Research Article
Electrical Characterization and Modeling of a Gelatin/Graphene System

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A gelatin/graphene composite has been analyzed by means of current density-voltage and the electrical impedance measurements. The DC electrical behavior has been interpreted in terms of an equivalent Thévenin model taking into account the open circuit voltage and the series resistance. A model based on the effect of the electrical double layer and on the diffusion of the charge carriers is used for the analysis of the experimental data, obtained in the frequency domain. The model reveals for any applied voltages a marked diffusion process at low frequencies. In particular, where the charge transfer mechanism is dominant, the time distribution of the reaction rates reveals that several multiple step reactions occur in the materials, especially at high values of the applied forward bias voltages.

1. Introduction
In the last decade, the emerging field of the “green” electronics has promoted the research to identify compounds of natural origin for the production of synthetic materials and biopolymers for biodegradable and biocompatible applications [1, 2]. In order to improve their thermal, mechanical, and electrical properties, compared to conventional inorganic materials, the bionanocomposites have been fabricated with a dispersion of nanosized fillers into the polymer matrix [3, 4]. Here, we present results using gelatin as biopolymer and graphene as a conductive filler. Gelatin is an animal protein and forms a structure with a high molecular weight and it is in many aspects similar to rigid-chain synthetic polymers [5]. The addition of graphene sheets gives the possibility to functionalize the resulting bionanocomposite in order to optimize the electrical properties for the fabrication of biodegradable energy storage devices [6]. In this work, gelatin and gelatin/graphene systems have been investigated, using current density-voltage measurements and electrical impedance spectroscopy.

2. Materials and Methods
Isopropanol, glycerol, and all aqueous solutions were prepared with Milli-Q water. Gelatin is from bovine skin type B with a gel strength of about 225 g Bloom. Aqueous suspensions of graphene have been prepared by exfoliation in low boiling point solvents of graphite flakes with a technique described in [7]. The gelatin solution was prepared by dissolving the gelatin in water and glycerol at 80°C. The incorporation of graphene particles was carried out by stirring the previous gelatin solution with the aqueous suspension of graphene for about 30 min at the same temperature. The resulting nanocomposites have a graphene concentration of 0.1%. The slurry obtained was firstly casted on a glass surface at room temperature and then dried for 72 h in a vacuum chamber at 25°C. The electrical measurements of the composites have been performed in a two-point contact geometry using a Keithley model “2400” source measurement unit. The impedance spectroscopy characterization has been done using an “HP 4199” impedance/gain-phase analyzer in the frequency region between 100 Hz and 100 KHz with an
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Gelatin/graphene
Al foil
Ag paste
+
−

Figure 1: Cross section geometry of the device.

![Figure 1](image)

AC-signal amplitude of 50 mV. All the measurements were performed at room temperature. An aluminum foil has been used as back contact and the top-contact has been fabricated by silver paste with an average area of 0.08 cm$^2$, as shown in Figure 1.

3. Results and Discussion

In Figure 2 the current density-voltage ($J$-$V$) characteristics of the gelatin/graphene system and of the pure gelatin have been compared. The blends have been characterized using a two-contact electrode geometry, as shown in Figure 1, and in a voltage range between 0 and 5 V. The devices show negative values of the current density under short circuit conditions. This "background current density" can be explained by the existence of the double layer capacitance and it is related to the nonfaradaic current during the discharge process. In this voltage range, the current density dependence from the bias voltage suggests that the addition of the graphene modifies the capacitance at the interface between the metallic contact and the bionanocomposites. As shown in Figure 2, it leads to an increase of the "background current density." In addition, the current density in the whole voltages range is increased due to the graphene sheets that lead to a higher conductivity of the blend. The current density signals have negative values up to voltages of about 1 V and subsequently they become positive. When the bias voltage is further increased, the current density is limited to a value of about 0.1 $\mu$A/cm$^2$ until an electrochemical reaction occurs in the device at a bias voltage of 1.8 V. Further on the current density increases rapidly, reaching a value of 0.1 mA/cm$^2$ at 3 V. When further increasing the forward bias voltage up to 5 V a moderate monotonic current increase has been observed.

The corresponding values of the open circuit voltage ($V_{OCV}$) are 0.97 V and 1.13 V for the pure gelatin and the gelatin/graphene system, respectively. According to the Thévenin theorem [8], the linear electric circuit may be represented as a series connection between an ideal voltage source $V_{OCV}$ and the internal resistance $R_S$, as shown in Figure 3.

In order to evaluate the value of $R_S$, the voltage is measured with a resistance load $R_L$ of 10 MΩ. The output voltage $V_X$ is 0.4 V and 0.2 V, respectively, for the blends with and without graphene content, as shown in Figure 4. Consequently, $R_S$ is defined as

$$R_S = R_L \times \left( \frac{V_{OCV}}{V_X} - 1 \right), \quad (1)$$

and the computed values of $R_S$ are 18.25 MΩ and 38.50 MΩ. In the case of an ideal battery, the value of this internal resistance is zero. As reported in the literature, the value of $R_S$ changes as a function of the temperature, ageing conditions, chemical properties, and discharge current [9]. Its value depends also on the ionic component, in particular on the electrolyte conductivity, ion mobility, charge transfer, and surface area of the electrode [9]. In our case, the insertion of
Figure 4: Time evolution of the output voltage with a load resistance ($R_L$) of 10 MΩ, measured at room temperature.

Figure 5: AC-equivalent circuit of the systems under analysis.

layers of graphene reduces the overall resistance by 50%, thus producing a strong enhancement of the output voltage.

In order to evaluate the faradaic process inside the devices, its AC electrical behavior can be modeled as a Randles circuit [10]. The double layer capacitance $C_{dl}$ modeling includes a constant phase element (CPE$_1$), whereas the Warburg impedance $Z_W$ is modeled as a series connection between a charge transfer resistance $R_{CT}$ and a further CPE element (CPE$_2$), as shown in Figure 5.

The resulting impedance in the Laplace domain is defined as

$$Y(\omega) = (j\omega)^{-\alpha}Q_1 + \frac{(j\omega)^{-\beta}Q_2}{1 + R_{CT}(j\omega)^{\beta}Q_2} \tag{2}$$

where $R_{CT}$ is the charge transfer resistance. The CPE parameters $\alpha$, $\beta$, $Q_1$, and $Q_2$ are frequency independent.

Figures 6 and 7 report the AC electrical impedance measurements of the gelatin based devices with and without the graphene addition, measured at room temperature and for different bias voltages ($V_{BIAS}$). The best fit to the experimental data using (2) is shown in Figures 6 and 7 as solid lines and dotted lines for different $V_{BIAS}$ values.

The fitting procedure with (2) gives the results reported in Tables 1 and 2. The impedance spectrum contains two distinct regions: at low frequencies, the prevalent mechanism is the diffusion of the electrons and ions, while, for frequencies above 2.5 KHz, the charge transfer mechanism becomes dominant. Here, the equivalent AC circuit can be reduced to a simple parallel connection of CPE$_1$ and $R_{CT}$.
Table 1: Best fitting values of parameters in (2) for pure gelatin based devices.

<table>
<thead>
<tr>
<th>( V_{\text{BIAS}} ) (V)</th>
<th>( \alpha )</th>
<th>( Q_1 ) (p( \Omega^{-1}\text{s}^\alpha ))</th>
<th>( \beta )</th>
<th>( Q_2 ) (( \mu\Omega^{-1}\text{s}^\beta ))</th>
<th>( R_{\text{CT}} ) (K( \Omega ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.878</td>
<td>66.33</td>
<td>0.643</td>
<td>0.215</td>
<td>57.64</td>
</tr>
<tr>
<td>1</td>
<td>0.878</td>
<td>67.70</td>
<td>0.714</td>
<td>0.140</td>
<td>58.67</td>
</tr>
<tr>
<td>3</td>
<td>0.889</td>
<td>55.40</td>
<td>0.472</td>
<td>0.843</td>
<td>56.71</td>
</tr>
<tr>
<td>5</td>
<td>0.907</td>
<td>41.10</td>
<td>0.186</td>
<td>6.81</td>
<td>47.07</td>
</tr>
</tbody>
</table>

Table 2: Best fitting values of parameters in (2) for gelatin/graphene blend based devices.

<table>
<thead>
<tr>
<th>( V_{\text{BIAS}} ) (V)</th>
<th>( \alpha )</th>
<th>( Q_1 ) (p( \Omega^{-1}\text{s}^\alpha ))</th>
<th>( \beta )</th>
<th>( Q_2 ) (( \mu\Omega^{-1}\text{s}^\beta ))</th>
<th>( R_{\text{CT}} ) (K( \Omega ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.895</td>
<td>42.36</td>
<td>0.671</td>
<td>0.186</td>
<td>92.20</td>
</tr>
<tr>
<td>1</td>
<td>0.895</td>
<td>42.20</td>
<td>0.648</td>
<td>0.233</td>
<td>95.16</td>
</tr>
<tr>
<td>3</td>
<td>0.899</td>
<td>39.26</td>
<td>0.495</td>
<td>0.680</td>
<td>95.02</td>
</tr>
<tr>
<td>5</td>
<td>0.923</td>
<td>26.47</td>
<td>0.147</td>
<td>6.298</td>
<td>72.94</td>
</tr>
</tbody>
</table>

Table 3: Extracted parameters from Nyquist spectra fitting using (3) and (4) for gelatin and gelatin/graphene blends.

| \( V_{\text{BIAS}} \) (V) | \( C_{\text{dl}} \) (pF) | \( D \) | \( \tau \) (\( \mu\text{s} \)) | \( C_{\text{dl}} \) (pF) | \( D \) | \( \tau \) (\( \mu\text{s} \)) |
|-----------------|----------------|---------|------|----------------|---------|------|------|
| 0               | 374.3          | 2.14    | 0.68 | 182.5          | 2.12    | 0.91 |
| 1               | 382.0          | 2.14    | 0.71 | 181.8          | 2.12    | 0.93 |
| 3               | 267.5          | 2.12    | 0.65 | 160.0          | 2.11    | 0.92 |
| 5               | 153.4          | 2.10    | 0.50 | 77.3           | 2.08    | 0.64 |

As reported by Hsu and Mansfeld [11], the value of the “true” capacitance related to the \( C_{\text{dl}} \) can be extracted directly to the value of \( Q_1 \) as follows:

\[
C_{\text{dl}} = Q_1 \left( \omega_{\text{max}} \right)^{-\alpha}. \tag{3}
\]

Here, \( \omega_{\text{max}} \) represents the frequency at the top of the semi-circle shown in the Nyquist plots of Figures 6 and 7. The resulting values of \( C_{\text{dl}} \) are listed in Table 3 for different \( V_{\text{BIAS}} \) values.

For both devices, the \( \alpha \) values can be associated with the frequency dependency of the CPE\(_1\) due to the surface roughness of the sample [12] or due to the nonuniformly distributed electrical properties of the surface [13]. A model of self-similar fractal electrodes, proposed by Nyikos and Pajkossy [14], gives the following relation between the exponent \( \alpha \) and the effective fractal dimension \( D \):

\[
\alpha = \frac{1}{(D - 1)}. \tag{4}
\]

The surface of the sample is not perfectly smooth and, for a rough surface, values of \( D \) between 2 and 3 are normally assumed. In our case, the values of \( \alpha \) are ranged between 0.89 and 0.92 for the bionanocomposite sample and between 0.87 and 0.90 for the pure gelatin sample. Therefore, the resulting values of \( D \) have a value of approximately 2.1 for all applied bias voltages and for both type samples, as also reported in Table 3. This confirms the role of the glycerol as a good plasticizer, resulting in a rather smooth surface. The same holds also for the sample with the addition of the graphene layers for all \( V_{\text{BIAS}} \) values. On the other hand, the contribution of the CPE\(_1\) element can also arise from different values of the multistep reaction rates at many different surface sites [13]. In our case, the time constant \( \tau' = R_{\text{CT}} \times Q_1 \) ranges between 0.9 \( \mu\text{s} \) and 0.5 \( \mu\text{s} \) for the analyzed devices, as shown in Table 3.

The dependence of this time constant on bias voltage can be related to the different reactions inside the bulk material and at the interfaces with the metal contacts. For bias voltages below 1 V, for both devices, the reaction rates are the same. A strong increase of the \( V_{\text{BIAS}} \) induces a marked decrease of the time constant to values of about 0.5 \( \mu\text{s} \). This means that the reactions involved in the device are changed. This is also confirmed by the results, shown in Figure 2, where an enhancement of the current density up to a value of 0.1 mA/cm\(^2\) at 5 V is found. Moreover, the filler addition to gelatin hinders the charge transfer process with a consequent increase of the \( R_{\text{CT}} \) value. Conversely, the value of the “true” capacitance \( C_{\text{dl}} \) is reduced to about 50% of its original value. Therefore, the resulting value of \( \tau \) does almost not change with the addition of the graphene sheets to the biopolymer. A marked drop of the \( \beta \) value with the increasing of the \( V_{\text{BIAS}} \) is probably due to the diffusion of the ionic species [15].

Only with a value of \( \beta \) of about 0.5, the equivalent impedance (CPE\(_2\)) becomes a pure \( Z_W \) and describes the linear semi-infinite diffusion, which obeys the second Fick’s law. Therefore, at low frequency, being the diffusion of the charge carriers, the dominant mechanism, a clear modification of the AC electrical impedance is evident, as shown in Figures 6 and 7. At high frequencies, the diffusion part becomes negligible as compared to the charge transfer mechanism.

4. Conclusion

The electrical characterization of a gelatin/graphene system has been performed at room temperature using impedance spectroscopy and current density-voltage measurements. An addition of graphene sheets to the biopolymer results in an enhancement of the electrical power transfer to the load due to a decreasing series resistance, without a decrease of the cell open circuit voltage. The modeling of the frequency behavior of the electrical impedance reveals for any applied voltages a marked diffusion process at low frequencies. In the frequency region, where the charge transfer mechanism is dominant, the time distribution of the reaction rates reveals that several multiple step reactions occur in the device, especially at high values of the applied forward bias voltages. The new gelatin/graphene nanocomposite material is a promising material for low cost power electronic applications, with the particular advantage to use only naturally occurring biopolymers with limited postprocessing necessity. A further improvement of the quality of the graphene samples, for example, by increasing the number of graphene layers and hence the associated surface area, should lead to a better energy storage capability.
Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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