

Figure S1. The shape of the voltammograms of 10^{-3} M $K_3Fe(CN)_6$ aqueous solution is strongly dependent on the mass content of graphite in the composite electrode. 1M KCl . T = 298 K. At 20m/s of scan rate. E is referred to Ag/AgCl/KCl sat. electrode.

Graphite + Polyethylene (GHDPE) composite electrode manufacturing process

Commercial high density polyethylenes are linear polyolefins that allow a high packing of macromolecules. In this work, the polymeric matrix used for the preparation of these materials is a technical grade high density polyethylene (HDPE, Alcudia, REPSOL S.A., Puertollano, Spain) with the appropriate additives for its workability and stability. HDPE is a thermoplastic material with a melting point of around 142 °C, so it is necessary to work above this temperature in order to be able to process it. The steps to obtain the materials are as follows:

- 1-. Mixing: this is carried out in a roller mill.
- 2-. Crushing: this is carried out cold with a blade mill.
- 3-. Pressing: in a hot plate press.
- 4-. Cutting: with a milling machine and a diamond saw.
- 5- Assembly of the electrodes.

1. Mixing of graphite and PE in the roller mill

The roller mill (COLLINS, WALZWERK 110, Maitenbeth, Germany) consists of two parallel cylinders of approximately 12 cm diameter rotating in opposite directions. The mixing process requires the control of four independent parameters:

a) Temperature: It is possible to set the temperature of both rollers separately, as well as the end and core temperature of each roller. To avoid too many free parameters, a working temperature of 150°C is chosen, well above the melting point of the polymer, which allows a sufficiently low viscosity of the graphite/PE mixture. For high graphite contents (70, 65% by weight), the temperature can be as high as 160°C. It is not advisable to exceed this temperature as it is possible to observe the formation of encrustations at the ends of the roller, undoubtedly due to the degradation of the polymer.

b). Speed: this parameter is usually varied continuously during the mixing process. The values used range from 10 to 30 rpm, with 20 rpm being the value normally used when graphite is added to the melt.

c) Friction: gives in % the ratio of the speeds between the rollers. It can be positive or negative. If it is positive, the rear roller rotates faster than the front roller by the specified %, and vice versa if the friction is negative. This difference in speed increases the speed gradient in the gap between the rollers, where the actual mixing takes place. The friction is normally set to 0% during the mixing process, but its value is varied when it is desired to change the mixing from one roller to the other.

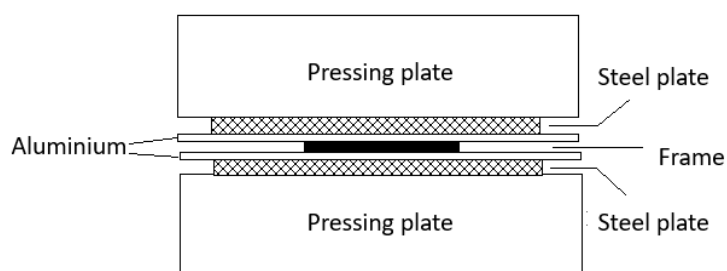
d) Roller gap: in accordance with the above parameters, the roller gap can exceed all of them. During the mixing process, the roller gap is constantly varied to match the rheological properties of the mix to the speed of the rollers and to improve the uniformity of the product. For the mixing process, the roller gap is usually 0.5 mm and can be as wide as 2.0 mm, depending on the amount of material and the loading ratio.

2. Knife Mill

Once the mixture has been mixed as described in the previous point, the material is allowed to cool and then crushed. This is done in a mill using a 2.0 mm mesh screen. The reason for grinding to this size is that at high graphite contents the molten mixture has a high viscosity and the large particles tend to stick to the walls but do not flow through the gaps between the particles. By reducing the particle size and applying high pressures, this problem is greatly reduced.

3. Material pressing

This stage consists of collecting the material crushed in the previous stage and producing a uniform plate. This was done using a hydraulic press (COLLINS, PRESSE 300 Maitenbeth, Germany) whose plates can be heated well above the melting temperature of the material. To prepare the plates, a steel frame with a central clearance of $120 \times 100 \times 4$ mm (48 cm^3) is selected and the material is arranged in a stacking structure as shown in the diagram. The steel plates ensure flatness and uniformity of the applied pressure, while the aluminum plates prevent the material from sticking to the press plates.



Press diagram: Arrangement of the different parts of the press for the production of GHDPE composite sheets.

In order to obtain the plates, different pressure-temperature programmes have been tested, and the best results have been obtained with the five-stage programme shown below:

Time (min)	3	2	4	8	20
Pressure (Bar)	2	20	60	200	60
Temperature (°C, hot/cold)	180/23	180/23	----	----	----

The heating process of the press plates is carried out without pressure, while the cooling process takes place in the last pressure stage. The temperature of 180°C and the pressure of 200 bar ensure melting and uniformity of the plates obtained. In general, the volume of material placed inside the steel frame is much higher than the quantity required ($\approx 48 \text{ cm}^3$). For this reason, the pressure-temperature programme ensures the uniformity of the finished slab. In any case, an approximate value of the density of the material obtained is calculated in order to compare it with its expected value, according to

the equations used to calculate the proportion of graphite by volume.

4. Sample cutting and preparation

This step is carried out using an automatic milling machine. This step is necessary to ensure dimensional uniformity between the different samples. The size of the samples is 50 x 6 x 4 mm. These bars are then embedded in a cylinder of epoxy resin to ensure their isolation and from successive transversal cuts we obtain the electrodes.

5. Preparation of the electrodes

Once the GHDPE composite rods have been insulated with epoxy resin, small 1 cm cylinders are cut with a diamond saw. One face is polished and coated with a layer of colloidal Ag paint. This surface is contacted with a Cu wire, the end of which is flat to ensure adhesion. The contact is then sealed with an epoxy adhesive. The working surface is polished with 600 emery paper.

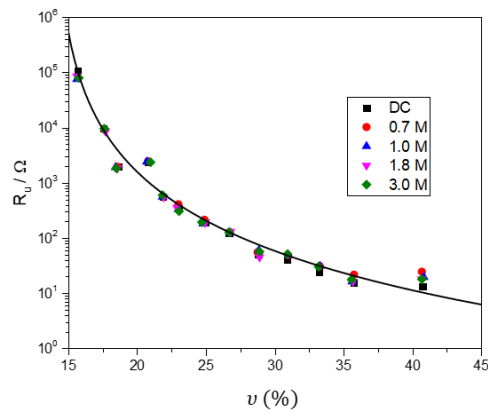


Figure S2. The resistance measured (DC curve) agrees well with these measured by EIS ($E = 0.4$ V) of samples with different graphite content immersed in aqueous KCl solutions if the KCl concentration is sufficiently high. $R_u \propto (v - v_c)^{-t}$ From experimental measures of the dependence of the resistance on graphite content, values $v_c = 0.14$ and $t = 3.4$ are calculated. In composite materials, the critical percolation volume v_c marks the internal formation of conductive clusters inside the solid material, which in turn involve conductive graphite terminations on the surface of the composite electrode in contact with the solution

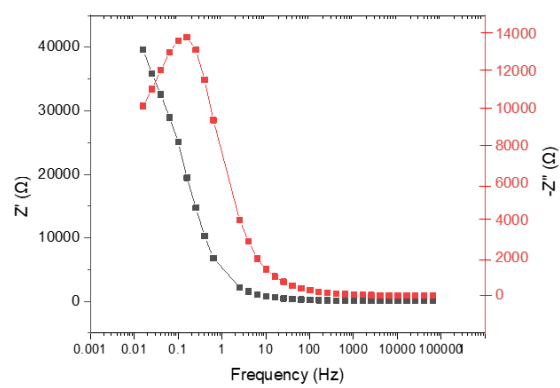
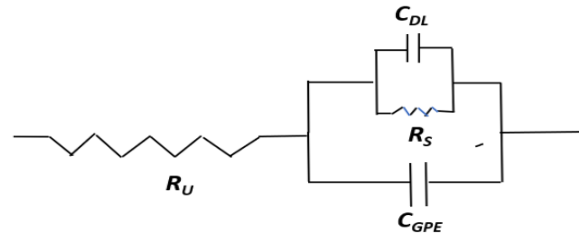
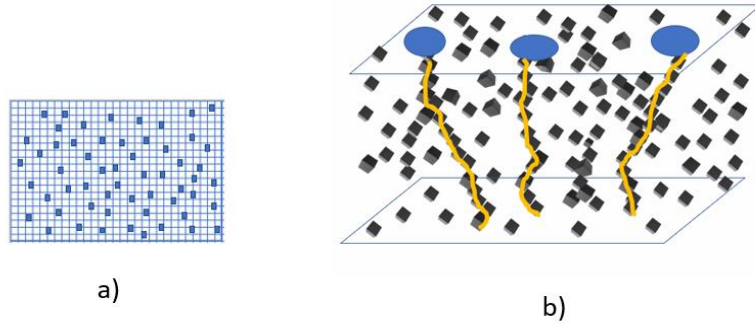


Figure S3. Faradaic processes associated with the presence of oxygen in the solution complicate the interpretation of the composite electrode/solution interface. $\nu = 0.25$. $T = 298$ K. $E = -0.4$ V. $\Delta E = 10$ mV. 0.4 M KCl.



$$Z' = \frac{(C_{DL} + C_{GPE})^2 R_U R_S^2 \omega^2 + R_U + R_S}{(C_{DL} + C_{GPE})^2 R_S^2 \omega^2 + 1}$$

$$-Z'' = \frac{(C_{DL} + C_{GPE}) R_S^2 \omega}{(C_{DL} + C_{GPE})^2 R_S^2 \omega^2 + 1}$$

c)

Figure S4. The total surface area of the particles and their separations depend on the shape and size distribution. The charge of the composite material accumulates on the composite/dissolution surface, generating parallel associated graphite/dissolution microcapacitors on the electrode surface (a) for relatively low proportions of graphite above the first percolation threshold, (c) the contributions of the graphite/polyethylene and graphite/dissolution interfaces could not be separated, as their sum is obtained experimentally $C_{DL} + C_{GPE}$ (red equation) modelling with parallel capacitors.