INGENIERÍA DE MATERIALES

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

MATERIALS ENGINEERING

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

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Resumen

El óxido de titanio (TiO_2) 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 TiO_2 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 espectroscopia 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 TiO_2 en substitución de un oxígeno y forma el $TiO_{2-x} A_x$.

Palabras clave: *Celdas solares, fotocatálisis, relajación dieléctrica,* TiO_2.

Abstract

Titanium Dioxide (TiO_2) 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 TiO_2 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 TiO_2 lattice, replacing an oxygen and forming $TiO_{2-x} A_x$.

Keywords: *Dielectric relaxation, photocatalysis, solar cells,* TiO_2.

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, anticorrosive 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

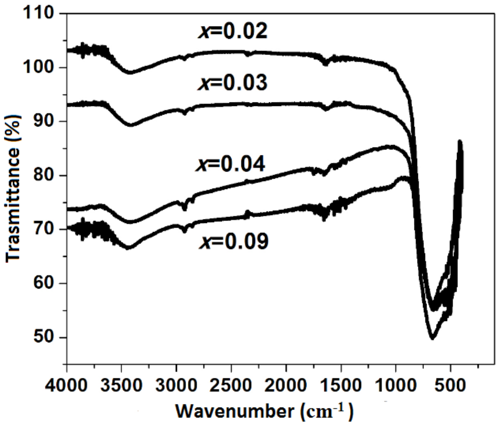

Figure 1. FTIR spectra of the samples of TiO$_2$ in different mole fractions of activated carbon.

Figure 1 shows the IR spectra of the samples of TiO$_2$ 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

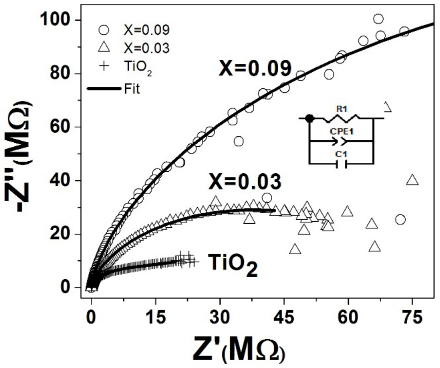

Figure 2. Nyquist plot for the composite formed for TiO$_2$ mixed stoichiometrically with activated carbon mole fractions, obtained at a temperature of 313 K and a potential of 0.5V.

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 TiO$_2$ 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 $\sigma_0 = d / RA$ 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 fount that for the obtained composite, the resistance values decrease considerably with increasing content of activated carbon, from 4.40E + 08 Ω to TiO$_2$, to 1.69E + 07Ω for the highest concentration of carbon X = 0.09. The values found for the capacitor were in the order of picofarads and no appreciable change with the concentration of activated carbon was found. P values of constant phase element parameter reflect a distribution of relaxation times, which is related to phenomena of correlation of carriers in the crystal lattice of the material.

Table 1. *Parameter values of the equivalent circuit for the* TiO_2 *mixed stoichiometrically with activated carbon mole fractions, obtained at a temperature of 313 K.*

Concen-tration	R1(MΩ) ±0.02	CP1-T	CP1-P	C1 (PF) ± 0.02
X=0,09	1.69E+07	6.94E-11	0.73	4.72E-12
X=0,03	2.25E+07	2.73E-10	0.55	3.87E-12
TiO_2	4.40E+08	7.70E-11	0.64	9.41E-12

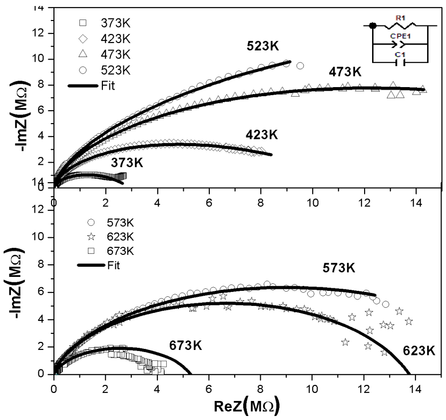

Figure 3. *Nyquist plot for a mole fraction of X=0.09 under nitrogen, in a temperature range of 323K-623K and potential 0.5V.*

In Figure 3 the Nyquist plot, -Z '' (milliohms) vs Z '(milliohms) for TiO_2 mixed with activated carbon for a molar ratio of X = 0.09, obtained under nitrogen at a temperature range between 323K, 723K and a pressure 0.2 psi. The different discrete symbols correspond to the experimental data representing the dielectric response of the composite, while the continuous curve represents the adjustment data obtained by the same equivalent circuit used in the above analysis. The electrical response as a function of temperature has a well-defined region in the entire frequency range, which is shaped like a not ideal semicircle due to the predominance of the dielectric response of the material over the conductor behavior. The values obtained for the different adjustment parameters are presented in Table 2. It is found in the upper diagram of Figure 3 that the volume resistance value R1 increases progressively with increasing temperature from 323-523 K. Moreover it shows that the resistance decreases as the temperature increases from 523K, which is a typical behavior of semiconductor materials. Moreover, the volume Capacitance of the sample is mostly of the order of picofarads and varies very little with increasing temperature. It is found that the value of parameter P of the constant phase element, decreases significantly from 323-523 K, showing that the system becomes more capacitive and the relaxation of induced dipoles in the material is highly correlated with increasing temperature, whereas for temperatures above 523 K, it retakes values close to one, showing that the relaxation of oriented dipoles is very close to the Debye type behavior.

Table 2. *Parameter values of the equivalent circuit for the* TiO_2 *mixed stoichiometrically with activated carbon to a mole fraction X=0.09 under nitrogen.*

T (K)	**R1(MΩ) ±0.02**	**CP1-T**	**CP1-P**	**C1 (PF) ± 0.02**
323	0.50	2.20E-09	0.55	13.1
373	3.00	3.15E-06	0.49	50.00
423	12.41	3.43E-06	0.42	32.11
473	29.53	1.79E-06	0.47	32.11
523	54.68	1.90E-06	0.47	32.11
573	19.59	7.93E-07	0.61	31.08
623	13.78	1.88E-07	0.74	12.85
673	13.78	1.88E-07	0.74	12.85

In the Figure 4 it is shown the Nyquist plot, -Z '' (milliohms) vs Z '(milliohms), for TiO_2 mixed with activated carbon for the same molar ratio X = 0.09, but now the data is obtained in helium atmosphere in a temperature range of 323K to 473K and a pressure-0.2 psi. Experimental data were modeled with the same equivalent circuit (continuous curve) and is found that the resistance increases with increasing temperature, opposite to the observed behavior under nitrogen. Capacitance values (Table 2) of the sample are in the order of picofarads and does not change appreciably with temperature increases, as observed under 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.

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.*

T(K)	R1(MΩ)± 0.02	CP1-T	CP1-P	C1(PF) ±0.02
323	2.51	4,12 E-9	0.50	11.40
373	0.58	1,51E-09	0.77	9.51
423	0.46	3,23E-10	0.77	2.14
473	0.34	2,35E-09	0.77	8.00

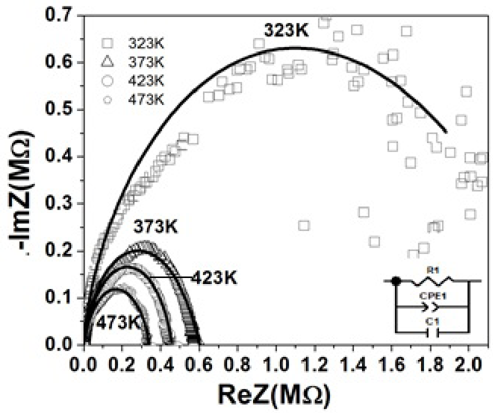

Figure 4. *Plot Nyquist for the composite formed forTiO2 mixed stoichiometrically with activated carbon with mole fraction of X=0.09 under helium in a temperature range of 323K - 473 K.*

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

$$M^*(\omega)=M_\infty\left[1-\int\left(-\frac{d\phi}{dt}\right)e^{-i\omega t}dt\right] \qquad (1)$$

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

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

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

The imaginary modulus *M''(ω)* 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 ωp corresponds to Mmax, given the more probable relaxation time τp 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 β of the exponential KWW function. The β exponent values found in the fit, change depending on the temperature and range from a value of β = 0.68 at 323 K, to β = 0.47 to 523 K. These values of β 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 TiO_2, 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 $TiO_{2-x}A_x$ (Sauthier et al., 2012).

Table 4. *Adjustment parameters obtained by the model KWW for the* TiO_2 *mixed stoichiometrically with activated carbon to a mole fraction X=0.09 under nitrogen.*

T(K)	B ± 0.01	Log Wn(Hz)±0.01	M"max
323	0.68	5.05	11.05
373	0.67	4.28	10.42
423	0.62	3.80	10.62
473	0.53	3.55	10.62
523	0.53	3.57	9.62
573	0.47	3.75	10.02

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.

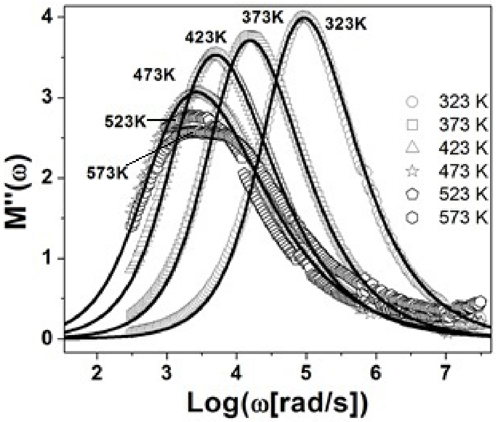

Figure 5. *Imaginary part of the electrical module in function of frequency for a molar fraction X=0.09 under nitrogen and temperatures 323K to573K.*

Table 5. *Adjustment parameters obtained by the model KWW for the composite system* TiO_2 *mixed stoichiometrically with activated carbon mole fraction X=0.09 under helium.*

T(K)	β ±0.01	Log Wn(Hz) ±0.01	M"max
323	0.45	5.25	34.60
373	0.45	5.70	37.00
423	0.45	5.81	37.50
473	0.45	6.00	40.00
523	0.45	7.60	36.80
573	0.63	8.00	78.60
623	0.64	8.30	13.60
673	0.64	8.70	9.60
723	0.64	8.80	7.60

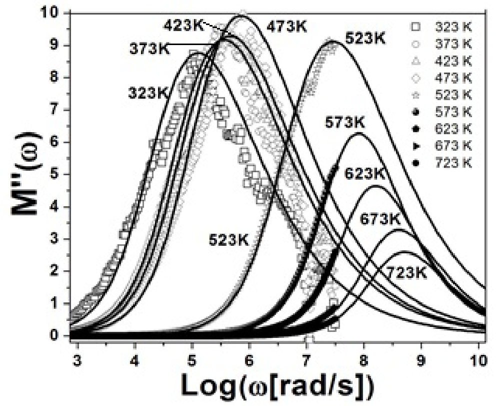

Figure 6. *Imaginary part of the electrical module in function of frequency for a molar fraction X=0.09 under helium and temperatures 323K to723K..*

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 TiO_2. 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 TiO_2 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 TiO_2 to substitute an oxygen and form $TiO_{2-x}A_x$.

5. References

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