow-Assisted Electrochemical Systems

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Abstract

Colloidal carbon based suspension electrodes are gaining increased attention for large-scale energy storage applications, and particularly for flow-assisted electrochemical energy storage systems. In the latter, they serve as flowable electrodes in an electrolyte solution of flow batteries, or flow capacitors. They can also be used for applications other than energy storage such as capacitive deionization of water. However, developments of such suspensions remain challenging. The suspensions should combine low viscosity and high electronic conductivity for optimized performances. In this work, we report a flowable aqueous carbon dispersion which exhibits a viscosity of only 2 Pa.s at a shear rate of 5 sec\textsuperscript{-1} for a concentration of particles of 7 wt\%. At this concentration, the suspension forms a conductive network and displays an electronic conductivity of 65 mS/cm, nearly two orders of magnitude greater than previously related materials. The investigated suspensions are stabilized by sodium alginate and arabic gum in the presence of ammonium sulfate. Experiments under flow demonstrate that the suspensions remain highly conductive upon shearing. Their use in flowable systems for the storage and discharge of electrical charges is demonstrated.

1 - Introduction

Extensive research is undertaken for the management of energy with new technologies that exploit renewable sources [1,2]. In the last decade, carbon black dispersions have been used as active material in different flow-assisted electrochemical energy storage systems (FAESs) [3-5]. In these systems, the carbon black dispersions serve as flowable electrodes in semi-solid flow batteries (SSFB) dispersed in an electrolyte solution [6] or as active materials in the electrochemical flow capacitor (EFC) [7] or in the flow capacitive deionization of water (CDI) [8].
The major challenges towards efficient applications include the optimization of the rheological and electrical performances of flowable active material, namely, new classes of fluids that exhibit low viscosity and high electronic conductivity. Several studies proposed carbon black dispersions as good candidates for flowable electrodes. For instance, Li and coworkers [9] have reported a conductivity value of 5 mS/cm for a dispersion of commercial Ketjenblack 0.2 wt% used in semi-solid flow cell (SSFC). Subsequently, higher loadings of carbon filler were studied to achieve higher conductivities. For example, Paroda et al. [10], with a conductivity of 14 mS/cm, Dannison et al. [11] and Hatzell et al. [12] with conductivities of 0.01 mS/cm and 0.3 mS/cm, and more recently Parant et al. [13] with a conductivity of a few mS/cm. In this latter work, the authors found an optimal formulation with commercial acetylene carbon black at a concentration of 8.0 wt% in water. They have also tested other carbon black materials but with less success because these other materials become too viscous with increasing concentration.

Indeed, in addition to electronic conductivity, viscosity is another critical property of carbon based flowable electrodes. A low viscosity minimizes the energy needed for pumping and flowing the active fluids. Paroda et al. [10] have reported a viscosity equal to 8 Pa.s for a carbon concentration of 15 wt%, while Presser et al. [7] reported a viscosity of only 2 Pa.s for a concentration of 10 wt% of highly monodispersed carbon beads. Hatzell et al. [12] have reported a viscosity value of 10 Pa.s for a concentration of 20 wt%. Campos et al. [14] reported flowable carbon dispersions with a viscosity of 12 Pa.s for a concentration of 23 wt% of carbon material. Parant et al. [13] reported a viscosity above 30 Pa.s at a shear rate of 5 s⁻¹ for optimal acetylene black materials. These results show that achieving a compromise of high conduction and flowability remains challenging. [15-19].

The above state of the art is summarized in Table 1. Direct comparisons between these results and the ones presented in this work are not straightforward because of the different methodologies and materials presented in the literature. Nevertheless, the above data provide guidance for ranges of conductivity and viscosity to be improved to progress further towards actual applications of flowable carbon dispersions.
Table 1 – Examples of conductivity and viscosity from literature on colloidal carbon based suspensions.

| Concentration (wt%) | Conductivity $\sigma$ (mS/cm) | Viscosity $\eta$ (Pa.s) @ 5 sec$^{-1}$ |
|---------------------|--------------------------------|--------------------------------------|
| Presser et al. (7)  | 10                            | not reported                         |
| Li et al. (9)       | 0.2                           | 5                                    | 1.5 |
| Paroda et al. (10)  | 15                            | 14                                   | 8   |
| Dannison et al. (11) | 16                           | 0.01                                 | not reported |
| Hatzell et al. (12) | 20                            | 0.3                                  | 10  |
| Parant et al. (13)  | 8                             | 4                                    | 30  |
| Campos et al. (14)  | 23                            | not reported                         | 11  |

We study in the present work dispersions reminiscent of the systems investigated by Parant et al. [13]. We use indeed arabic gum as surfactant, and sodium alginate as polymeric stabilizer. The choice of arabic gum is due to its high dispersion ability, while sodium alginate prevents sedimentation of carbon particles over time as it increases the viscosity of the solution. Beyond these similarities, we present here a different formulation process, which includes the grinding of the carbon powder and the addition of a strong excess of ammonium sulfate and the use of Ketjenblack carbon. These modifications allow the viscosity to be kept at a low level and the electronic conductivity to be substantially increased up to 65 mS/cm, almost two orders of magnitude greater when compared to [13] for a concentration of carbon black of 7.0 wt%. The viscosity for this dispersion is of only 2 Pa.s, a value well below many of the above mentioned dispersions. We study the properties of these systems under flow, and show their potential application to store, and release charges under flow.

2 – Materials and methods

2.1 – Sample preparations

Carbon black dispersions are prepared by mixing the carbon particles (Ketjenblack EC 600JD AkzoNobel) within an aqueous solution. The latter contains 1.5 wt% of arabic gum (Molekula, CAS Number 9000-01-5), 0.5 wt% sodium alginate (Aldrich, CAS Number 9005-38-3), and 2 M ammonium sulfate (Aldrich, CAS Number 7783-20-2). Arabic gum acts as a highly effective
surfactant for the dispersion of carbon particles whereas sodium alginate serves as stabilizer against sedimentation. The used stabilizers ensure a constant conductivity of the dispersion over time. The solution was heated for 1 h at 80 °C under magnetic stirring until complete dissolution of polymers.

Subsequently, the grinding of the carbon powder was processed with the aid of a mortar in order to obtain a fine control of the size of the particles. This step is followed by a heat treatment of the powders in the oven at 180 °C for 2 h. This procedure facilitates the wettability of the carbon particles and consequently their dispersibility. After cooling, carbon black particles were added to the aqueous solution with the desired proportions, and the blend is kept under stirring for several minutes until the carbon black is totally wetted by the aqueous solution.

Finally, to homogenize the dispersion, mechanical shear stress was applied with a high shear mixer (Silverson L4RT) for 30 min at a given rotation speed of 5000 rpm, as shown in Figure 1a, corresponding to an applied shear rate of 3500 sec$^{-1}$. The obtained colloidal dispersion is shown in Figure 1b.

![Figure 1](image)

Figure 1 – (a) Scheme of the formulation protocol. (b) Colloidal carbon based flowable electrodes at 7.0 wt%.

### 2.2 – Rheology characterizations

The viscosity and the shear stress were measured with an AR1000 controlled stress rheometer from TA instrument. The geometry used is a PMMA disc-plate of 60 mm in diameter, with a gap of 800 µm relative to the bottom plate as shown in Figure S1a in supplementary...
information. Several tests were conducted on the choice of the gap to demonstrate that the results are independent on the width gaps larger than 500 µm.

A ramp of shear rate is applied from 500 sec$^{-1}$ to 0.1 sec$^{-1}$, with 10 points per decade. Each shear rate is maintained during 30 seconds and the viscosity is measured by averaging the measurements over the last 5 seconds. The temperature is set with a Peltier system at 20° C.

### 2.3 – Electronic conductivity measurement

In order to determine the electrical percolation threshold, DC chronoamperometry measurements have been performed at different concentrations of carbon in the dispersion. The conductivity involves ionic and electronic contributions. Ionic conductivity is not negligible due to the presence of charged species from the dissolved polymers (sodium alginate and arabic gum) and ammonium sulfate. But the electronic conductivity can be determined at “zero frequency” [13]. To this end, the current is measured after a certain time in order to eliminate the contribution of current involved in the polarization of the electrodes by the free ions in solution.

The measurements are carried out with a two-plate capacitor cell connected to a potentiostat/galvanostat (Metrohm Autolab/PGSTAT101). The platinum electrodes of this cell are symmetrical with a square surface $A= 3 \text{ mm} \times 3 \text{ mm}$ and separated by a distance $d=3 \text{ mm}$. The cell probe is immersed in the carbon dispersion over a height of 1.5 cm. A DC voltage of ± 1 V is applied to the electrodes and the current is measured for a long period of time (2000 sec) until the polarization current decreases to zero. The stabilized current $I_{\text{plateau}}$ allows us to measure the electrical resistance between the two electrodes, and the electronic conductivity knowing the cell geometry:

$$\sigma_e = \frac{I_{\text{plateau}}}{|E|} \cdot \frac{d}{A} \quad (1)$$

where $I_{\text{plateau}}$ is the stabilized current measured at 2000 sec, $|E|$ is the applied voltage, $d$ is the distance between the electrodes and $A$ is the surface area of the electrodes.
2.4 – **AC electrical measurements under shear**

The electrical impedance measurements under shear were performed by using a Couette cell (Caplim Rheophysique West 3400) connected to the impedancemeter as shown in Figure 2a. This experimental set-up enables the analysis of the dynamic properties of the sample in a wide range of shear rates up to 1000 sec\(^{-1}\). This apparatus consists of a specific cylindrical sample-holder in Polyether ether ketone (PEEK) using blocking circular gold electrodes with surface areas of 770 mm\(^2\), resistance of 0.3 Ω and thickness of 0.6 mm. In order to obtain the apparent shear rate values from the Couette cell revolutions, a conversion protocol was carried out. Through the speed of revolution \(\omega\), the apparent shear rate \(\dot{\gamma}\) is deduced using the following equation:

\[
F_\dot{\gamma} = \frac{R_2^2 + R_1^2}{R_2^2 - R_1^2} \quad (2)
\]

where the apparent shear rate \(\dot{\gamma}\) is:

\[
\dot{\gamma} = F_\dot{\gamma}\omega \quad (3)
\]
Figure 2 – (a) Experimental setup for the AC electrical measurements under shear. (b) Schematic representation of the sample-holder geometry in AC electrical measurements under shear ($R_1 = 0.01691 \text{ m}$, $R_2 = 0.01751 \text{ m}$ and $F_\gamma = 28.69$).

3 –Results and Discussion

3.1 – Microstructure morphologies

Carbon black dispersions were deposited between glass slides for optical imaging by using an optical microscope (Leica DM 2500P) at room temperature. Figure S2 shows optical micrographs of Ketjenblack dispersions at different concentrations. It is possible to observe the agglomeration of the carbon black particles in large clusters with an average diameter of 5 μm. The size of the clusters grow with the concentration of particles. But it is difficult to confirm any percolation behavior in these conditions of confinement. Electrical measurements are preferentially used for this purpose.

3.2 – Rheological properties

The rheological behaviors of the samples are presented in Figure 3, where the shear stress and viscosity are plotted as a function of the shear rate from 0.1 to 500 sec$^{-1}$. We recall that the gap between the two plates was chosen so that the measurements are independent of its value. In this situation, wall slip can be considered as negligible [20]. The continuous phase exhibits a Newtonian viscosity of 0.05 Pa.s. It is observed that this viscosity is slightly lower than
that reported by Parant et al. [13]. The difference can be attributed to the presence of the electrolyte in strong excess which alters the rheological behavior of the continuous phase.

The addition of carbon particles induces the appearance of a yield stress, and the final dispersions show a shear-thinning behavior with viscosity values lower than 100 Pa.s at low shear rate, for carbon black concentrations up to 7.0 wt%. A Herschel-Bulkley model for yield stress fluids can be applied to fit the rheology curves using the following equation:

$$\sigma(z) = \sigma_0 + k\gamma(z)^n$$

where, $\sigma(z)$ is shear stress, $\sigma_0$ the yield stress, $\dot{\gamma}(z)$ the shear rate, $k$ the consistency index and $n$ the flow index. Even for a small addition of carbon black particles, the final suspensions display a yield stress and a shear thinning behavior. These results suggest the formation of a network by the dispersed particles. The fitting parameters obtained by the Herschel-Bulkley model are given in Table 2 for each carbon dispersion. The viscosity measured at 5 sec$^{-1}$ is also shown in the table.

![Figure 3](image)

Figure 3 - Rheology measurements of the Ketjenblack aqueous dispersion composed of 1.5 wt% arabic gum, 0.5 wt% sodium alginate and 2 M (NH$_4$)$_2$SO$_4$. Several percentages of carbon are presented. (a) Viscosity of dispersions in Pa.s versus shear rate. (b) Shear stress of dispersions versus shear rate. Shear stress curves have been fitted using the Herschel-Bulkley law (red lines).
Table 2 – Viscosity values in Pa.s measured at 5 sec\(^{-1}\) and Herschel-Bulkley parameters deduced from the fit of the rheological data obtained in plate plate geometry.

|                     | Continuous Phase | Ketjenblack 3.0 wt% | Ketjenblack 5.0 wt% | Ketjenblack 7.0 wt% | Ketjenblack 9.0 wt% |
|---------------------|------------------|---------------------|---------------------|---------------------|---------------------|
| \(\eta\) @ 5 sec\(^{-1}\) | 0.005            | 0.02                | 0.3                 | 2                   | 45                  |
| \(\sigma_0\)        | 0                | 0.059               | 0.74                | 7.18                | 194.50              |
| \(k\)               | 0.005            | 0.14                | 0.17                | 1.25                | 8.56                |
| \(n\)               | 1.000            | 0.86                | 0.71                | 0.68                | 0.67                |

3.3 – Electronic conductivity

Ketjenblack carbon dispersions are prepared at several filler weight percentages: from 2 wt% to 9 wt%. Figure 4 shows the evolution of the electronic conductivity of the carbon dispersions as a function of the filler content. At low carbon content, the dispersions are considered as not electronically conductive since their conductivity is about 0.01 mS/cm, or below. We note that it is difficult to measure electronic conductivities lower than 0.01 mS/cm with our method. This is due to a residual ionic conductivity that is impossible to avoid, even after a long stabilization of the current. This residual conductivity may involve faradic processes at the surface of the electrodes.

Nevertheless, there is a substantial increase in electronic conductivity with increasing the concentration of particles. As shown in Figure 4, the conductivity curve displays a s-shape with a percolation threshold around 5.5 wt%. A conductive network is formed at this threshold which allows the suspension to be considered as electronically conductive. Electrical percolation is generally associated to rheological percolation with a large increase in viscosity [21-25]. Nevertheless, the percolation behavior and the steepness of the curves depend on finite size effects [26]. The finite size of the sample is relative to other characteristic lengths including the size of the particles, and the minimal distance the particle clusters have to be within, so that they can be considered as electrically or elastically connected. In addition, these dimensions can display polydispersity which also affects the percolation behavior [27]. Here, we see that the conductivity increases more sharply with concentration than the viscosity.
The increase of conductivity is also sharper than the increase of yield stress (see Figure S1b supplementary information). Those differences result from distinct physical mechanisms. Electrical connectivity is related to the ability of electrons to be transported from one cluster to another cluster, whereas rheological connectivity is related to hydrodynamic interactions and to the ability to transfer elastic stress. Even if details of the particle interactions and of configurations of adsorbed polymers at their interface are not known, it can be expected that electrical transport and rheological behavior involve mechanisms with distinct length scales. Therefore, the shape of the percolation curves can appear as different. But globally they reflect the formation of networks that can both sustain elastic stress and transport electrical charges with increasing the concentration of carbon black particles.

However, the present dispersions at 7.0 wt% remain fluid enough to easily flow in our test set-up without showing any phenomena of occlusion or clogging. For this reason, it was chosen as a specific concentration of carbon dispersions able to act as a percolated carbon flowable electrode. More importantly, and as shown later, the suspensions remain electrically conductive under flow, meaning that the conductive network is not disrupted by the shear.

Figure 4 – (a) Electronic conductivity of dispersion of Ketjenblack in arabic gum 1.5 t% and sodium alginate 0.5 wt% in 2 M (NH₄)₂SO₄ as a function of the filler content of carbon (wt%). (Error bars correspond to the standard deviation of 3 measurements). (b) DC chronoamperometry measurements of conductivity of the carbon dispersions. The current values related to the electronic conductivity are the stabilized values at the plateau. A square voltage of ±1 V is applied to the electrode for 2000 seconds in order to avoid the polarization currents due to the presence of free ions in the system.

3.4 – Electronic conductivity under shear
AC electrical measurements under shear have been performed using the set-up described in part 2-4. Figure 5 shows the effect of the shear rate on the electrical conductivity of the sample under study.

![Figure 5](image)

Figure 5 – Electro-rheological behavior of a Ketjenblack 7.0 wt% dispersion in arabic gum 1.5 wt% - sodium alginate 0.5 wt% in (NH$_4$)$_2$SO$_4$ 2 M. The values of the normalized electronic conductivity are shown at the frequency of 100 Hz (black line), 1 kHz (red line) and 10 kHz (blue line). The data are normalized by the static reference value at 0 shear rate.

Unlike other studies in which the electrical properties under shear flow often reveal a breaking-and-reforming mechanism of aggregates [19,28-29] our system does not show any significant variation of the electrical properties under shear. These results suggest that the flow does not strongly alter the structure of the electrical network.

3.5 – Electrochemical characterization of flowable electrodes

For the electrochemical characterizations, the flowable carbon dispersions were tested in a two-electrodes symmetric cell configuration. The carbon flowable electrodes have the same volume. They are separated from each other by using an anion exchange membrane (SnakeSkin® Dialysis Tubing 1000 MWCO).

Figure 6a shows the cyclic voltammetry (CV) curves of the carbon dispersions at different scan rates. A large capacitive current is observed due to the charging of the particles.
Nevertheless, the electrical behavior of the sample does not show a typical rectangular shape characteristic of the charging of a capacitor formed by the adsorbed ionic double layers. The distortion of the CV curves suggests that there is a large resistive contribution in the system. The resistances are due to different factors, such as the intimate contact of the dispersions with the current collectors for the injection and collection of charges, and the contact resistances between the particles [12]. Figure 6b shows the specific gravimetric capacitance $C_{sp}$ of the sample calculated using the equation:

$$C_{sp} = \frac{2i}{m \left( \frac{dV}{dt} \right)}$$

(5)

where, $i$ is the value of measured current in the cyclic voltammetry curves and $\frac{dV}{dt}$ is the scan rate [7]. $C_{sp}$ is found to be rate-dependent, with the highest values obtained at low scan rate.
In particular, a specific capacitance of 20 F/g is calculated at 1 mV/s as shown in Figure 6c. The influence of scan rate presumably originates from the specie diffusion kinetics related to the porosity of the material with a broad range of characteristic sizes. The smallest pores are less accessible than bigger ones. At fast scan rates, it is likely that the small pores do not contribute to the storage of charges, resulting in a lower effective capacitance.

It is observed that the materials maintain their charges over a long time after charging. As shown in Figure 6d, the voltage across a cell containing 5 g of materials cell in an open-circuit configuration [30-34] decreases by less than 10% after 10000 sec for a suspension that has been charged at 1V during 20 min. The self-discharge is of about 20% for a suspension charged...
during 5 min at the same voltage. The self-discharge arises from losses in the circuit in which an oscilloscope is implemented, from redistribution of ions at the surface of the particles and from possible uncontrolled redox reactions with impurities.

3.6 – Flow assisted charge and discharge

In order to verify the ability of these flowable electrodes to transport and store charges, flow assisted charge and discharge processes have been performed. During the charging process, the introduction of the new uncharged dispersion into the electrochemical cell, leads to a leak of current and to a decrease of the voltage across the cell below the values observed at rest. Conversely, during the discharge process, the reintroduction of charged carbon dispersions in the active area of the electrochemical cell leads to an increase of the voltage across the cell above the values observed at rest. This behavior is investigated by using the home-made experimental setup shown in Figure 7. The two-compartment electrochemical cell was connected by means of silicone tubes to 4 syringes. The latter act as the reservoirs of the charged and uncharged dispersions. This electrochemical cell is connected to a RC circuit which is directly connected to a wave-form voltage generator (Trueform 33500B, Keysight). The charging process is performed at 1 V for 200 seconds by using a load resistance of 178 Ω. In this phase, the uncharged carbon dispersion is pumped by syringe-pumps through the electrochemical cell, where electric charges are supplied to the dispersions.
Figure 7 – (a) Experimental set-up for flow assisted charge and discharge. (b) Geometry and materials used in the electrochemical two-compartments cell.

The charged carbon dispersions are collected in the other two syringes. During the discharge process, the circuit is short-circuited by means of a switch. The voltage across the electrochemical cell, was recorded by an oscilloscope (Tektronix DPO 2022B). Figure 8a show the charge and discharge processes of the formulated flowable carbon electrodes. These processes are characterized by two specific times, $t_1$ and $t_2$. During the charging process, the voltage across the cell reaches its maximum value at $t_1 = 200 \text{ sec}$. This initial process is followed by a second one of discharge, of the same duration, in which the voltage across the cell reach its minimum at $t_2 = 400 \text{ sec}$.

The black curve represents the profile of charge and discharge of the dispersion in static conditions. As shown in Figure 8a, at $t_1 = 200 \text{ sec}$ the voltage across the cell reaches the value

| Electrodes    | Carbon paper Toray 120 |
|---------------|------------------------|
| Volume cell   | 0.48 cm$^3$            |
| Active area for each channel | $l = 10 \text{ mm}$  |
|               | $w = 8 \text{ mm}$    |
|               | $h = 3 \text{ mm}$    |
| Membrane separator | SnakeSkin® Dialysis |
| Material      | PMMA                   |
of 0.86 V, and approaches zero after discharge at \( t_2 = 400 \text{ sec} \). At a flow rate of 1 mL/min (red curve), the effect of flow keeps the voltage across the cell constant at a lower value than a static one. At \( t_1 = 200 \text{ sec} \) the process of discharge of the particles begins. During this process in dynamic conditions, the voltage reaches a value greater than that under static conditions.

![Figure 8](image)

Figure 8 – (a) Charge and discharge processes of flowable carbon electrodes. (b) Stored and converted charge profiles during the charge-discharge processes at different flow rates. (c) Scheme of the electrochemical circuit during the charging process in DC at 1 V. (d) Scheme of the electrochemical circuit during the discharging process in short circuit conditions.

Similar trends are found for the other flow rates up to 9 mL/min. Table 3 shows the final charge and discharge values of the flowable electrodes. These results represent a proof of concept of the use of flowable electrodes to store and transport charges.
Table 3 - Voltage across the cell under charge and discharge at time \( t_1 \) and \( t_2 \). The materials are charged from 0 sec to \( t_1 \) and discharged from \( t_1 \) to \( t_2 \).

|          | Static | 1 mL/min | 3 mL/min | 5 mL/min | 7 mL/min | 9 mL/min |
|----------|--------|----------|----------|----------|----------|----------|
| \( t_1 = 200 \) sec | 0.86 V | 0.81 V   | 0.78 V   | 0.74 V   | 0.72 V   | 0.67 V   |
| \( t_2 = 400 \) sec | 0 V  | 0.005 V  | 0.014 V  | 0.018 V  | 0.035 V  | 0.053 V  |

From such charge-discharge measurements it is possible to calculate the stored charges within the system and to analyze the effect of the flow using equation 6.

\[
\int \frac{V_{in} - V_{out}}{R} \, dt = \int \frac{V_R}{R} \, dt = \int idt = Q
\] (6)

Where \( V_{in} \) stands for the potential applied to the circuit, and \( V_{out} \) for the potential across the electrochemical cell at time \( t \). The stored charge evolution during the charge and discharge processes of the carbon flowable electrodes under flow is shown in Figure 8b. At time \( t_1 = 200 \) sec the amount of charge is equal to 0.19 C in static conditions. The effect of flow results in an increase of stored charges during the charging process, but also of restored charges during discharge. Charge values during the two processes are given in Table 4. From these considerations, it is possible to carry out a deeper analysis of the effect of flow on the charge and discharge processes of the carbon flowable electrodes.

Table 4 – Stored and restored charges in C during the processes of charge and discharge at time \( t_1 \) and \( t_2 \). Charges stored up to \( t_1 \), restored charges from \( t_1 \) to \( t_2 \).

|          | Static | 1 mL/min | 3 mL/min | 5 mL/min | 7 mL/min | 9 mL/min |
|----------|--------|----------|----------|----------|----------|----------|
| \( t_1 = 200 \) sec | 0.19 C | 0.23 C   | 0.26 C   | 0.28 C   | 0.31 C   | 0.37 C   |
| \( t_2 = 400 \) sec | 0.13 C | 0.14 C   | 0.15 C   | 0.16 C   | 0.17 C   | 0.20 C   |

Figure 9a shows the evolution of the normalized maximum charge stored at time \( t_1 \) against the flow rate. Normalization by the flow rate allows the efficiency of the charging process to be evaluated. Indeed, for a similar efficiency, one would expect an amount of stored charges proportional to the flow rate, considering that the amount of charges is directly proportional to
the amount of materials transported through the cell. Here, it is observed that the efficiency is greater at low flow rate, meaning that the amount of charges per carbon particle decreases with the flow rate. Nevertheless, in spite of a lower efficiency, the net amount of stored charges still increases with the flow rate. The system still transports a greater amount of charges at high flow rate, even if fewer charges are transported at the level of each carbon particle. The value of maximum charge acquired by the system as function of the flow rate is shown in Figure 9b.

![Graph showing charge vs. flow rate](image)

**Figure 9 –** Effect of the flow on the stored charge in dynamic conditions. (a) Normalized maximum charge stored at time \( t_1 = 200 \) sec against the flow rate. More clusters are involved in the transport of charges at high flow rate, but the charge per clusters is lower than that at low flow rate. As a net result, the total amount of charges is still greater at high flow rate. (b) Maximum charge acquired by the system as function of the flow rate.

Last, it is also interesting to estimate the power supplied during discharge through the load resistance. This power is given in Figure S3 for a load resistance of 178 \( \Omega \), and at time \( t_2 = 400 \) sec. The power remains rather low but increases strongly with the flow rate. It reaches a value of 0.02 mW for a flow rate of 9 mL/min.

4 – Conclusion

The overall objective of this work focuses on the study and implementation of a highly conductive colloidal carbon based suspension as flowable electrode for flow-assisted electrochemical systems (FAESs). We have used an aqueous dispersion of carbon materials in
the presence of arabic gum as surfactant and sodium alginate as stabilizer. We have shown that the addition of ammonium sulfate at high concentration allows a substantial improvement of properties compared to previous studies. In order to improve the rheological and electrical performances of these carbon dispersions, a different formulation protocol was adopted. The materials presented in this work display a high electronic conductivity of 65 mS/cm, two orders of magnitude higher than related flowable carbon dispersions proposed in the literature. The formulated dispersion shows a high viscosity, but still lower than most values reported in the literature. The specific gravimetric capacitance of 20 F/g is not high, but the materials have been shown to be efficient to store and restore charges in flow conditions. Overall, the progresses made in terms of the conductivity and viscosity allow for a faster charging of the electrodes and easier circulation with less energy lost in pumping the fluids. Future work should be focused on improving the capacitance, using for example more porous carbon black, to make the present formulations still more efficient for future energy management technologies.
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Highly Conductive Colloidal Carbon Based Suspension for Flow-Assisted Electrochemical Systems

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Supplementary Information

1- Rheology measurements

To measure the viscosity and the shear stress as a function of the shear rate, an AR1000 controlled stress rheometer from TA instrument was used. The geometry used is a PMMA disc-plate of 60 mm in diameter and with a gap of 800 µm relative to the bottom plate as shown in Figure S1a. The formulated carbon dispersions exhibit a flowable behavior with low values of yield stress up to the concentration of 7.0 wt% of active material. Above this concentration the dispersion turns into unflowable dough in which the yield stress rises sharply as shown in figure S1b.

![Rheometer](image1)

(a) Rheometer (TA instrument) set-up for viscosity and shear stress measurements. (b) Yield stress values obtained by using the Herschel-Bulkley law of the Ketjenblack aqueous dispersion composed of 1.5 wt% arabic gum, 0.5 wt% sodium alginate and 2 M (NH4)$_2$SO$_4$. (Inset: Photos showing three different concentrations of Ketjenblack dispersions: dilute dispersion, flowable gel and unflowable dough).
2 - Microstructure Morphologies

Ketjenblack dispersions samples were deposited between glass slides for optical imaging by using a Leica DM 2500P microscope. Below, the optical micrographs of some dispersions at different concentrations of carbon black.

![Optical micrographs of Ketjenblack dispersions in arabic gum 1.5 wt% - sodium alginate 0.5 wt% in (NH₄)₂SO₄ 2 M. (A) 2.0 wt%, (B) 3.0 wt%, (C) 4.0 wt%, (D) 5.0 wt% (E) 6.0 wt%, (F) 7.0 wt%, (G) 8.0 wt%, (H) 9.0 wt% (Scale bar 50 μm).](image)

3 – Power during discharge

The power supplied in a load resistance $R$ of 178 Ω is calculated as $RI^2$, where $I$ is the discharge current. The obtained values are shown in figure S3.

![Power supplied through a load resistance of 178 Ω at time $t$=400 sec as function of flow rate.](image)