Estudios de relajación dieléctrica a altas temperaturas en dióxido de titanio modificado con carbón activado

Dielectric relaxation studies in activated carbon doped Titanium Dioxide at high temperatures

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Resumen
El óxido de titanio (TiO₂) ha sido objeto de diferentes investigaciones en los últimos años, debido a su aplicabilidad en celdas solares, por sus interesantes propiedades ópticas, eléctricas y magnéticas. En este trabajo se presenta el estudio de la respuesta dieléctrica de pastillas prensadas de TiO₂ mezclado con carbón activado para diferentes fracciones molares. El comportamiento eléctrico de los compósitos es analizado cuando las muestras se someten en atmósfera de nitrógeno y de helio y se estudia mediante espectroscopía de impedancia compleja, en el intervalo de frecuencias de 50Hz a 5 MHz y desde temperatura ambiente hasta 723 K. Por los resultados del comportamiento dieléctrico de las muestras, se evidencia que una atmósfera de nitrógeno produce un dopaje aniónico, donde un anión (A) del nitrógeno entra en la red del TiO₂ en substitución de un oxígeno y forma el TiO₂-x Ax.

Palabras clave: Celdas solares, fotocatálisis, relajación dieléctrica, TiO₂.

Abstract
Titanium Dioxide (TiO₂) has been an object of different investigations in the recent years, principally to its applications in solar cells due to its interesting optic, electric and magnetic properties. In this work is presented the dielectric response study of activated carbon doped TiO₂ in pressed pills in different Molar relations. The electric behavior of the composites is obtained by bringing the samples to a Nitrogen and Helium atmosphere and studying with complex impedance spectroscopy, in the 50Hz to 5 MHz frequency interval and from room temperature to 723 K. The experimental results showed that the Nitrogen atmosphere leads to an anionic doping, in which an nitrogen anion (A) gets into the TiO₂ lattice, replacing an oxygen and forming TiO₂-x Ax.

Keywords: Dielectric relaxation, photocatalysis, solar cells, TiO₂.
1. Introduction

Titanium dioxide has been extensively investigated, because of its physicochemical properties that allows it to be a suitable material for a variety of applications (Sergiu et al., 2007; Feng et al., 2008; Yoon et al., 2009). It is a light sensitive semiconductor which absorbs electromagnetic radiation in the region near ultraviolet and it is very stable chemically. By the above features it is the most commonly used photocatalyst and it is currently used as degrader of organic molecules in the water purification process. It is also used as white pigment for its dispersion properties, antiscorrosive coating, gas sensor and generally in the ceramics industry (Kubacka et al, 2008; Garcia et al., 2009). This compound have three crystalline phases: rutile (tetragonal structure), anatase (octahedral structure), brookite (orthorhombic structure), which according to the requirement of the electrostatic valence rule, each oxygen atom is shared by three octahedra. For rutile each octahedron has two sides common with other octahedra; in brookite three and for anatase four sides shared by others octahedra. The TiO$_2$ has a band gap of 3.0 eV for rutile phase and 3.2 eV for the anatase phase. These values require ultraviolet radiation (UV) to be activated. Recent research (Barberio et al., 2014. Irie et al., 2003; Ochoa et al., 2009) focus on the possibility of reducing the bandgap size of anatase using doping materials such as nitrogen and carbon, thus taking advantage of the catalytic effect on a significantly larger wave spectrum. For the titanium dioxide doping, carbon has proved to be suitable as external atom, where the incorporation has reduced bandgap of 3.2 eV (pure anatase) to 2.32 eV (carbon doped phase), with which the required wavelength for excitation has been increased to 535 nanometers (Irie et al., 2003; Yoon et al., 2009). Thus, titanium dioxide mixed with carbon has significantly higher effectiveness than pure titanium dioxide. Due to this reported effect caused by the activated carbon on the TiO$_2$ matrix, it is also expected to affect the dielectric properties of the material, because of this, in this paper is studied the effect in the electrical properties of oxide titanium produced by the carbon impurities, for this was realized the electrical characterization of such composites in the form of pressed pellets obtained from commercial powder and different mole fractions of activated carbon using the technique of complex impedance spectroscopy. For it, are analized the Nyquist plots and formalism of the imaginary part of the electrical module in the time domain (Williams & Watts, 1970) for study the dynamic processes of dielectric relaxation of the carriers.

2. Experimental procedure

To prepare the TiO$_2$ mixed with activated carbon samples, it was used TiO$_2$ anatase phase with 99.5% purity (Aldrich), grain size 21 nm ~ and activated carbon powder (Aldrich). It also has been calculated the necessary amount of each for obtain mole fractions of X = 0.09, 0.04, 0.03 and 0.02 using stoichiometric calculation. After this procedure the precursors were mixed by hand macerated in an agate mortar for about three hours, until homogeneity was obtained. Compounds obtained were pressed at room temperature to obtain pill form in a hydraulic press. Infrared spectroscopy of the composites were performed on a spectrometer FTIR mark Shimadzu Prestige 21 with transparent tablets containing the sample and KBr as a binder (90 wt%), the qualitatively determination of the presents functional groups was done using a number of 16 sweeps and a resolution of 4 cm$^{-1}$. Measures of the complex electrical impedance at high temperatures are performed in a measuring cell adapted to a tubular three-zone furnace Carbolite TZF, this furnace can reach temperatures up to 1473 K. For data acquisition of electrical impedance was used the HIOKY 3532-50 LCR HITESTER equipment in a frequency range between 40Hz and 5MHz and an applied voltage signal of 0.5V. The sample was placed in the measuring cell between two circular shape flat electrodes of gold. Measurements were made from 323K to 723 K at intervals of 50K, in two different atmospheres, nitrogen and helium, with a constant flow and a pressure of 0.2 psi. Finally, adjustments to the experimental curves were obtained by equivalent electrical circuits in
the theoretical modeling software Zview2 and by using the decay function of the electric field KWW.

3. Analysis and results

3.1 Characterization for infrared spectroscopy with transformed of Fourier

Figure 1 shows the IR spectra of the samples of TiO₂ in different mole fractions of activated carbon. For macerated manually obtained compounds, the spectra shows a band at 3440 cm⁻¹, this is associated with the H-OH vibrational mode stress and where the transmittance or infrared absorption carbon increases with decreasing concentration. It was found a band at 2908 cm⁻¹ which is due to C-H bonds of aromatic groups, due to the presence of activated carbon, it has been observed that this band decreases drastically by reducing the carbon content. The band at 1630 cm⁻¹ corresponds to the water bending mode (Vargas et al., 2011). Looking specifically at the 1000 to 400 cm⁻¹ region of the spectrum, a broadband is defined as the activated carbon content increases. The characteristics bands of this region are located at 680 cm⁻¹ and can be associated with the vibrational mode of the functional group Ti-O-Ti and the functional group Ti-O (Ochoa et al., 2009). In general, in Figure 1 an increase of intensity with decreasing carbon content is observed, this shows that the formation of the various bounds is stronger at low mole fractions of carbon.

3.2 Complex electrical impedance characterization

Figure 2 shows the Nyquist plot, -Z'' vs. Z' for the behavior of the impedance of the composite system TiO₂, mixed stoichiometrically with activated carbon mole fractions X = 0.09, 0.03 and TiO₂ undoped to a temperature of 313 K at atmospheric pressure and without inert gas. At this temperature the typical impedance spectrum consists of a non-ideal semicircle around the frequency range, whose center is displaced under the real axis due to the sample volumetric response and it is not shown the double layer capacitance effect on the interface electrode / electrolyte, characterized by a linear response at low frequency. The non-ideal semicircle observed is modeled using an equivalent circuit (continuous curve) shown on the right side of Figure 2. The circuit consists of a resistor R, a capacitance C and constant phase element (CPE) connected in parallel. Once the resistance of the composite is obtained, it is possible to obtain the values of conductivity-dc of the sample using the σₐ = d / RA equation, where A and d are the area and thickness of the sample respectively. The values of the setting parameters obtained by the proposed equivalent circuit are presented in Table 1. It is found that for the obtained composite, the resistance values decrease considerably with increasing content of activated carbon, from 4.40E + 08 Ω to TiO₂, to 1.69E + 07Ω for the highest concentration of carbon X = 0.09. The values found for the capacitor were in the
orden de picofarads y no se observó cambio apreciable con la concentración de carbón activado. Los valores de la constante de fase reflejan un comportamiento de retraso de baja frecuencia que está relacionado con la correlación de los portadores en la red cristalina del material.

En la Figura 3 se muestra el diagrama de Nyquist, \( -Z'' \) (milliohms) vs \( Z' \) (milliohms) para \( TiO_2 \) mezclado con carbón activado para una fracción molar de \( X = 0.09 \), obtenido bajo nitrógeno en un rango de temperatura de 323K-523K y potencial 0.5V. Los datos experimentales se modelaron con el mismo circuito equivalente (curva continua) y se observa que la resistencia aumenta con la temperatura, lo cual es el comportamiento opuesto al observado en la atmósfera de nitrógeno. Los valores de capacidad (Tabla 2) del material están en orden de picofarads y no cambian apreciablemente con la temperatura, como se observa bajo nitrógeno.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>( R_1(M\Omega) )</th>
<th>CP1-T</th>
<th>CP1-P</th>
<th>C1 (PF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X = 0.09</td>
<td>1.69E+07</td>
<td>6.94E-11</td>
<td>0.73</td>
<td>4.72E-12</td>
</tr>
<tr>
<td>X = 0.03</td>
<td>2.25E+07</td>
<td>2.73E-10</td>
<td>0.55</td>
<td>3.87E-12</td>
</tr>
<tr>
<td>( TiO_2 )</td>
<td>4.40E+08</td>
<td>7.70E-11</td>
<td>0.64</td>
<td>9.41E-12</td>
</tr>
</tbody>
</table>

Tabla 1. Parámetros del circuito equivalente para el \( TiO_2 \) mezclado estóximétricamente con fracciones molares de carbón activado, obtenido a una temperatura de 333 K.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>( R_1(M\Omega) )</th>
<th>CP1-T</th>
<th>CP1-P</th>
<th>C1 (PF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>323</td>
<td>0.50</td>
<td>2.20E-09</td>
<td>0.55</td>
<td>13.1</td>
</tr>
<tr>
<td>373</td>
<td>3.00</td>
<td>3.15E-06</td>
<td>0.49</td>
<td>50.00</td>
</tr>
<tr>
<td>423</td>
<td>12.41</td>
<td>3.43E-06</td>
<td>0.42</td>
<td>32.11</td>
</tr>
<tr>
<td>473</td>
<td>29.53</td>
<td>1.79E-06</td>
<td>0.47</td>
<td>32.11</td>
</tr>
<tr>
<td>523</td>
<td>54.68</td>
<td>1.90E-06</td>
<td>0.47</td>
<td>32.11</td>
</tr>
<tr>
<td>573</td>
<td>19.59</td>
<td>7.93E-07</td>
<td>0.61</td>
<td>31.08</td>
</tr>
<tr>
<td>623</td>
<td>13.78</td>
<td>1.88E-07</td>
<td>0.74</td>
<td>12.85</td>
</tr>
<tr>
<td>673</td>
<td>13.78</td>
<td>1.88E-07</td>
<td>0.74</td>
<td>12.85</td>
</tr>
</tbody>
</table>

Tabla 2. Parámetros del circuito equivalente para el \( TiO_2 \) mezclado estóximétricamente con fracciones molares de carbón activado a una fracción molar de \( X = 0.09 \) bajo nitrógeno.

En la Figura 4 se muestra el diagrama de Nyquist, \( -Z'' \) (milliohms) vs \( Z' \) (milliohms) para \( TiO_2 \) mezclado con carbón activado con la misma fracción molar X = 0.09, ahora los datos son obtenidos en atmósfera de helio en un rango de temperatura de 323K-473K y un presión-0.2 psi. Los datos experimentales se modelaron con el mismo circuito equivalente (curva continua) y se observa que la resistencia aumenta con la temperatura, lo cual es el comportamiento opuesto al observado en helio. Los valores de capacidad (Tabla 2) del material están en orden de picofarads y no cambian apreciablemente con la temperatura, como se observa bajo helio.
nitrogen. Moreover, the value of the P parameter of the constant phase element is very close to one, showing that the orientation of the dipoles induced by applying external electric field is not highly correlated and approaches to a Debye behavior.

\[ \phi(t) = e^{-\left(\frac{t}{\tau}\right)^\beta}; \quad 0 < \beta \leq 1 \quad (2) \]

Where \( 0 < \beta < 1 \) is an exponent indicating the Debye relaxation deviation (\( \beta = 1 \)) and \( \tau \) represents a characteristic relaxation time.

The dynamics of the induced dipole orientation when applying the external electric field is analyzed with the electric modulus formalism and the following relationship,

\[ M'(\omega) = M_\infty \left[ 1 - \int \left( \frac{d\phi}{dt} \right) e^{-i\omega t} dt \right] \quad (1) \]

Where, \( M'(\omega) \) is the electrical modulus and \( M_\infty \) represents the value of its real part at high frequencies. In the equation is used the Kohlrausch-Williams-Watts (KWW) function (Williams & Watts,1970).

### Table 3. Parameter values of the equivalent circuit for the composite system formed for TiO_2 mixed stoichiometrically with activated carbon with mole fraction X=0.09 under helium.

<table>
<thead>
<tr>
<th>T(K)</th>
<th>R1(MΩ)±</th>
<th>CP1-T</th>
<th>CP1-P</th>
<th>C1(PF)±</th>
</tr>
</thead>
<tbody>
<tr>
<td>323</td>
<td>2.51</td>
<td>4.12 E-9</td>
<td>0.50</td>
<td>11.40</td>
</tr>
<tr>
<td>373</td>
<td>0.58</td>
<td>1.51E-09</td>
<td>0.77</td>
<td>9.51</td>
</tr>
<tr>
<td>423</td>
<td>0.46</td>
<td>3.23E-10</td>
<td>0.77</td>
<td>2.14</td>
</tr>
<tr>
<td>473</td>
<td>0.34</td>
<td>2.35E-09</td>
<td>0.77</td>
<td>8.00</td>
</tr>
</tbody>
</table>

Figure 4. Plot Nyquist for the composite formed for TiO_2 mixed stoichiometrically with activated carbon with mole fraction of X=0.09 under helium in a temperature range of 323K - 473 K.

Figure 5. Plot Bode phase for the composite formed for TiO_2 mixed stoichiometrically with activated carbon with mole fraction of X=0.09 under helium in a temperature range of 323K - 473 K.

The imaginary modulus \( M''(\omega) \) for the TiO_2 plus activated carbon composite with \( x=0.09 \) concentration, obtained in a first heating under a nitrogen atmosphere and applying a potential of 0.5 V, shown in Figure 5. The points correspond to the experimental data and solid line corresponds to the adjustment obtained using equation 1. The imaginary module has a maximum whose value decreases and the peak position with the frequency shifts to the low frequency region at increases of the temperature, evidencing the existence of a relaxation process associated with the orientation of dipoles of the composite system, which is thermally deactivated. The relaxation frequency \( \omega_p \) corresponds to \( M_{max} \), given the more probable relaxation time \( \tau_p \) by the condition \( \tau_p \omega_p = 1 \) (Macdonald et al., 2005). The asymmetric and broad shape of the imaginary part of the electrical module is described by the exponent \( \beta \) of the exponential KWW function. The \( \beta \) exponent values found in the fit, change depending on the temperature and range from a value of \( \beta = 0.68 \) at 323 K, to \( \beta = 0.47 \) to 523 K. These values of \( \beta \) clearly indicate that the relaxation process of induced dipoles goes away of a Debye type behavior for an increasing temperature. The ease or difficulty of a molecule to be reoriented in a solid depends on its shape and its interactions with their environment, according with the applied temperature and the inclusion of dopant in the material the relaxation time will change. Usually, in the measures at a range of frequencies higher than the characteristic relaxation frequency, the contribution to the electrical modulus is not observed. Physically, it happens that the applied frequency for measurement is too high and the dipoles cannot follow the oscillations of the applied electric field, therefore these dipoles do not participate in the polarization of the material (Jonscher, 1999). The fact that the peak of the module moves to lower frequencies and is much wider with increasing temperature, responds to the stabilization of the amorphous walls of TiO_2 with consequent...
delay of the crystallization temperature caused by
the presence of carbon. Furthermore, for high mole
fractions of carbon, a presumably crystallization has
occurred due to the high dispersion of the carbon
particles in the matrix of TiO₂, being strongly delayed
the temperature of transformation. Moreover for an
nitrogen atmosphere is produced an anionic doping
where an anion (A) of Nitrogen enters the TiO₂
network to substitute an oxygen atom and form
TiO₂⁺A⁻ (Sauthier et al., 2012).

In Figure 6 is shown the M (ω) imaginary part of the
modulus for a system formed by TiO₂ with a molar
fraction of activated carbon X = 0.09, obtained by
heating the sample in a helium atmosphere and
applying a potential of 0.5 V , as shown in figure 5
the points correspond to the experimental data and
the solid line corresponds to the setting obtained
using equation 1. When the sample is subjected to a
helium atmosphere, the modulus imaginary part has
a maximum whose value remains approximately
constant and contrary to what is presented in a
nitrogen atmosphere, the peak position in function
of the frequency shifts to the high frequency
region with increases of the temperature, giving
evidence of the existence of a relaxation process
associated with the orientation of dipoles of the
composite system, which it is thermally activated.

The values of β exponent found in the fit increases
progressively with increasing temperature from a
value of β = 0.45 at 323 K, to β = 0.64 at 523 K. The
values of β exponent obtained for a sample in the
presence of an atmosphere of helium are completely
different from those obtained for a sample under a
nitrogen atmosphere, indicating the great influence
of the kind of atmosphere in the processes of dipole
orientation induced in the composite. The values of
the setting parameters are reported in Table 5, the
lines in various boxes, means that it is not possible
to obtain the value because the experimental curve
of the imaginary part of the electrical modulus does
not have a maximum well defined or it cannot be
solve in the frequency range of the impedance meter.
Similar behavior is studied for other composites,
with different mole fractions of activated carbon.

Table 4. Adjustment parameters obtained
by the model KWW for the TiO₂ mixed
stoichiometrically with activated carbon
to a mole fraction X=0.09 under nitrogen.

<table>
<thead>
<tr>
<th>T(K)</th>
<th>B ± 0.01</th>
<th>Log Wn(Hz)±0.01</th>
<th>M’’max</th>
</tr>
</thead>
<tbody>
<tr>
<td>323</td>
<td>0.68</td>
<td>5.05</td>
<td>11.05</td>
</tr>
<tr>
<td>373</td>
<td>0.67</td>
<td>4.28</td>
<td>10.42</td>
</tr>
<tr>
<td>423</td>
<td>0.62</td>
<td>3.80</td>
<td>10.62</td>
</tr>
<tr>
<td>473</td>
<td>0.53</td>
<td>3.55</td>
<td>10.62</td>
</tr>
<tr>
<td>523</td>
<td>0.53</td>
<td>3.57</td>
<td>9.62</td>
</tr>
<tr>
<td>573</td>
<td>0.47</td>
<td>3.75</td>
<td>10.02</td>
</tr>
</tbody>
</table>

Table 5. Adjustment parameters obtained by
the model KWW for the composite system
TiO₂ mixed stoichiometrically with activated
carbon mole fraction X=0.09 under helium.

<table>
<thead>
<tr>
<th>T(K)</th>
<th>β ±0.01</th>
<th>Log Wn(Hz) ±0.01</th>
<th>M’’max</th>
</tr>
</thead>
<tbody>
<tr>
<td>323</td>
<td>0.45</td>
<td>5.25</td>
<td>34.60</td>
</tr>
<tr>
<td>373</td>
<td>0.45</td>
<td>5.70</td>
<td>37.00</td>
</tr>
<tr>
<td>423</td>
<td>0.45</td>
<td>5.81</td>
<td>37.50</td>
</tr>
<tr>
<td>473</td>
<td>0.45</td>
<td>6.00</td>
<td>40.00</td>
</tr>
<tr>
<td>523</td>
<td>0.45</td>
<td>7.60</td>
<td>36.80</td>
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<tr>
<td>573</td>
<td>0.63</td>
<td>8.00</td>
<td>78.60</td>
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<td>0.64</td>
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<td>13.60</td>
</tr>
<tr>
<td>673</td>
<td>0.64</td>
<td>8.70</td>
<td>9.60</td>
</tr>
<tr>
<td>723</td>
<td>0.64</td>
<td>8.80</td>
<td>7.60</td>
</tr>
</tbody>
</table>
4. Conclusions

The addition of activated carbon in the matrix of the obtained titanium oxides does not produce significant changes in the vibrational modes of TiO₂. The values of the proposed equivalent circuit parameters show that the sample under nitrogen atmosphere presents higher resistance values with the increase of the temperature, opposite to the process that presents the sample under helium atmosphere, which means that the TiO₂ mixed with activated carbon, can be used as gas sensor. Meanwhile the value of the β exponent of KWW model shows a relaxation process of induced dipole which is disfavored with increasing temperature when the sample is subjected to a nitrogen atmosphere. The results of the dielectric response of the studied composites, suggest that nitrogen produces a anionic doping, where an anion (A) of Nitrogen enters in the network of TiO₂ to substitute an oxygen and form TiO₂-xAx.

5. References


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