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## **Carbon Black/Electrolyte Interface study by Electromagnetic and Electrochemical Techniques in $\gamma\text{Al}_2\text{O}_3$ /Poly(vinylidene fluoride)/Carbon Black Composite Materials: Application for Lithium-Ion Batteries**

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## 1 **Abstract**

2 This work aims at better understanding the interactions existing between the liquid electrolyte  
3 and the solid composite electrode in a Li-ion battery. We substituted the common active  
4 material (e.g.  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  or  $\text{LiFePO}_4$ ) by an insulating (inactive)  $\gamma\text{-Al}_2\text{O}_3$  compound in  
5 order to detect and evidence the interaction between the carbon black electronic additive and  
6 the liquid electrolyte. Our study presents the characterization of charge (electrons and ions)  
7 transport at different scales by combining a high-frequency analysis performed by broadband  
8 dielectric spectroscopy (BDS, up to  $10^{10}$  Hz), along with a low-frequency analysis performed  
9 by electrochemical impedance spectroscopy (EIS, down to  $10^{-3}$  Hz). Two carbon black  
10 materials with two different specific surface areas ( $80 \text{ m}^2.\text{g}^{-1}$  and  $65 \text{ m}^2.\text{g}^{-1}$ , respectively) were  
11 studied. The electronic percolation threshold and the kinetics of impregnation of the  
12 hierarchical composite electrode by the liquid electrolyte have been determined with respect  
13 to the carbon black content. The significant influence of the adsorption of ions at the carbon  
14 black surface on the electrons transport is particularly highlighted and explained.

15

## 16 **1. Introduction**

17 Nowadays, Li-ion batteries are used for electrical energy storage in a wide set of applications  
18 such as electronic portable devices, hybrid vehicles and more recently full-electric vehicles.<sup>1</sup>  
19 Much effort has been devoted, in the last decade, to the development of new compounds,  
20 new architectures and new technologies<sup>2</sup> (e.g. Li-air, Na-ion, Li-S) and new electrolytes<sup>3,4</sup>.  
21 Among the various commercial electrochemical energy storage systems, Li-ion batteries  
22 exhibit the best performance today.<sup>5</sup> However, despite the significant benefits that Li-ion  
23 batteries offer as an energy storage system, the electrode processing technology suffers from  
24 limitations with regard to power and energy densities of the final product.<sup>6</sup> As a result, 50%  
25 of batteries weight and volume consist of non-electroactive parts (collectors, separators,  
26 electrolyte). The limitations mainly originate from altered charge transport in these complex  
27 multi- and hierarchical materials (Fig. 1).<sup>7,8</sup> In addition to the active material (AM), carbon  
28 black (CB) and polymeric binder (PB) are widely used as additives to enhance the electronic  
29 conduction and overall cohesion respectively within the electrode. Electronic and ionic  
30 conductivities are the two major parameters leading to good or poor electrochemical  
31 behaviour.<sup>9,10</sup> Up to now, most of the studies demonstrates that the rate limitations, for  
32 commercially available active materials, are mainly due to the electrode architecture and not  
33 to mass transport in the active materials. However, to date, only a few studies have reported  
34 on the direct measurement of the electrical properties (including both electronic and ionic  
35 charge transport of the electrode), from the macroscopic to the nanometric scales. In fact,  
36 regarding the electronic transport, the *dc* electronic conductivity ( $\sigma_{dc}$ ) is most often the only  
37 parameter to be measured in the dry state (*ex situ*).  $\sigma_{dc}$  is a macroscopic averaged value that  
38 provides poor information on the real electrical transport properties, especially in powdered  
39 materials, such as composite electrodes, consisting of different individual particles and their  
40 clusters. Then, the particles are separated by resistive and capacitive barriers (e.g. cluster or  
41 particle boundaries), that limit the electronic transfer. Furthermore, only a few studies have  
42 tried to measure the *dc* electronic conductivity in the wet state, i.e. *impregnated*  
43 *electrode*.<sup>6,11,12,13,14</sup> One must also consider the role of interfaces (adsorption of ions to the  
44 surface of active material and carbon particles), and the subsequent physical interactions at  
45 these interfaces.<sup>6,9,10</sup> The conductivity of the wet electrode drops as compared to the dry  
46 electrode due to the nanometric size of the carbon black particles that leads to a particularly

47 high specific surface area. Indeed, due to surface effects, the adsorbed  $\text{Li}^+$  cation and  $\text{PF}_6^-$   
48 anion will modify the overall carbon black conductivity. Moreover, EC-DMC dipoles from the  
49 electrolyte and PvdF-HFP dipolar species interact more to one another. In a previous work,  
50 the active material was substituted by an insulating compound ( $\gamma\text{-Al}_2\text{O}_3$ ) and studied by  
51 broadband dielectric spectroscopy (BDS) in order to understand only the interactions between  
52 the carbon black and the electrolyte.<sup>6</sup> Previous experimental data have revealed that the ion  
53 adsorption leads to a decrease of the electronic conductivity of the samples due to the  
54 existence of energy barriers contrary to the dry samples in which the electronic transfer can  
55 be achieved by tunneling.

56 In this report, we now focus on the electrolyte/carbon black interface study in a  
57  $\gamma\text{Al}_2\text{O}_3$ /Poly(vinylidene fluoride)-HFP/Carbon black composite material by using two types of  
58 carbon black powders with different specific surface areas. The electronic conductivity, for  
59 both dry and impregnated (by electrolyte) samples, was measured using broadband dielectric  
60 spectroscopy (BDS). Moreover, these measurements were combined with electrochemical  
61 impedance spectroscopy (EIS) in order to have access to the broadest range of frequencies,  
62 from GHz to mHz. These measurements allowed us i) to fundamentally understand the  
63 influence of the electrolyte ions adsorption on the conduction properties, ii) to determine the  
64 electronic percolation threshold with respect to the carbon black content and finally iii) to  
65 propose a model for kinetics impregnation of the composite solid electrode by the liquid  
66 electrolyte.

## 67 **2. Experimental**

### 68 **2.1. Chemicals and sample preparation**

69 Standard chemicals were used as received. Reactive gas ( $\text{N}_2$  alpha 1), for porosity  
70 measurements, was supplied by Air Liquide. One of either two carbon black powders with  
71 differing specific surface areas of  $80 \text{ m}^2.\text{g}^{-1}$  (denoted CB1) and  $65 \text{ m}^2.\text{g}^{-1}$  (denoted CB2) was  
72 used as a conductive agent additive for each specific sample. CB1 was supplied by Alfa Aesar  
73 and CB2 (Super C65) by IMERYS Graphite & Carbon. Anhydrous  $\gamma$ -alumina was supplied by  
74 Merck and poly(vinylidene fluoride *co*-hexafluoropropylene) (PVdF-HFP) used as polymeric  
75 binder (PB) was supplied by ARKEMA (Kynar flex 2751-00). The composite mixture was  
76 produced in batches of 200 mg with the following compositions: i) 7 wt% of PB, ii) from 6.5 to  
77 20 wt% of CB and (iii)  $\gamma$ -alumina, its content being readjusted to maintain the total mass

78 constant (200 mg). PB was first dissolved in 3 mL of acetone for 4 hours. A CB/ $\gamma$ - $\text{Al}_2\text{O}_3$  mixture  
79 was ground using a mortar and pestle and subsequently added to the solution. The mixture  
80 was then stirred magnetically overnight for 12 hours and subsequently evaporated on a heat-  
81 plate at 40°C. EIS and BDS studies were conducted with following carbon black loading:

82 a) for CB1: 8 wt% (i.e. volume fraction = 5.3 %), 10 wt% (i.e. volume fraction = 6.9 %), 12.5 wt%  
83 (i.e. volume fraction = 7.8 %) and 15 wt% (i.e. volume fraction = 9.2 %);

84 b) for CB2: 6.5 wt% (i.e. volume fraction = 4.5 %), 8 wt% (i.e. volume fraction = 5.3 %), 10 wt%  
85 (i.e. volume fraction = 6.9 %), 12.5 wt% (i.e. volume fraction = 7.8 %) and 15 wt% (i.e. volume  
86 fraction = 9.2 %).

87 The mean total porosity is  $44 \pm 3$  % after densification (see below) and the amount of PVdF-  
88 HFP was kept unchanged at 7 wt% (i.e. volume fraction of  $5.8 \pm 0.3$  %) for all the studied  
89 samples.

90 The concentrations of the various components will then be indicated in volume percent in the  
91 next sections.

## 92 **2.2. Morphological and surface characterizations**

93 The specific surface area of the composite material was determined using the Brunauer-  
94 Emmett-Teller (BET) method based on the measurement of  $\text{N}_2$  gas adsorption/desorption  
95 isotherms, with a Belsorp II analyzer from BEL Japan Inc. The morphology of the composite  
96 electrode was characterized by scanning electron microscopy using a Zeiss FEG-SEM equipped  
97 with an in-lens detector.

## 98 **2.3. Electrochemical impedance spectroscopy setup**

99 Regarding the electrochemical impedance spectroscopy (EIS) measurements, the powdered  
100  $\gamma$ - $\text{Al}_2\text{O}_3$ /CB/PB mixture was trapped in a 13-mm diameter stainless-steel grid that served as a  
101 current collector. It was then calendered under a pressure of about 258 MPa to produce a  
102 pellet (*thickness = 0.78-1.15 mm, diameter = 7 mm and weight  $\approx$  44-65 mg*). The resulting  
103 sample served as a working-electrode, whereas a lithium disk and a lithium rod were used as  
104 counter and reference electrodes, respectively. These three electrodes were assembled in an  
105 EL-cell (from BioLogic) with two layers of porous glass paper separator soaked with the  
106 aforementioned LP30 electrolyte. All cells assembling was carried out in a Jacomex glovebox  
107 (under controlled Ar atmosphere:  $\text{O}_2 < 1$  ppm,  $\text{H}_2\text{O} < 1$  ppm). EIS measurements were  
108 performed using a VMP3 system from BioLogic. The frequency range scanned was  $10^{-3}$  to

109  $5 \times 10^4$  Hz, with a sinusoidal perturbation voltage amplitude of 30 mV, and a cell voltage drift  
110 before experiment less than  $1 \text{ mV} \cdot \text{h}^{-1}$ .

#### 111 **2.4. Broadband dielectric spectroscopy setup**

112 Sample pellets of powdered  $\gamma\text{-Al}_2\text{O}_3/\text{CB}/\text{PB}$  (*thickness = 0.65-0.85 mm, diameter = 7 mm and*  
113 *weight  $\approx 37\text{-}48 \text{ mg}$ ) were produced by applying a pressure of about 258 MPa to carry out BDS*

114 measurements. Complex conductivity and permittivity spectra were recorded over a broad  
115 frequency range (*from  $10^6$  to  $10^{10}$  Hz for all measurements*), using both an Agilent 4294A  
116 impedance and a Keysight E8364B network analysers. The experimental device consisted of a  
117 coaxial cell (*APC7 standard*), for both dry and wet samples measurements, in which the  
118 cylindrical sample was coated in front and back side by a 200-nm gold film (*diameter: 3.04 mm*  
119 *and 7 mm, respectively*) and positioned between the coaxial waveguide and a short circuit (*see*  
120 *K.A. Seid et al. <sup>9</sup> for a complete description*)<sup>15,16</sup>. The relative complex permittivity  $\varepsilon(\omega) =$   
121  $\varepsilon'(\omega) - i\varepsilon''(\omega)$  of the sample was obtained from its admittance  $Y_s$ . A LP30 solution (1 M  $\text{LiPF}_6$   
122 solution in an ethylene carbonate/dimethyl carbonate mixture (EC/DMC 1/1 w/w)) was used  
123 as the electrolyte for soaking the electrodes.

### 124 **3. Results and discussion**

#### 125 **3.1. Architecture of $\gamma\text{-Al}_2\text{O}_3/\text{CB}/\text{PVdF-HFP}$ composite materials**

126 The general morphology of the composite dry materials is shown in Figure 2. For different CB1  
127 loadings, from 5.3 % to 9.2 % in volume fraction, the SEM micrographs revealed micro-sized  
128 clusters corresponding to alumina, homogeneously distributed along the surface of the  
129 electrode. CB1 is made of nanometric spherical particles of about 10 nm which constituted  
130 the smallest dispersible compounds. After processing, these particles are connected by  
131 chemical bonds to form linear agglomerates of 300-500 nm in diameter. Agglomerates of CB  
132 particles are visible, and hereafter denoted as clusters. These clusters are physically bonded  
133 together. The PB is deposited at the surface of the  $\gamma\text{-Al}_2\text{O}_3$  and formed with the CB a  
134 continuous three-dimensional network that connected the different components of the  
135 composite electrode all-together. Similar morphology was observed for CB2-based  
136 composites. BET adsorption/desorption measurements (Figure 3) allowed the determination  
137 of the mesopores diameter, which for both CB-containing dry electrodes, was in the range of  
138 2.4 nm. The specific surface areas of each CB used in the study were of  $80 \text{ m}^2 \cdot \text{g}^{-1}$  and  $65 \text{ m}^2 \cdot \text{g}^{-1}$   
139 for CB1 and CB2, respectively. Note that CB2 is a highly conductive carbon, particularly



140 designed to be integrated in Li-ion battery electrodes, whereas CB1, exhibiting a larger specific  
141 surface area, is used for comparison, to evaluate the influence of the possible interactions at  
142 the electrolyte/CB interface. However, the SEM micrographs revealed the same geometry and  
143 morphology of the resulting composite dry electrode for both CB. SEM and  
144 adsorption/desorption analyses did not provide sufficient information, regarding the  
145 electrode architecture, with respect to its electrical properties at the nano-scale. The  
146 electronic contacts within the composite electrode are likely to be described as tunnel  
147 junctions. Indeed, a tiny variation in the gap thickness may make the difference between a  
148 conductive and non-conductive path. Moreover, at the microscale, the CB can only be seen as  
149 a network of clusters. Hence, it is difficult to obtain a quantitative description of the  
150 morphology and the geometry of the composite electrode, due to the dense, complex, and  
151 hierarchical structure of the different compounds. In the following sections, we focus on the  
152 correlation of the evolution of conductivity measured by electrochemical and electromagnetic  
153 techniques with respect to a change in the carbon black composition.

### 154 **3.2. Electrochemical impedance spectroscopy**

155 The wet electrodes were further characterized at lower frequencies ( $10^{-3}$  to  $5 \times 10^4$  Hz) by  
156 complex electrochemical impedance spectroscopy (EIS).<sup>17,18,19</sup> This technique is  
157 complementary to the broadband dielectric spectroscopy technique (see next section) since  
158 it allows the conductivity characterization at lower frequencies.<sup>20,21</sup> Figure 4 displays the  
159 Nyquist diagram of complex impedance  $Z$  normalized by the surface area of carbon black (*i.e.*  
160 *specific surface with respect to carbon black weight*) that is under study. Note that the EIS  
161 measurements were performed immediately after the electrodes being soaked by the  
162 electrolyte. Nyquist plots exhibit two main relaxation phenomena as shown in the equivalent  
163 circuit (Figure 5). No relaxation related to charge transfer (electrochemical kinetics) is  
164 expected here as neither the inactive alumina nor the carbon black exhibits any  $\text{Li}^+$   
165 intercalation at the operating voltage applied (3.1 V vs.  $\text{Li}^+/\text{Li}$ ).

166 To qualify the contact at the current collector/electrode interface, the areal density of  
167 contacts at the interface,  $\Sigma$  (*contact number by surface unit*) can be introduced. The contact  
168 resistance (*in  $\Omega \cdot m^2$* ) is given as  $R_C = R_{cr} + R_f$ , where  $R_{cr}$  is the constriction resistance and  $R_f$  is  
169 the resistance of the native oxide film present at the extreme surface of the metallic current  
170 collector.  $R_f$  is not expected to vary with the electrode composition.<sup>22,23</sup> The constriction  
171 resistance  $R_{cr}$  expected to vary as:

$$172 \quad R_{cr} \propto \frac{1}{\sigma_{dc} \times \Sigma} \quad (1)$$

173 where  $\sigma_{dc}$  is the global conductivity of the electrode.<sup>24</sup> No semi-circles were observed for all  
 174 CB contents below 5.3%, corresponding to the lack of efficient electronic percolation. The total  
 175 impedance recorded is so large ( $> 1 \text{ k}\Omega \cdot \text{m}^2$ ) that no accurate quantitative information could  
 176 be extracted from these measurements. Beyond 5.3% of CB, the electronic percolation was  
 177 clearly achieved, consistent with the results obtained in broadband dielectric spectroscopy  
 178 measurements (*see § 3.3*). A higher content in CB also leads to a lower corresponding  
 179 impedance. Thus, electronic conduction increased with CB loading, also consistent with the  
 180 BDS analysis (*see § 3.3*).

181 In addition, the electronic percolation for CB1 was reached with a slightly smaller loading of  
 182 carbon black. This could be related to the higher specific surface area of the corresponding  
 183 carbon. Moreover, the relaxations at the lower frequencies exhibit larger resistances for CB1  
 184 (*i.e. 170-180  $\Omega \cdot \text{m}^2$* ) than CB2 (*i.e. 60-70  $\Omega \cdot \text{m}^2$* ) counterpart with the same CB loading 9.2%.  
 185 Two assumptions would be considered to explain this phenomenon at the macroscopic scale  
 186 (*i.e. sample size*), given the frequency band used in EIS. The first one could be assigned to  
 187 larger resistances due to greater interactions (adsorption) between carbon and electrolyte,  
 188 stemming from the higher surface exchange offered by the larger specific surface area of CB1.  
 189 The second one would focus on the formation of a solid electrolyte interphase (SEI) which  
 190 would passivate the carbon surface. This second hypothesis is only retained if the sample has  
 191 remained in contact with the electrolyte for about a day. As the sample is soaked and  
 192 measured right after, the SEI may possibly exist in very small amount. In both cases, this should  
 193 give rise to an increase the contact resistance, and subsequently lowering the global  
 194 conductivity.

195 The two relaxations observed experimentally and shown in Figure 5a were correlated  
 196 with two inflexion points in the corresponding phase-Bode diagram (not shown here),  
 197 reinforcing the assumption that two distinct phenomena are taking place. These two  
 198 relaxations are thus modelled with an electrical equivalent circuit, consisting in two ( $R//Q$ )  
 199 elements in series,  $R$  being a resistor, and  $Q$  a constant phase element (CPE), expressing the  
 200 non-ideality of a capacitor ( $Z_{CPE} = 1/Q(i\omega)^\alpha$ ). Two additional elements have been added: a  
 201 resistance,  $R_{int}$ , containing a part of the aforementioned contact resistance,  $R_c$ , and the bulk  
 202 liquid electrolyte resistance (finite ionic motion in the liquid phase), and an open Warburg

203 element  $W$ , for modelling the semi-infinite ionic diffusion (medium frequency straight line at  
204  $45^\circ$  in Nyquist plot) and ions accumulation (low frequency capacitive behaviour at  $90^\circ$  in  
205 Nyquist plot) in the electrode vicinity (confined electrolyte). The corresponding equivalent  
206 circuit is displayed as inset in Figure 5a. For the CB contents of 6.9%, 7.8% and 9.2%, these  
207 ratios being chosen to ensure the electronic percolation), two contributions  $R//Q$  have been  
208 always distinguished (through the phase inflexion detection <sup>25</sup>) as shown in Figure 5b.  $R_1$   
209 denotes the resistance measured at high frequency, in the range of 5 kHz (1<sup>st</sup> relaxation),  
210 whereas  $R_2$  denotes the resistance measured at lower frequency, in the range of 1 kHz (2<sup>nd</sup>  
211 relaxation).  $R_1$  was lower for samples with more CB content. Conversely  $R_2$  remains more  
212 constant as a function of time. Therefore,  $R_1$  seemed to be more associated with the electronic  
213 conductivity. In particular, concerning the compositions of CB, 6.9% and 7.8%, the  $R_1$   
214 resistance decreases (from  $\sim 100$  to  $50 \Omega.m^2$ ) with time during the three first days followed  
215 by a daily increase ( $\sim 18 \Omega.m^2.day^{-1}$ ). Actually, the  $R_1$  first decrease may be attributed to the  
216 impregnation delay of the composite electrode by the liquid electrolyte, leading to an  
217 improvement of exchange surfaces within the materials. The subsequent increase could be  
218 attributed to a deterioration of the contacts, possibly from a cohesion loss between the  
219 various components of the electrodes, and the formation of agglomerates, associated with a  
220 decrease in active surface area. This phenomenon was not observed for the composition of  
221 CB 9.2%. In this latter case,  $R_1$  resistance slightly increased (of about  $3 \Omega.m^2.day^{-1}$ ) all along  
222 the impregnation. This shows that a higher CB loading combined with a higher specific surface  
223 area seems to be less affected by the liquid electrolyte impregnation, maintaining a constant  
224 quality of contacts and exchange surfaces. Thus,  $R_1$  contributes to the contact resistance,  $R_c$   
225 especially through  $R_{cr}$  mainly associated with the grain-to-grain contact. On another hand,  $R_2$   
226 could be assigned to the formation of the solid electrolyte interphase (SEI) due to the  
227 passivation of the surface of the composite electrode by the liquid electrolyte degradation  
228 products (such as solvents, and inorganic salts).  $R_2$  increases slightly, for the 2 lower CB  
229 loadings 6.9 and 7.8%, during the six first days of the study and then remained constant ( $\sim$   
230  $50 \Omega.m^2$ ), whereas  $R_2$  for the highest CB loading 9.2% is mostly constant since the beginning,  
231 at a much lower value ( $\sim 10 \Omega.m^2$ ). The stability of  $R_2$  may be ascribed to the completion of  
232 the SEI formation, known to be obtained on carbon-based materials.<sup>26</sup> Due to its dielectric  
233 nature and location (surface thin film),  $R_2$  may also contribute to the contact resistance,  $R_c$ .  
234 Thereafter, the determination of the real value of this contact resistance,  $R_c$  is very tricky, as

235 one can notice several contributions arising from different phenomena. Moreover, as  
236 previously shown, a change in the surface area and/or porosity of the solid phase is also  
237 responsible for noticeable changes in terms of exchange surface and passivation of the  
238 composite electrodes, making this determination very complex and fluctuant with time.  
239 However, it has been highlighted here that the choice of the carbon additive, the formulation  
240 (loading) and the wetting of the electrode are interdependent parameters, playing through  
241 the overall contact resistance, and SEI formation. Now considering the low frequencies (*i.e.* <  
242 1 Hz), in the Nyquist plots, it can also be noticed (Figure 6a) that the semi-infinite diffusion  
243 domain (45° straight line) is function of both the CB content and the time of impregnation, but  
244 is less affected by the CB specific surface area (Figure 8). This is directly related to the  
245 architecture (porosity/tortuosity) of the composite electrodes, which obviously depends less  
246 on the carbon surface than on the carbon content and time (liquid electrolyte impregnation  
247 opens porosities). Actually, this domain refers to the confined electrolyte inside the vicinity of  
248 the composite electrode. When noticeable on the Nyquist plot, it means the porosities are  
249 opened and wide enough to ensure good ionic transport.<sup>27</sup>

250 According to the EIS measurements performed just after wetting the electrode and up  
251 to 22 consecutive days as presented on Figure 6, this domain slowly appears with 6.9% CB  
252 (only visible after 22 days), whereas it is already visible (after 1 day) with 9.2% CB. This is  
253 consistent with the mesoporosity of the dry electrodes, previously highlighted by BET. The  
254 amount of pores, proportional to the CB content, which can be filled by the liquid electrolyte  
255 will lead to a certain swelling of the electrode, enlarging the ionic diffusion pathways. That is  
256 why a protocol of electrode formation (shaping) is so important before cycling a Li-ion  
257 batteries to ensure good ulterior performance, especially for the ionic mass transport.

### 258 **3.3. Broadband dielectric spectroscopy**

259 The broadband dielectric spectroscopy (BDS) allows for the characterization of different types  
260 of polarization and charge carrier motion under the influence of an electromagnetic field  
261 across the sample, at different scales. This technique is mainly known for polymers and ionic  
262 conductive materials but has been less used for electronic conductive materials. When  
263 submitted to a time-dependent electric field  $E(t)$ , the electrical response of a material is due  
264 to charge density fluctuations. In a harmonic regime, the relationship between the frequency-  
265 dependent complex conductivity  $\sigma(\omega) = \sigma'(\omega) + i\sigma''(\omega)$  and relative permittivity  $\varepsilon(\omega) = \varepsilon'(\omega) -$   
266  $i\varepsilon''(\omega)$  is defined by:

$$\sigma(\omega) = \sigma_{dc} + i\omega\varepsilon_0\varepsilon(\omega) \quad (2)$$

where  $\sigma_{dc}$  is the macroscopic direct-current conductivity,  $\varepsilon_0 = 8.842 \times 10^{-12} \text{ F.m}^{-1}$  the vacuum permittivity and  $\omega = 2\pi\nu$  the angular frequency ( $\nu$  being the frequency, expressed in Hz).

In electronic conductors, several types of polarization occur, coming from the crystal structure, particle nanostructure and sample microstructure<sup>5,28</sup>. In practice, the principle of this technique is based on the study of an electromagnetic wave at a given frequency  $\nu$ , transmitted through the studied sample, going across it and reflected by a short circuit at the rear of it. Thus, the value of the reflection coefficient  $S_{11}$  measured depends on the dielectric properties of the sample materials. After calibration (using short, open, and load  $Z_0 = 50 \Omega$ ), it is possible to measure  $S_{11}$  from the cell containing the sample and the corresponding admittance  $Y_S$  (in S) is obtained from  $S_{11}$  (without unit) as follows:

$$Z_0 Y_S = \frac{1 - S_{11}}{1 + S_{11}} \quad (3)$$

which is directly related to the complex permittivity  $\varepsilon$  by the following approximate and pedagogic relationship at low frequencies (at high frequencies, *i.e.* above  $10^8$  Hz, the relationship becomes much more complex<sup>29</sup> for *ex-situ* and *in-situ*<sup>9</sup>; these more complex relationships are then used in this article across the frequency range):

$$Y_S = iC\omega \quad (4)$$

where  $C = \varepsilon_0\varepsilon S/d$  ( $S$  being the area of the circular inner conductor (3.04 mm in diameter) and  $d$  the thickness of the sample, as a classical formula for a planar capacitor).

*Ex situ* measurements of the conductivity were carried out for both series of carbons, CB1 and CB2. Conductivities of dry CB1 composite samples were higher than their counterparts CB2 for CB volume fraction above 4.5% (Figure 7a-b). dc-conductivities of the samples with CB1 are easily obtained because the real parts of conductivity are not frequency dependent. On the other hand, conductivities of samples with CB2 are frequency dependent in the higher frequency range (Figure 7a). In this last case, the frequency dependence of the conductivity was previously attributed to space-charge polarization of CB2 clusters (agglomerates).<sup>6</sup> The electronic percolation threshold (*ex situ*) was reached for CB volume content of about 4.5% for the two types of carbon black (Figure 7c). For a dry percolated sample, this shows that a higher specific surface of the additive CB1 has a greater impact on the electronic conductivity by significantly increasing it. Indeed, the greater amount of surface area exposed by the carbon powder results in a thinner thickness of binder deposited on the

298 surface and between the carbon particles. We mainly focused in the following on electrodes  
299 with a CB1 content above this percolation threshold, although it was observed that larger  
300 amounts of carbon black increased the brittleness of the sample making it difficult to handle  
301 from a practical view point.

302 *In situ* measurements were then performed on wet samples to characterize the  
303 influence of the electrolyte on electronic transfers in CB1 (as CB2 was previously studied<sup>8</sup>).  
304 Figure 7d shows that the conductivity of wet samples with CB1 is lower than that of  
305 corresponding dry samples above the percolation threshold. This drop is all the more  
306 important as the proportion of CB1 increases. This same trend was previously observed for  
307 samples containing CB2<sup>6</sup>. Moreover, the presence of electrolyte also greatly transforms the  
308 real part  $\epsilon'$  of the permittivity, especially at higher frequencies where it tends to be negative  
309 (*see Supporting Information S1*). On the other hand, the higher values of  $\epsilon'$  at lower  
310 frequencies are due to the presence of the electrolyte given the existence of polarizations  
311 caused by ion motions and ionic double-layer capacitances (*see Supporting Information S1*).  
312 Moreover, the dielectric spectra are composed of different relaxations induced by charge  
313 carrier motions in conducting materials. These relaxations are due to the existence of  
314 interfaces (e.g. sample/current collector, cluster/cluster, particle/particle in CB) giving rise to  
315 associated space-charges. It results contact resistances, which limit the charge transfers at the  
316 different size scales of the samples. Nyquist plots of complex permittivity ( $\epsilon''$  vs.  $\epsilon'$ ) are  
317 relevant to highlight the different space-charge relaxations by decomposing the spectra with  
318 a homemade software. Dielectric relaxation intensities and frequencies give generally access  
319 to space-charge capacitances and charge carriers mobilities, respectively. Nyquist plots of  
320 complex resistivity ( $\rho''$  vs.  $\rho'$ ) and conductivity ( $\sigma''$  vs.  $\sigma'$ ) are suitable to determine dc-  
321 conductivities of the samples and the CB clusters by decomposing the spectra given the  
322 presence of multiple interfaces.

323 The Nyquist plots of complex permittivity ( $\epsilon''$  vs.  $\epsilon'$ ) for the different wet samples (i.e.  
324 with CB1 volume content of 5.3%, 6.9%, 7.8% and 9.2%) are shown in Figure 8. The dielectric  
325 spectra are decomposed into two contributions P1 and P2. The low-frequency part (P1) of  
326 each starting spectrum is well fitted by a quasi-vertical straight line corresponding to the  
327 contribution  $A(i\omega)^{s-1}$  with  $s$  here less than 0.06. This response is due either to a more or less  
328 disordered long-range conductive network or to distributions of contact resistances and  
329 capacitances caused by metallization and electrolyte (see further). By subtracting the P1

330 contribution, a circular arc highlights a dielectric relaxation (P2 contribution) accurately fitted  
 331 by a Cole-Cole given by

$$332 \quad \varepsilon(\omega) = \varepsilon_{hf} + \frac{\varepsilon_s - \varepsilon_{hf}}{(1 + i\omega\tau_2)^{1-\alpha_2}} \quad (5)$$

333 where  $\varepsilon_s$  is the static permittivity of the sample,  $\varepsilon_{hf}$  the sample background (or higher  
 334 frequency) permittivity,  $\tau_2$  the relaxation time and  $\alpha$  a fitting parameter ( $0 < \alpha_2 < 1$ ). The  
 335 relaxation frequency of P2 is given as  $\nu_2 = (2\pi\tau_2)^{-1}$  and  $\Delta\varepsilon_2 = (\varepsilon_s - \varepsilon_{hf})$  is the dielectric strength  
 336 of the relaxation. This type of relaxation is not evidenced for the dry samples, because it might  
 337 appear beyond the frequency band used here (i.e.  $\nu \gg 10^{10}$  Hz). The fitting parameters  $\alpha_2$  are  
 338 0.18, 0.18, 0.02 and 0.23 for respective CB1 volume contents of 5.3%, 6.9%, 7.8% and 9.2%.  
 339 Variations of  $\nu_2$ ,  $\Delta\varepsilon_2$  and  $\varepsilon_{hf}$  with CB1 content are shown in Figures 9a, 9b and 9c, respectively.  
 340 The evolution of  $\nu_2$ ,  $\Delta\varepsilon_2$  and  $\varepsilon_{hf}$  as function of the CB1 content  $\phi_{CB}$  is not monotonic. Indeed,  
 341  $\nu_2$  and  $\varepsilon_{hf}$  go through minimum values for  $6.9\% < \phi_{CB} < 7.8\%$  while  $\Delta\varepsilon_2$  goes through a  
 342 maximum value for the same  $\phi_{CB}$  content. A transition in the electrical properties of soaked  
 343 samples is evidenced because of the presence of the electrolyte, and the interactions between  
 344 the carbon black CB1 and the electrolyte species. These interactions are certainly due the  
 345 influence of the adsorbed species on the electrical properties of CB1. Figure 9a shows that the  
 346 relaxation frequencies  $\nu_2$  for  $\phi_{CB} = 5.3\%$ ,  $7.8\%$  and  $9.2\%$  ( $10^9 < \nu_2 < 10^{10}$  Hz) are of the same  
 347 order of magnitude as that of the dipolar rotation of the solvent EC: DMC which takes place  
 348 at  $6 \times 10^9$  Hz at room temperature. There is an exception for  $\phi_{CB} = 5.3\%$  where  $\nu_2$  is roughly  
 349 one order of magnitude lower at room temperature (i.e.  $\nu_2 = 2.2 \times 10^8$  Hz). However, it seems  
 350 unlikely to admit such a variation in the relaxation frequency of the solvent molecules with  
 351 the CB1 content. One has to wonder why these movements are not highlighted. Indeed, the  
 352 electrolyte is shunted by the percolated network of CB because of the high electronic  
 353 conductivity of the latter. The P2 relaxation would then be due to the polarization of the CB1  
 354 clusters, which is made possible thanks to the formation of an electronic space charge whose  
 355 capacitance  $C_{sc} \propto \Delta\varepsilon_2 \propto w^{-1}$  where  $w$  stands for the space-charge layer thickness<sup>10,30,31</sup>. This  
 356 fast relaxation would be thus correlated to electronic motions within CB1 clusters. This  
 357 hypothesis is supported by permittivities of the wet samples lower than that of the  
 358 corresponding dry samples, which shows that the solvent has no influence on their values for  
 359 frequencies above  $10^8 - 10^9$  Hz (Figures 9d-e and Figures S1a-b). Otherwise, the presence of  
 360 the solvent should have increased the permittivity of the samples, if the CB1 had not shunted

361 it. The background permittivity  $\epsilon_{hf}$  of the wet samples, which is a function of those of  $\gamma$ -  
 362 alumina ( $\epsilon = 8.48$ <sup>32</sup>), PVdF-HFP ( $\epsilon \approx 10$  at 500 Hz<sup>33</sup>), carbon black CB1 and electrolyte ( $\epsilon \approx 40$   
 363 <sup>34</sup>), is negative (Figure 9a). Taking these permittivity values into account, it is very likely that  
 364 the intrinsic permittivity of CB1 is more negative than the background permittivity  $\epsilon_{hf}$  of the  
 365 wet samples. This result is consistent with the Drude model for the permittivity of the (quasi-  
 366 ) metallic compounds<sup>35</sup>. The high frequency permittivity of the dry samples (Figure 9d-e and  
 367 Figure S1) is not negative since it is between 10 and 20. Since the dry samples are more  
 368 conducting than the wet samples, their permittivity could become negative in microwave and  
 369 terahertz frequency range as for some composite materials containing carbon black (carbon  
 370 black / polymer mixtures and composite electrodes of carbon black /  $\text{LiV}_3\text{O}_8$  / PMMA)<sup>24,36</sup>.  
 371 The observed transition of the dielectric properties of CB1 (for  $6.9\% < \phi_{CB} < 7.8\%$ ) could be  
 372 largely due to competitive adsorption of ions ( $\text{Li}^+$  and  $\text{PF}_6^-$ ) between alumina and carbon black  
 373 as for CB2<sup>6</sup>. This type of transition was previously evidenced for a CB2 volume content  $\phi_{CB} \approx$   
 374  $7.5\%$ <sup>6</sup>. A surface charge reversal of the interface between CB2 and electrolyte (LP30) was at  
 375 the origin of this transition<sup>6</sup>. This phenomenon can be understood by the evolution of the  
 376 surface potential  $\Delta\psi$  which is often given by

$$377 \quad \Delta\psi = \Delta\psi_{ion} + \Delta\psi_{dipole} \quad (6)$$

378 where  $\Delta\psi_{ion}$  is the potential created by adsorbed ions and  $\Delta\psi_{dipole}$  the potential due to surface  
 379 dipoles. A zero-charge interface (zci) was set at the threshold  $\phi_{CB} \approx 7.5\%$  due to an equal  
 380 number of adsorbed  $\text{Li}^+$  and  $\text{PF}_6^-$  at the CB2 surface<sup>6</sup>. The potential is only due to surface  
 381 dipoles at zci, where  $\Delta\psi = \Delta\psi_{dipole}$ , since  $\Delta\psi_{ion} = 0$ . The PVdF-HFP can be present on the  
 382 surface of the CB and interact with the CB via its dipoles. Indeed, the PVdF – Graphite  
 383 interactions are between the fluorine atoms (electron attractor) of the PVdF and the surface  
 384 of the graphite. Indeed, the PVdF – Graphite interactions are between the fluorine atoms  
 385 (electron attractor) of the PVdF and the surface of the graphite. Two types of dipoles interact  
 386 thus with the CB surface at the zci: solvent dipoles (EC:DMC) and dipolar species of the PVdF-  
 387 HFP. Below the zci  $\text{PF}_6^-$  ions are preferentially adsorbed on CB, while above  $\text{Li}^+$  ions become  
 388 preferentially adsorbed on CB. Due to the neutral nature of the surface at the zci, only dipolar  
 389 species modify the conductivity of the electrode as compare to the dry electrode. The surface  
 390 of the CB plays a determining role in the interactions with ions and dipoles which directly  
 391 influence the electronic conductivity of the carbon and therefore the performance of the Li-



ion battery<sup>37,38</sup>. At a higher CB content, the PVdF-HFP is not present in sufficient quantity: the electrolyte and therefore the Li<sup>+</sup> ions have direct access to the surface of the CB. To support this hypothesis, a NMR study of G. M. Palmer<sup>39</sup> had previously shown preferential adsorption of Li<sup>+</sup> ions at the alumina surface because of their strong bond to the electron donating oxygen basic surface sites. Consequently, the actual transition observed for CB1 would be due to a surface charge reversal of the CB1 / electrolyte interface around the volume content as for CB2. This phenomenon will be hereafter supported by the following data of the conductivity of wet CB1 samples.

Nyquist plots of complex resistivity ( $\rho''$  vs.  $\rho'$ ) and conductivity ( $\sigma''$  vs.  $\sigma'$ ) of wet CB1 samples from  $10^6$  to  $10^{10}$  Hz at room temperature are shown in Figure 10. Complex resistivity plots for  $\phi_{CB} = 5.3$  and 9.2% (Figures 10a-b) show only one relaxation (circular arc) for each compound. This relaxation is the result of contact resistances and capacitances between the different CB1 clusters. The circular arcs intersect the  $\rho'$  axis at  $\rho_s$  (*low-frequency side*) and  $\rho_c$  (*high-frequency side*), which are respectively sample and CB cluster resistivities (Figures 10a-b). Their corresponding conductivities are thus given by  $\sigma_s = \rho_s^{-1}$  and  $\sigma_c = \rho_c^{-1}$  at room temperature. Complex conductivity plots for  $\phi_{CB} = 6.9$  and 7.8% (Fig. 11c-d) highlight some relaxations (*circular arcs*) below  $10^8$ - $10^9$  Hz and the contributions (*vertical straight lines*) of the negative residual permittivities  $\varepsilon_{hf}$  above  $10^8$ - $10^9$  Hz (Figures 10c-d). The relaxations (*circular arcs*) at  $5.7 \times 10^6$  Hz and  $5.7 \times 10^8$  Hz would be due to the existence of contact resistances between CB1 samples and the gold film on their surfaces. High-frequency parts of the circular arcs intersect the  $\sigma'$  axis at  $\sigma_s$  (*sample conductivities*). The straight lines intersect the  $\sigma'$  axis at  $\sigma_c$  (*CB cluster conductivities*) and therefore determine the CB cluster contribution to the complex conductivity,  $\sigma(\omega) = \sigma_c + i\omega\varepsilon_0\varepsilon_{hf}$ . The conductivities of dry and wet samples have completely different behaviours depending on the CB1 content. The conductivity of dry samples is a regular increasing function of the CB1 content, while that of wet samples increases, reaches a maximum ( $\approx 7.2\%$ ) and then decreases when this content increases (Figure 11a). The impregnation of the solid sample by the liquid electrolyte led thus to an overall reduced conductivity as previously observed for CB2<sup>6</sup>. Note that the conductivity of the wet samples made with CB2 remained an increasing function of CB2 content<sup>6</sup>. Regarding the impregnation kinetics some studies have shown that a poor wettability leads to increased ionic resistance and inhomogeneous lithium intercalation in the active material. The

423 electrolyte is supposed to fully fill the electrode pores, as typically assumed in the literature<sup>40</sup>.  
 424 Below the percolation threshold, the conductivity of the sample with CB2 was increased due  
 425 to the ionic conductivity of the electrolyte within the pores network<sup>6</sup>. However, beyond the  
 426 electronic percolation threshold, the decrease in conductivity can be explained as a result of  
 427 stronger interactions between charge carriers of CB (*electrons and holes*) and adsorbed  
 428 species of the electrolyte (*PVdF HFP and solvent dipoles, Li<sup>+</sup> and PF<sub>6</sub><sup>-</sup> ions*). The difference in  
 429 behaviour between wet samples with CB1 and CB2 would be explained by the larger specific  
 430 area of CB1, hence a stronger interaction with the adsorbed ions. Moreover, that this increase  
 431 in interactions could be attributed to the relative decrease in the PVdF-HFP content (the ratio  
 432 of PVdF-HFP volume/CB surface) which makes the CB surface more accessible to the  
 433 electrolyte, i.e. to the adsorption of Li<sup>+</sup>. The evolution of the cluster conductivity  $\sigma_c$  according  
 434 to  $\phi_{CB}$  shows two linear trends (passing through the origin) on either side of the zci at  $\phi_{CB} \approx$   
 435 7.3% (Figure 11b). The evolution of  $\sigma_c / \phi_{CB}$  according to  $\phi_{CB}$  (Figure 11c) justifies this linear  
 436 behaviour with a slightly higher slope for  $\phi_{CB} = 5.3$  and 6.9% than for  $\phi_{CB} = 7.8$  and 9.2%. The  
 437 ratio of the slopes is equal to 1.3. In order understand this trend, we recall that the CB clusters  
 438 are agglomerates of spherical particles in which the graphite layers make them sufficiently  
 439 conductive. The graphite is known as a compensated semi-metal with an equal number of  
 440 electrons and holes. It can be either n or p type conductor according to the type of doping  
 441 <sup>41,42</sup>. The conductivity of the graphite can be thus given by

$$442 \quad \sigma = \frac{Ne^2\tau_s}{m^*} \quad (7)$$

443 where  $\tau_s$  is the scattering time, N the number of charge carriers/unit volume,  $e = 1.6 \times 10^{-19}$  C  
 444 the electronic charge and  $m^*$  the effective mass of charge carriers (*electrons, holes*).<sup>34, 35</sup>  $m^*$   
 445 is either the hole effective mass  $m_h^* = 0.039m_e$  or the electron effective mass  $m_e^* = 0.054m_e$   
 446 where  $m_e \approx 9.11 \times 10^{-31}$  kg is the electron mass<sup>34, 35</sup>. Note that the graphite conductivity is not  
 447 achievable by BDS due to its very high value approximating it to a short circuit in the device.  
 448 By analogy, the CB1 cluster conductivity can be described by a similar expression than (6) with  
 449 much lower values of N and  $\tau_s$  due the existence of particle boundaries limiting both the  
 450 number of mobile charge carriers and their mobility. Assuming that N is proportional to  $\phi_{CB}$ ,  
 451 Eq. (6) becomes

$$452 \quad \sigma_c = \frac{B}{m^*} \phi_{CB} \quad (8)$$

453 with B a constant proportional to  $e^2\tau_s$ . If the transition at  $\phi_{CB} \approx 7.3\%$  corresponds to the  
 454 passage from a p-type ( $\phi_{CB} = 5.3$  and  $6.9\%$ ) to an n-type ( $\phi_{CB} = 7.8$  and  $9.2\%$ ) conduction, Eq.  
 455 (7) gives a slope ratio  $m_e^*/m_h^* = 1.4$  which is very close to experimental value 1.3 of  
 456 Figure 11c. The assumption that scattering time  $\tau_s$  is constant (see Eq. 7) is therefore validated  
 457 in Figure 11d by plotting  $B/m_e$  as a function of  $\phi_{CB}$  and using  $m_h^*$  and  $m_e^*$  below and above  
 458 the transition, respectively. The fact that the time is short and independent of  $\phi_{CB}$  shows that  
 459 it would depend only on the CB1 nanostructure especially because of the presence of  
 460 numerous interfaces (i.e. interparticles, interclusters) thus increasing the frequency of the  
 461 collisions between the charge carriers. The conductivity of the cluster is mostly performed in  
 462 the surface layer due to the charge excess (electrons or holes) in the space charge region. The  
 463  $Li^+$  or  $PF_6^-$  ions adsorbed on the CB surface induce an electric field which can make the graphite  
 464 (so CB) either n (electron) or p (hole) conductor due to its amphoteric nature (Figure 12a).  
 465 When the majority of the adsorbed ions are anions ( $PF_6^-$ ), there is an electron depletion layer  
 466 leading to excess holes into this surface (space charge) layer (Figure 12a). Otherwise, when  
 467 the majority of the adsorbed ions are cations ( $Li^+$ ), a hole depletion layer is established leading  
 468 to excess electrons in this surface (space charge) layer (Figure 12a). Figure 12b clearly shows  
 469 that the ratio  $\sigma_s/\sigma_c$  vs  $\phi_{CB}$  tends towards 1 (i.e.  $\sigma_s \approx \sigma_c$ ) near of the transition. Charge carriers  
 470 migrate more easily from one cluster to another when the surface is electrically neutral. When  
 471 the surface is electrically neutral (i.e. at the zci), the interaction between either holes or  
 472 electrons and ion counterpart does not occur anymore. Indeed, the passage from a cluster to  
 473 another is facilitated due to the neutral surface because the coulombic interactions do not  
 474 exist in this case. If there was no dipole, the conductivity would equal that of the dry material.  
 475 On either side of this transition, the surface conduction is then favored. As shown in Figure  
 476 9b, the evolution of  $\Delta\varepsilon_2$  as a function of  $\phi_{CB}$  can be explained from the Mott-Schottky relation,  
 477 which gives the thickness  $w$  of the space-charge (depletion) layer capacitance  $C_{sc}$  vs. the  
 478 surface potential  $\Delta\psi$ , i.e.  $w \propto (e\Delta\psi)^{1/2}$ . When the surface charge is zero at the zci (for  $\phi_{CB} =$   
 479  $7.3\%$ ), the potential  $\Delta\psi$  reaches a minimum value because it is only due to adsorbed dipoles  
 480 ( $\Delta\psi_{ion} = 0$ ). This explains the maximum value of  $\Delta\varepsilon_2 \propto w^{-1}$  at the zci for the CB1 volume fraction  
 481  $\phi_{CB} = 7.3\%$  and the transition from a p-type to a n-type surface conduction at microscopic scale  
 482 of CB1 clusters (or agglomerates).

483 Finally, in order to show the complementarity of EIS and BDS, the BDS data should be  
484 compared with those of the EIS (*for samples with CB1*) although there is no overlap of their  
485 frequency windows. Conductivity values  $\sigma'_{50\text{kHz}}$  and  $\sigma'_{1\text{mHz}}$  obtained by EIS at respective  
486 frequencies 50 kHz and 1 mHz and detailed in Supporting Information S2 are plotted in Figure  
487 12c. They are compared in Fig 13c to the conductivity value  $\sigma'_{1\text{MHz}}$  measured by BDS at 1 MHz  
488 (*see Figure 7d*) and to that of the sample  $\sigma_s$  obtained from dielectric spectra decomposition  
489 (*see Figures 10 and 11a*). The results show that the global conductivity  $\sigma'_{1\text{mHz}}$  is lower by about  
490 two orders of magnitude than the sample conductivity  $\sigma_s$  (Figure 12c). This difference  
491 between  $\sigma'_{1\text{mHz}}$  and  $\sigma_s$  results from the existence of a high interfacial resistance that would  
492 be attributed to the barrier created by the adsorbed ions forming a double layer and/or to a  
493 hypothetical very thin SEI layer partially covering the carbon black. At the opposite end of the  
494 EIS spectra, the conductivity  $\sigma'_{50\text{kHz}}$  is close to  $\sigma_s$  for  $\phi_{\text{CB}} = 9.2\%$ , while it is less than  $\sigma_s$  by  
495 almost an order of magnitude for the smaller CB1 fractions of CB1. Hence, the difference  
496 between  $\sigma'_{50\text{kHz}}$  and  $\sigma_s$  would be due to the direct contact resistance between the sample and  
497 the current collector because of the existence of an insulating gap (*PVdF-HFP and/or  $\gamma\text{Al}_2\text{O}_3$* )  
498 between them. This later contact resistance would become smaller beyond 9% of CB, content  
499 for which the contact between the current collector and the sample would be most favorable  
500 to the electronic transfer. EIS is more suitable for the study of ionic diffusion and the various  
501 contact resistances at the macroscopic scale. On the other hand, the BDS here allows the  
502 comprehensive study of carbon black conductivity and permittivity and thus to highlight the  
503 influence of the liquid electrolyte on these two parameters.

#### 504 **4. Conclusions**

505 This study establishes a link between the complex hierarchical geometry of carbon black-  
506 based composites (such as electrodes of Li-ion batteries) and subsequent limitations of the  
507 charge transport occurring at different scales. We substituted the common active material by  
508 an insulating compound to specifically highlight the interactions taking place at the liquid  
509 electrolyte/carbon black interface. We demonstrated that the carbon specific surface area, as  
510 well as its loading, provide an important impedance contribution and play a key role in the  
511 electronic percolation threshold, the contact resistance, the SEI formation, and the mass  
512 transport efficiency. Most importantly, we revealed an evolution of the electrical conductivity

513 between the dry and the wet states, which can be attributed to the adsorptions of the  
514 electrolyte salt species ( $\text{Li}^+$  cation and  $\text{PF}_6^-$  anion). This phenomenon creates an electrostatic  
515 double-layer at the interface between the carbon black and the electrolyte that perturbs the  
516 electronic transfers between carbon black clusters. Further experiments are now ongoing for  
517 determining the equivalent limitations with the active materials commonly used in  
518 commercial lithium-ion batteries for mobility applications.

### 519 **Conflicts of interest**

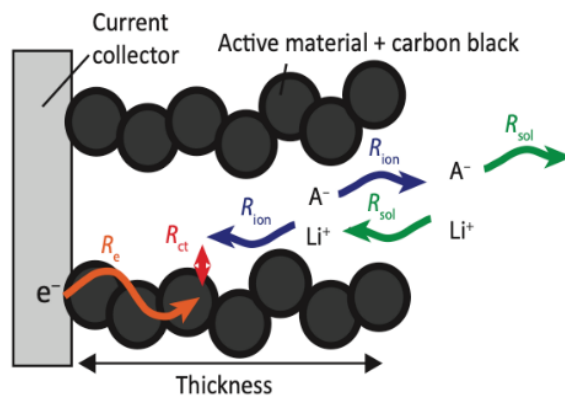
520 The authors have no conflict of interest to declare.

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525 project (ANR-15-CE05-0001) that are acknowledged.

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535 **Figure 1.** Schematic representation of charge carrier (ion/electron) transport in a hierarchical composite  
 536 electrode.  $R_e$ ,  $R_{ct}$ ,  $R_{ion}$  and  $R_{sol}$  are related to the resistance of electron within the percolated active  
 537 material/carbon black network, the charge transfer resistance, the resistance to ionic motion within the  
 538 electrolyte and solvent resistance, respectively.  $Li^+$  stand for Li ions whereas  $A^-$  stands for the counter anion (e.g.  
 539  $PF_6^-$ ).<sup>16</sup>

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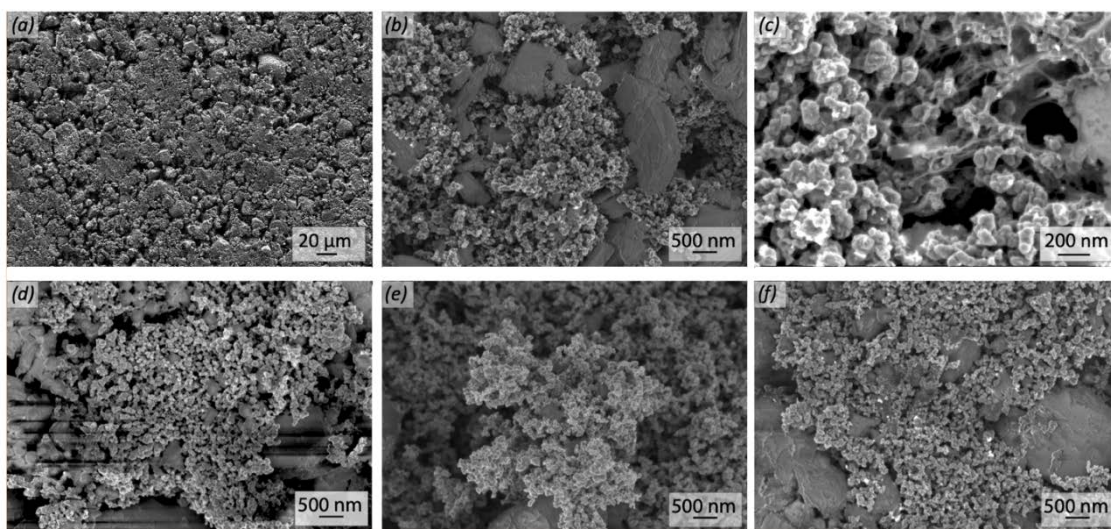
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556 **Figure 2.** SEM micrographs of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>/CB/PB composite samples for different volume contents of carbon black  
557 (CB1): (a-c) 5.3 %, (d) 6.9 %, (e) 7.8 %, (f) 9.2 %.

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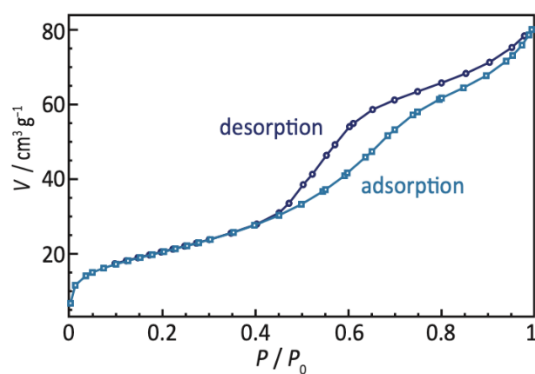
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571 **Figure 3.** Porosity measurement by BET technique ( $\text{N}_2$  adsorption/desorption) of a  $\gamma\text{-Al}_2\text{O}_3/\text{CB1}/\text{PB}$  composite  
572 electrode. Note that similar isothermal curve shape was observed using CB2.

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576 (a)

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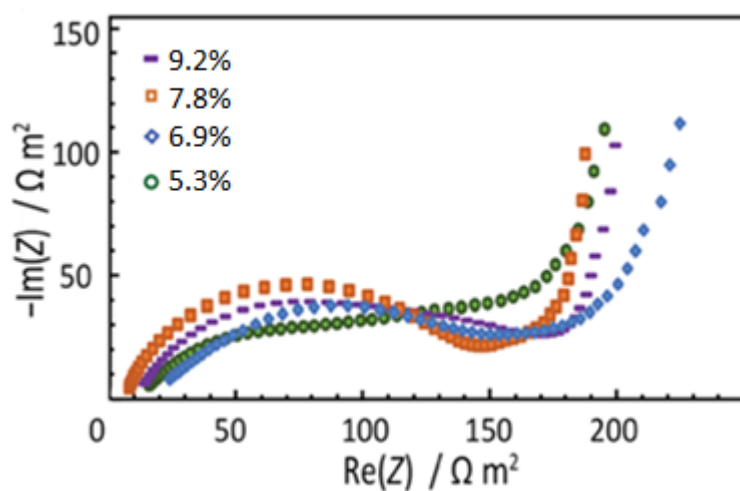
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591 (b)

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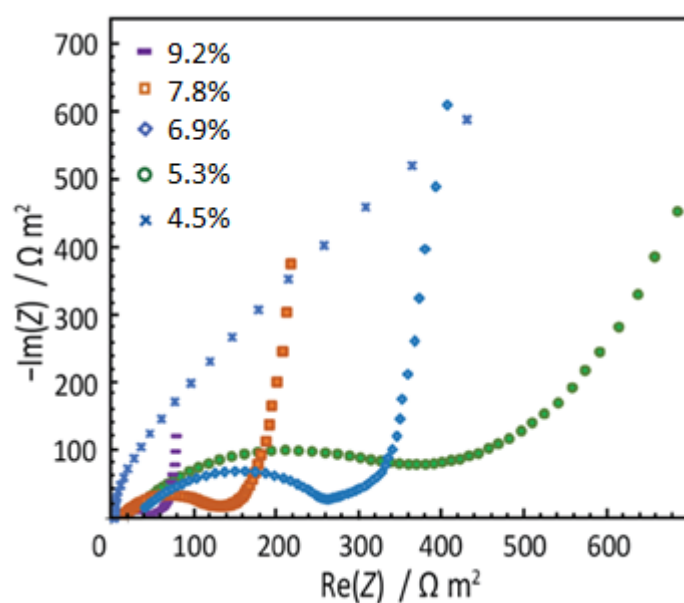
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612 **Figure 4.** Nyquist diagrams of a  $\gamma\text{-Al}_2\text{O}_3/\text{CB}/\text{PB}$  composite material with two different specific surface areas of  
 613 carbon black: (a) CB1 with  $80\text{ m}^2\cdot\text{g}^{-1}$  and (b) CB2 with  $65\text{ m}^2\cdot\text{g}^{-1}$ . Studied amounts of carbon black (volume  
 614 contents): 4.5 %, 5.3 %, 6.9 %, 7.8 % and 9.2 %.

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621 a)

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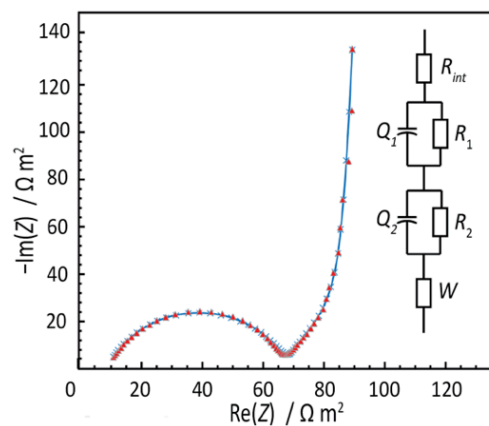
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630 b)

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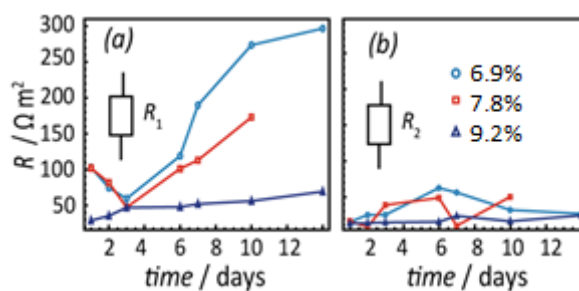
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637 **Figure 5.** a) Nyquist diagram (red) and corresponding fitting (blue) according to the electrical equivalent circuit  
 638 shown for a  $\gamma\text{-Al}_2\text{O}_3/\text{CB}/\text{PB}$  composite material containing 9.2 % in volume of CB2 (*specific surface area* =  
 639  $65 \text{ m}^2 \cdot \text{g}^{-1}$ ). b) Evolution of  $R_1$  (*high frequencies*) and  $R_2$  (*low frequencies*) contributions, respectively, as a function  
 640 of time with different CB2 volume contents: 6.9 %, 7.8 % and 9.2 %.  $W$ ,  $R$ ,  $Q$  stands for Warburg element,  
 641 resistance, and constant phase element of the electrical equivalent circuit modelling the relaxation phenomena  
 642 in the Nyquist diagram.

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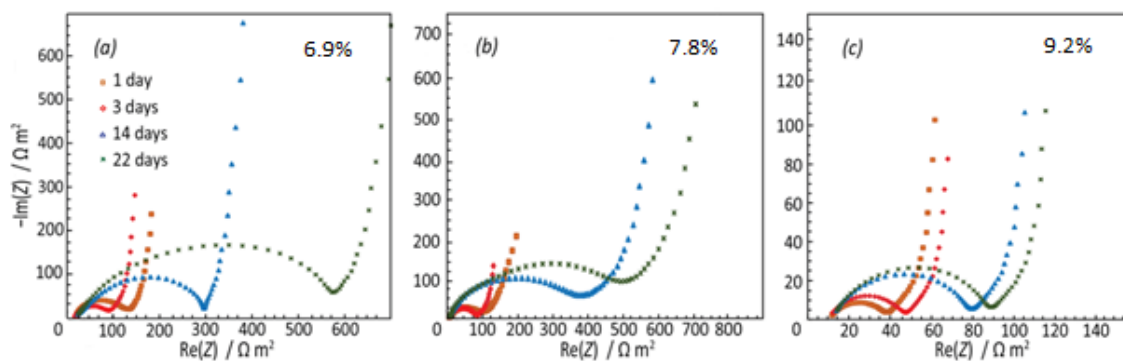
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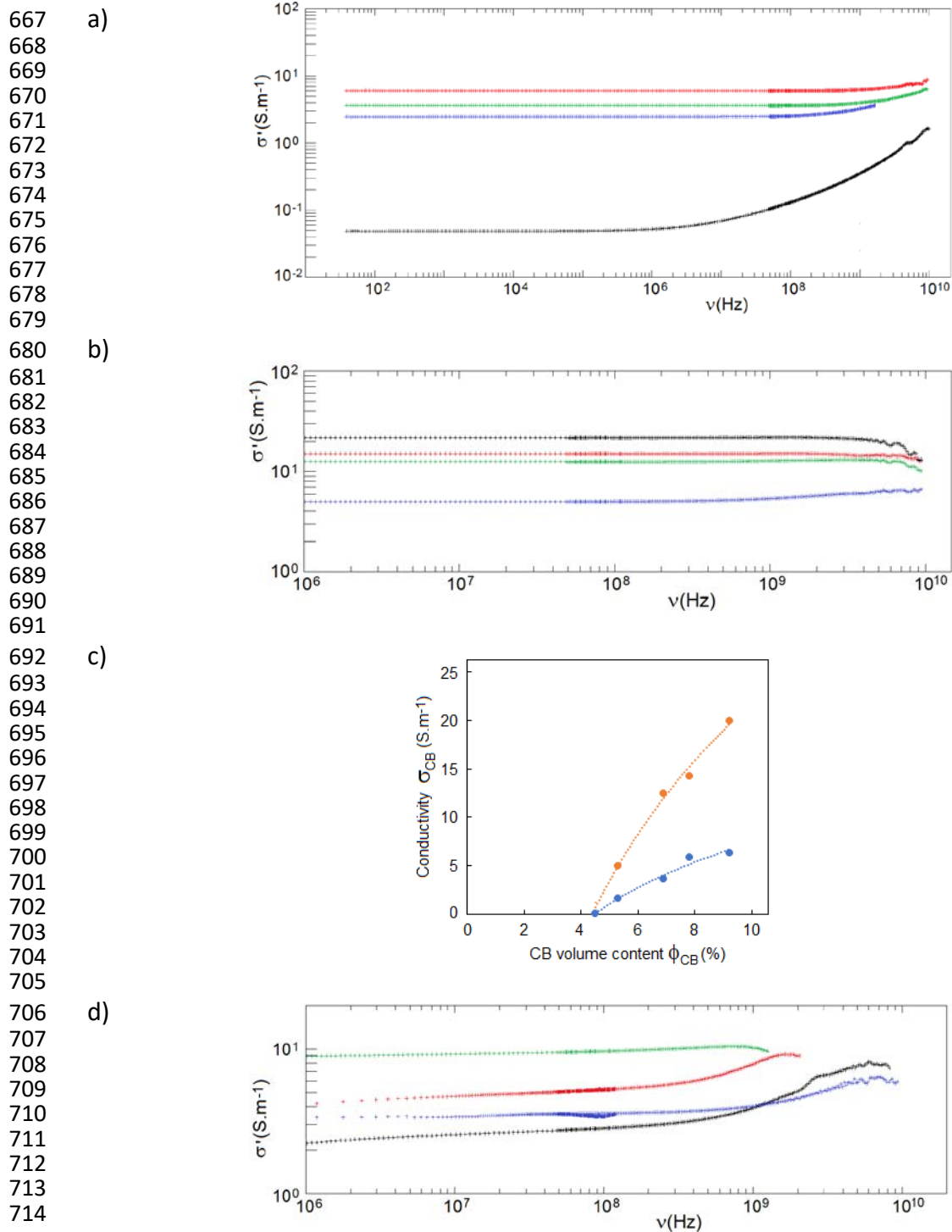
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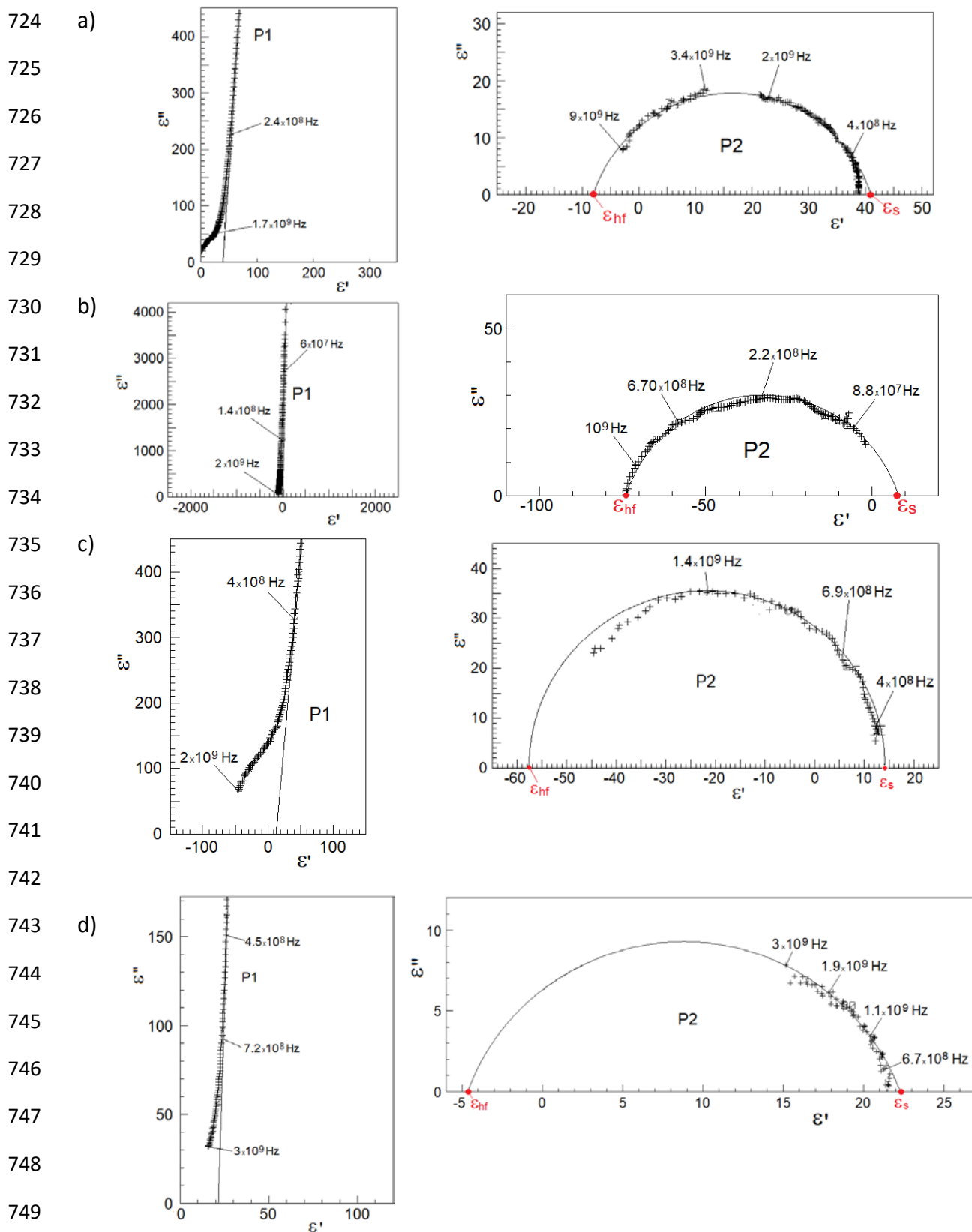
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**Figure 6.** Nyquist diagrams of a  $\gamma\text{-Al}_2\text{O}_3/\text{CB}/\text{PB}$  composite material as a function of time (from 1 to 22 days) for different volume contents of carbon black CB2 (*specific surface area* =  $65 \text{ m}^2.\text{g}^{-1}$ ): (a) 6.9 %, (b) 7.8 %, (c) 9.2 %.

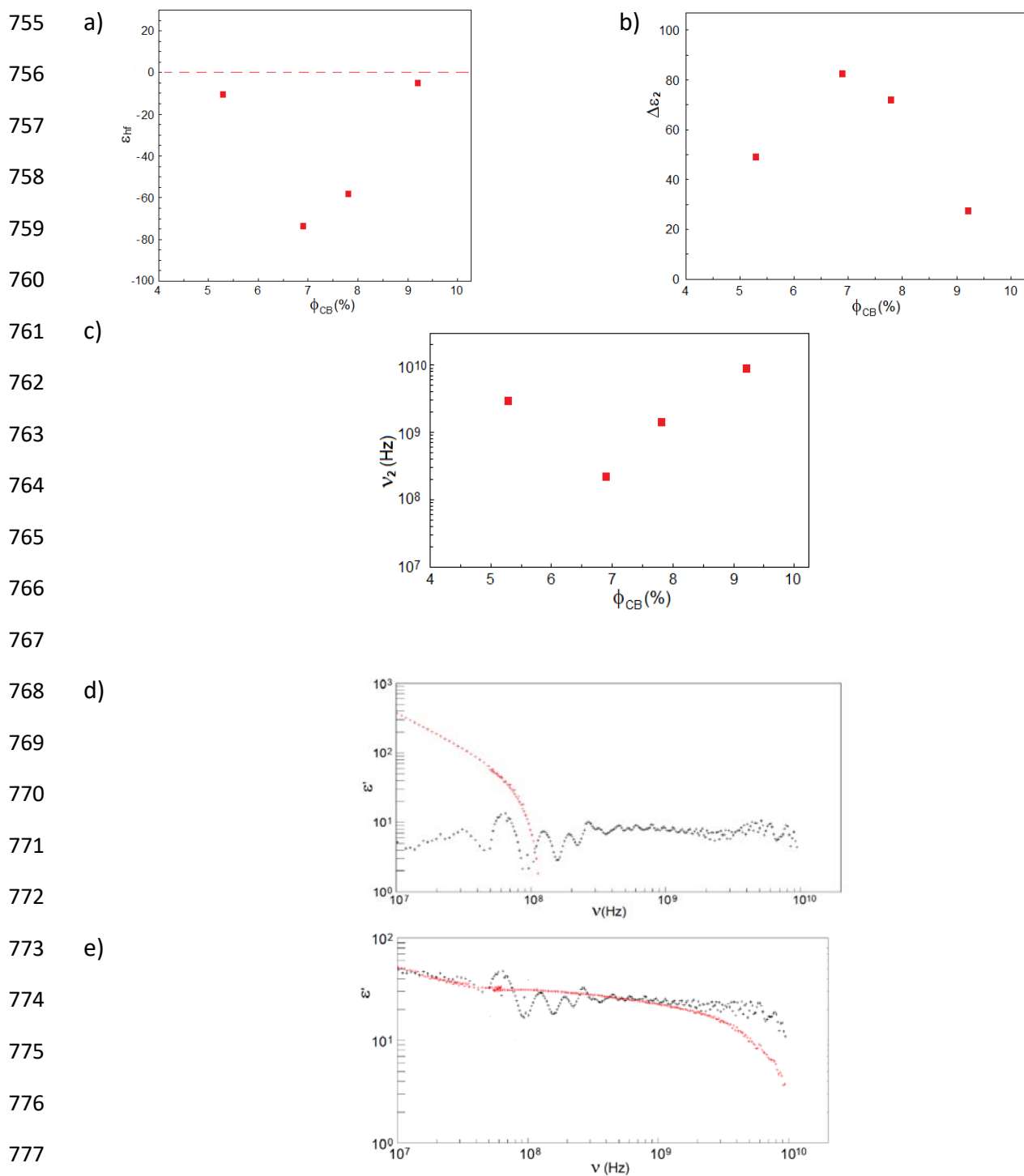


**Figure 7.** Conductivity as a function of frequency (*ex situ* measurement) of dry samples with two types of carbon black of different volume contents  $\phi_{CB}$ : (a) CB2 (*specific area* =  $65\text{m}^2.\text{g}^{-1}$ ) with  $\phi_{CB}$  = 4.5 % (++) , 5.3 % (++) , 6.9 % (++) and 7.8 % (++) ; (b) CB1 (*specific area* =  $80\text{m}^2.\text{g}^{-1}$ ) with  $\phi_{CB}$  = 5.3 % (++) , 6.9 % (++) , 7.8 % (++) and 9.2 % (++) ; (c) Dc- conductivity  $\sigma_{CB}$  (*ex situ* measurement) as a function of CB volume content  $\phi_{CB}$  (%) for samples with CB1 (●) and CB2 (●) (*CB percolation threshold*  $\phi_c \approx 4.5\%$ ); (d) Conductivity as a function of frequency (*in situ* measurement) of wet samples with CB1 carbon black at different volume contents  $\phi_{CB}$  = 5.3 % (++) , 6.9 % (++) , 7.8 % (++) and 9.2 % (++) .



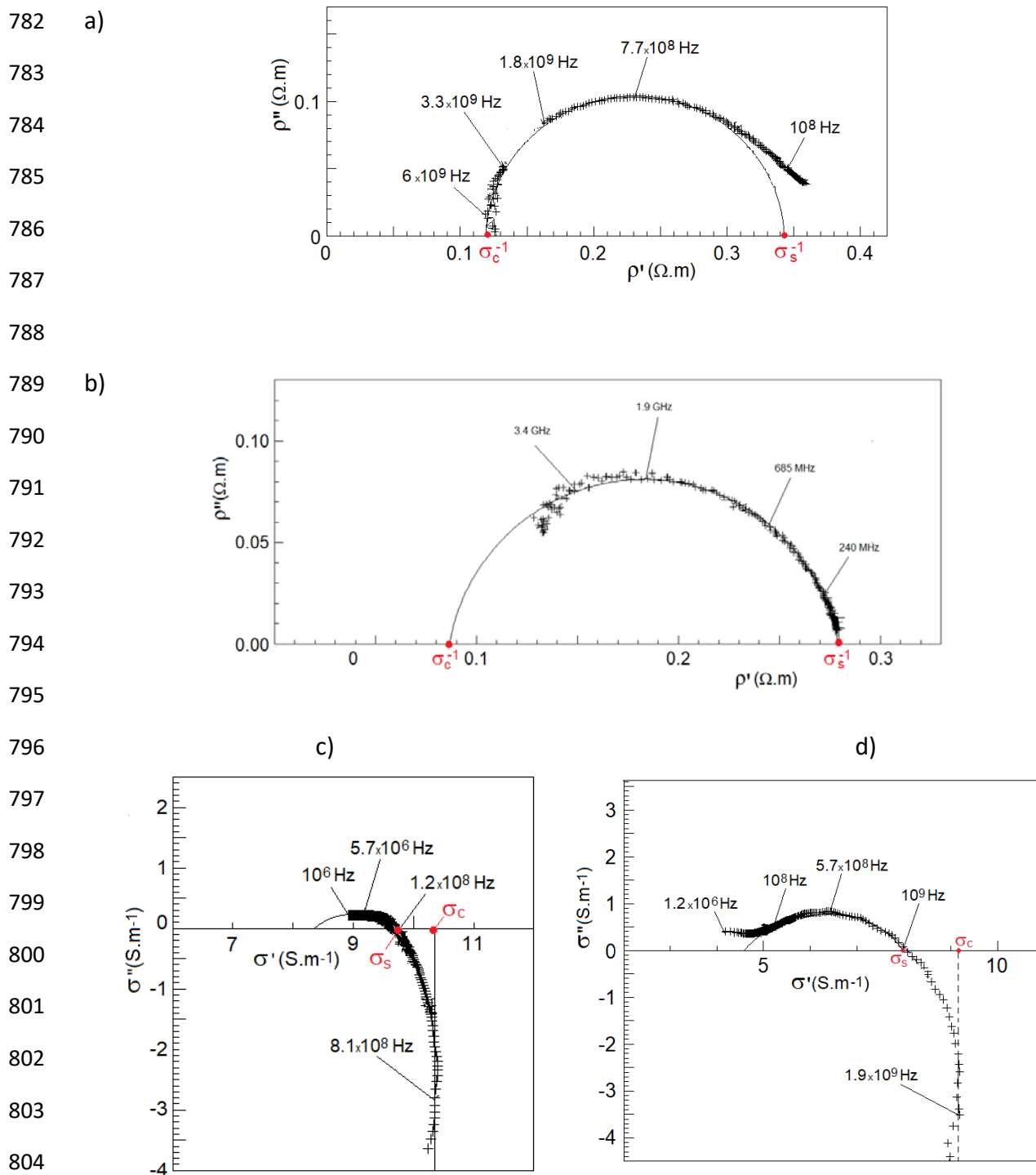
750 **Figure 8.** Nyquist plots of complex permittivity ( $\epsilon''$  vs.  $\epsilon'$ ) of wet samples at 293 K for CB1 volume contents: a)  
 751  $\phi_{CB} = 5.3\%$ , b)  $\phi_{CB} = 6.9\%$ , c)  $\phi_{CB} = 7.8\%$  and d)  $\phi_{CB} = 9.2\%$ . Decomposition of spectra highlights a low-frequency  
 752 contribution P1 (straight line) and dielectric relaxation P2 (circular arc) obtained upon subtracting P1.  $\epsilon_s$  is the  
 753 static permittivity of the sample and  $\epsilon_{hf}$  the background permittivity of the CB1 cluster.

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778 **Figure 9.** Parameters of dielectric relaxation P2 vs. CB1 volume fraction  $\phi_{CB}$  of wet samples: a) background  
 779 permittivity  $\epsilon_{hf}$ , b) dielectric strength  $\Delta\epsilon_2$ , c) relaxation frequency  $\nu_2$ . Real part  $\epsilon'$  of the permittivity vs. frequency  
 780  $\nu$  for dry (++) and wet (++) samples with CB1 volume fraction  $\phi_{CB}$ : d) 6.9 % and e) 9.2 %.

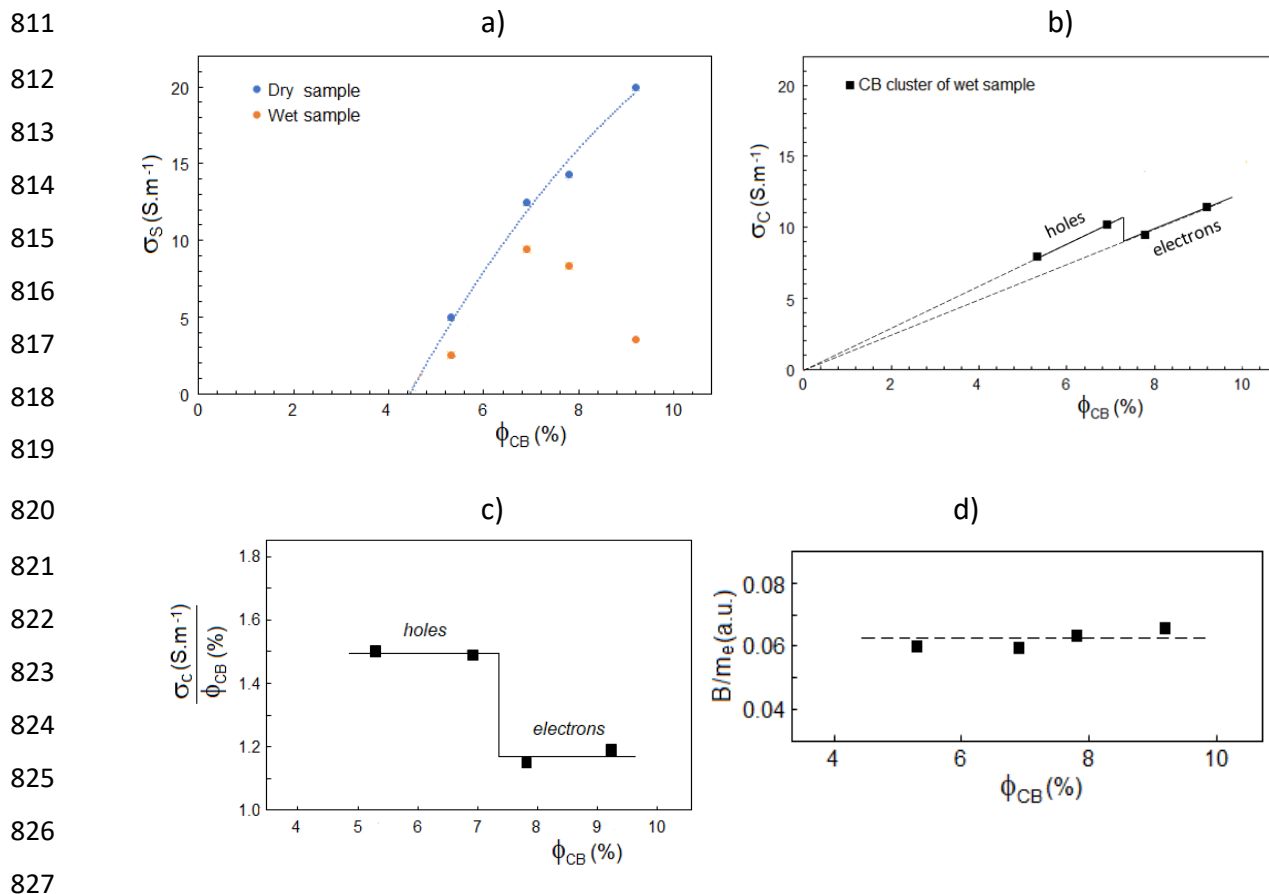
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806 **Figure 10.** Nyquist plots of complex resistivity ( $\rho''$  vs.  $\rho'$ ) of wet samples at 293 K for CB1 volume fraction: a)  $\phi_{CB}$   
 807 = 5.3 % and b)  $\phi_{CB}$  = 9.2 %. Nyquist plots of complex conductivity ( $\sigma''$  vs.  $\sigma'$ ) at 293 K for CB1 volume fraction: c)  
 808  $\phi_{CB}$  = 6.9 % and d)  $\phi_{CB}$  = 7.8 %.  $\sigma_s$  and  $\sigma_c$  correspond sample and CB1 cluster conductivities, respectively.

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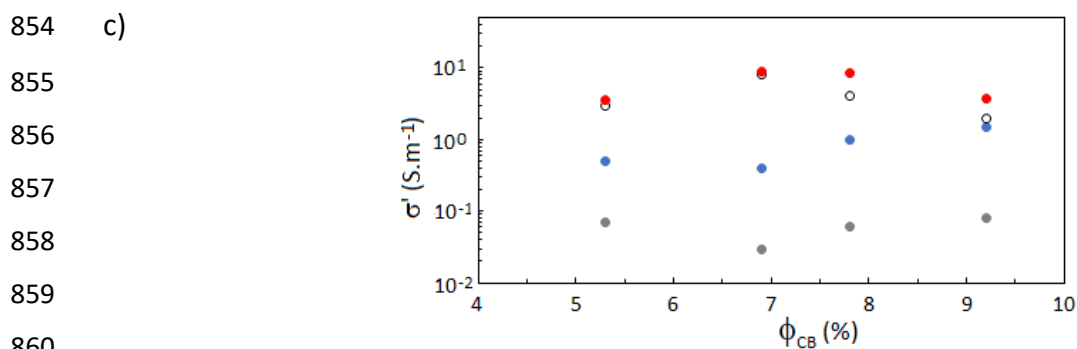
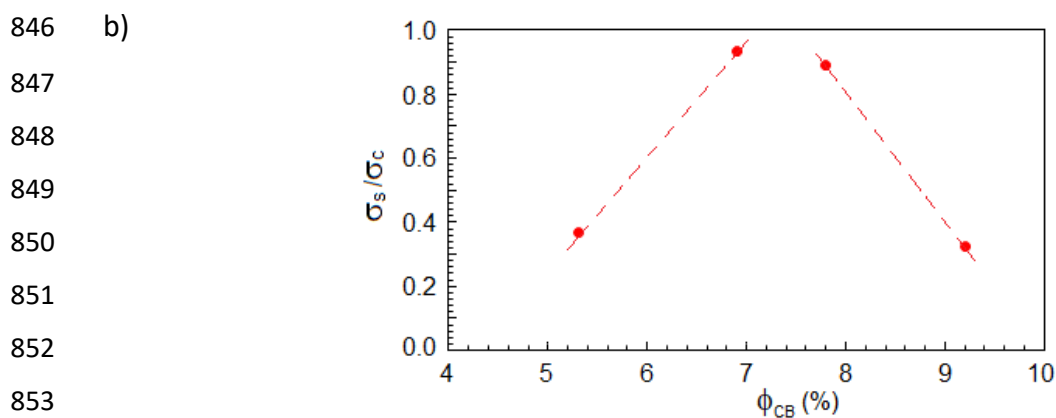
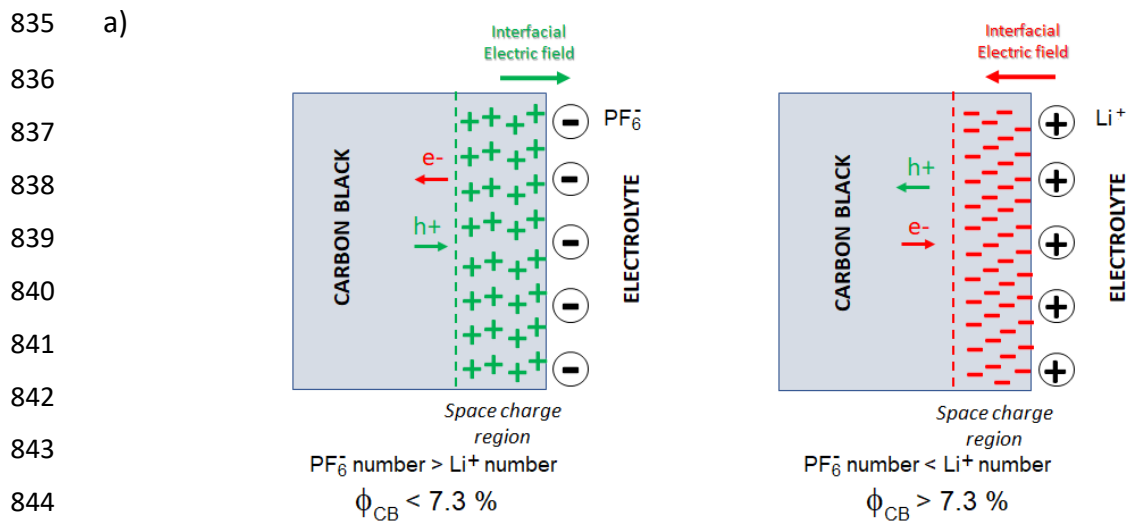


828 **Figure 11.** a) Conductivities  $\sigma_S$  of dry (●) and wet (●) samples vs. CB1 volume fraction  $\phi_{CB}$  at 293 K; b) Conductivity  
 829  $\sigma_C$  of wet sample vs. CB1 volume fraction  $\phi_{CB}$  at 293 K; c) Ratio  $\sigma_C / \phi_{CB}$  vs. CB1 volume fraction  $\phi_{CB}$  at 293 K; d)  
 830  $B/m_e$  vs. CB1 volume fraction  $\phi_{CB}$  at 293 K.  $\frac{B}{m_e} = \frac{\sigma_C}{\phi_{CB}} \frac{m^*}{m_e}$  where  $m_e \approx 9.11 \times 10^{-31}$  kg is the electron mass and  $m^*$   
 831 the effective mass of holes ( $m^* = m_h^* = 0.039m_e$ ) or electrons ( $m^* = m_e^* = 0.054m_e$ ).  $B/m_e$  is calculated using  
 832  $m_h^*$  for  $\phi_{CB} = 5.3$  and  $6.9\%$  and  $m_e^*$  for  $\phi_{CB} = 7.8$  and  $9.2\%$ .

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861 **Figure 12.** a) Modification of the sign of space charge layer at the carbon black (CB1) surface as function of the  
 862 CB1 volume fraction  $\phi_{\text{CB}}$ : left hand figure (majority of adsorbed  $\text{PF}_6^-$  anions resulting in an electron depletion  
 863 layer with excess holes) and right hand figure (majority of adsorbed  $\text{Li}^+$  cations resulting in a hole depletion layer  
 864 with excess electrons); b) Ratio  $\sigma_c/\sigma_s$  vs.  $\phi_{\text{CB}}$  where  $\sigma_c$  and  $\sigma_s$  are conductivities of cluster and sample (set of  
 865 CB1 clusters), respectively; c) Conductivities (real parts) vs. CB1 volume fraction:  $\sigma'_{1\text{mHz}}$  (●) and  $\sigma'_{50\text{kHz}}$  (●) obtained  
 866 by EIS at 1 mHz and 50 kHz (see Fig. 5a, Supporting Information S2 and Table S1),  $\sigma'_{1\text{MHz}}$  measured at 1 MHz by  
 867 BDS (○) (see Fig. 8d), and  $\sigma_s$  (●) (sample conductivity, see Fig. 11 and 12a).

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