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Influence of Sintering Temperatures on Structure and Electrical Conductivity of TiO_2 Cathode

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The influence of sintering temperatures on the structure and electrical property of TiO_2 cathode was investigated with regards to the crystal structure and composition, microstructure, oxygen vacancies, surface properties and electrical conductivity. The as-products were characterized by powder X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), digital four-point probe conductivity instrument (DFFPCI) and accelerated surface area and porosimetry system (ASAP). XRD analysis confirms that anatase phase TiO_2 at 700 ºC transformed to rutile phase TiO_2 and $TiO_{1.95}$ with the increase of sintering temperatures to 850 ºC and 950 ºC. The Ti°Cp binding energy of TiO_2, as studied by XPS, is discussed in terms of the valence state of the titanium ions. Digital four-point probe conductivity instrument analysis indicate that the electrical conductivity increase with the rise of temperature. Scanning electron microscopy and accelerated surface area and porosimetry system analysis indicate that the grain of the obtained TiO_2 increase but nitrogen storage properties decrease with the increase of sintering temperatures. Moreover, the experimental results show that the electrical conductivity of TiO_2 increases with the rise of the temperature.

Key Words: TiO_2, Cathode, Sintering temperature, Surface, Microstructure.

INTRODUCTION

Over the past decade, TiO_2 has attracted much attention due to its favourable physical, optical and electrical properties and various potential applications in various fields such as gas sensor[1,2], thin film capacitors[3,4], photocatalyst[5,6] and solar cells[7,8], *etc.* As is known to all, TiO_2 is an oxygen-deficient compound, temperature and oxygen partial pressure can greatly affect its crystal structure, chemical composition and properties. TiO_2 has three phases of brookite, anatase and rutile at different temperatures and the metastable phase anatase differs in electronic properties from the phase rutile. Moreover, rutile structure is thermodynamically more stable than the anatase structure and also is more dense. On the other hand, pure TiO_2 is electrically insulating or poorly conductive and its electrical conductivity is small ($< 10^{-13}$ S/cm). In general, sintering is a key step in the preparation of TiO_2 cathode and sintering temperature has a large effect on the phase, structure and electronic transport properties of the final products.

In recent years, many efforts have been devoted to investigate the formation of non-stoichiometric TiO_2 and various doping TiO_2 and its electronic properties, photoelectrochemical properties and wettability. For instance, Abdel-Aziz *et al.*[9] studied the dependence of the electrical conductivity in the temperature range (148-373 K) of polycrystalline TiO_2 and Ti_2O_3. Yakuphanoglu *et al.*[10] investigated the electrical, microstructure and crystal structure properties of Ni-doped TiO_2. Wang *et al.*[11] studied the nonlinear electrical behaviour and dielectric properties of (Ca, Ta)-doped TiO_2 ceramics which were obtained by sintering at 1300 ºC. Meng Fan-ming investigated influence of sintering temperature on nonlinear electrical properties of (Sr, Bi, Si, Ta)-doped TiO_2-based varistor ceramics which were obtained by sintering at 1350 ºC[12]. However, little attention has been paid to the detailed effects of the sintering temperatures on the microstructure, surface properties and electrical conductivity of TiO_2 cathode.

In this paper, we investigate the influence of sintering temperatures on the phase, microstructure, surface properties, oxygen vacancies and electrical conductivity properties of TiO_2 cathode. The chemical compositions of the as-prepared TiO_2 cathode sintered at diffferen temperatures are measured by XRD and XPS. The porosity and mean pore size of TiO_2 cathode at different temperatures are also investigated. Moreover, the effect of sintering temperature on the electrical conductivity properties of TiO_2 cathode are also investigated.

EXPERIMENTAL

Synthesis of TiO_2 cathode: TiO_2 (AP, 99.9 %) powders were sintered at a rate of 10 ºC/min in the tubular resistance furnace (SGM6816BK) under argon atmosphere for 5 h. After

that, they were cooled to room temperature. Then they were pressed by 16 MPa and sintered at different temperatures to make into 0.5 g TiO_2 pallets. The sintering temperatures were 700, 850 and 950 ºC respectively. The TiO_2 pellets sintered at different temperatures were assembled into the cathode. Finally, TiO_2 cathode were obtained.

Characterization: The phase composition, the surface topography and chemical analysis of TiO_2 sintered were performed by XRD-6000 X-ray diffraction (XRD) with CuK_α radiation (λ = 0.15406 nm) through a continuous scan mode with speed of 4 º/min, VEGA IILMU scanning electron microscope (SEM) and X-sight energy dispersive spectrum (EDS). The oxygen vacancies of samples sintered were characterized by ESCALAB250 X-ray photoelectron spectra (XPS) with AlKa (hγ = 1486.6 eV) as an excitation source. The XPS peak positions of each element were corrected by using of C1s (285.0 eV). The electrical conductivity of TiO_2 pallets were performed with a digital four-point probe conductivity instrument (DFPPCI; SX1934). The surface properties and pore-size distribution were determined by ASAP 2010 (accelerated surface area and porosimetry system).

RESULTS AND DISCUSSION

Effect of sintering temperatures on phase composition of TiO_2 cathode: Fig. 1 shows the XRD patterns of as-prepared TiO_2 pallets sintered for the same reaction time of 5 h at (a) 700 ºC, (b) 850 ºC and (c) 950 ºC, respectively. The crystalline phase of the pallets sintered at 700 ºC was dominantly anatase in Fig. 1(a), whereas the pellets treated at 850 and 950 ºC show peaks characteristic of both the rutile TiO_2 and rutile $TiO_{1.95}$ phase in Fig. 1(b) and Fig. 1(c). With increasing of sintering temperature, the intensities of the peaks increased to some extent. The crystal size of the prepared TiO_2 sintered at 700, 850 and 950 ºC were estimated to be 65.3, 92.0 and 103.0 nm in diameter by the Scherrer's equation, respectively. The biphase TiO_2 sintered at 850 ºC contains about 50 % of the rutile $TiO_{1.95}$ phase, while the biphase TiO_2 sintered at 950 ºC contains about 59 % of the rutile $TiO_{1.95}$ phase. The phase composition of the samples can be calculated from the equation[13]:

$$X_R = 1 - \left[1 + 1.26\left(\frac{I_R}{I_A}\right)\right]^{-1}$$

, where X_R is the weight fraction of rutile $TiO_{1.95}$ in the mixture, I_R and I_A are the peak intensities of the rutile $TiO_{1.95}$ and rutile TiO_2 diffractions, respectively.

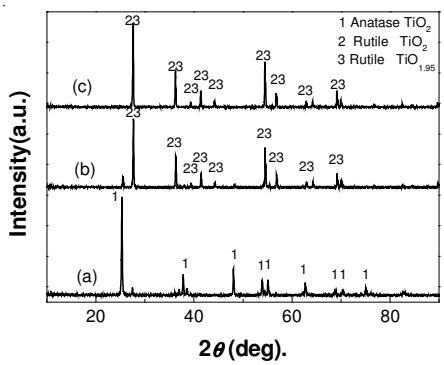
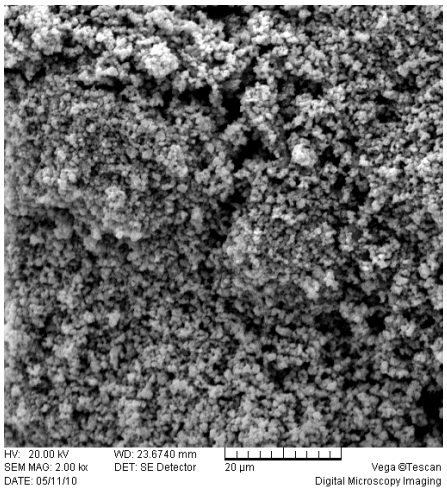


Fig. 1. XRD patterns of as-prepared TiO_2 cathode sintered for the same reaction time of 5 h at (a) 700 °C (b) 850 °C and (c) 950 °C

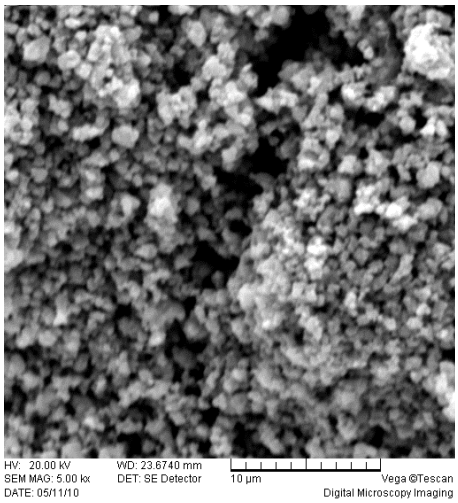
Effect of sintering temperatures on morphologies of TiO_2 cathode: The scanning electron micrographs (SEM) of TiO_2 pellets sintered at different temperatures for 5 h are presented in Fig. 2. It is seen in figures that with the increase of temperature, the TiO_2 grains are growing larger and tending to be homogenized, while the porosity decreases and monolithic structure tends to be more densification. The grains in microstructure may have an important effect on electronic properties of the samples. EDX of TiO_2 pallets sintered for the same reaction time of 5 h at (a) 700 ºC, (b) 850 ºC and (c) 950 ºC, respectively is shown in Fig. 3 and the corresponding contents of elements are given in Table-1, which indicate that the samples have polycrystalline and the sample includes three elements (Ti, O and Au). Gold is introduced in process of the sample prepared for SEM inspection. The results show that content of titanium increases and oxygen decreases with the rise of temperature.

TABLE-1
THE CONTENTS OF ELEMENTS FOR SAMPLES SINTERED AT DIFFERENT TEMPERATURES

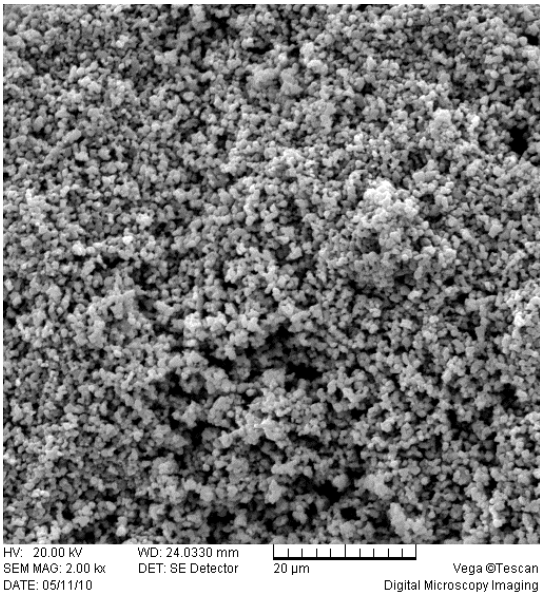
Temp. (ºC)	Content of elements (wt %)		
	Ti	O	Au
700	50.91	35.20	13.89
850	54.86	32.33	12.81
950	60.09	27.19	12.72



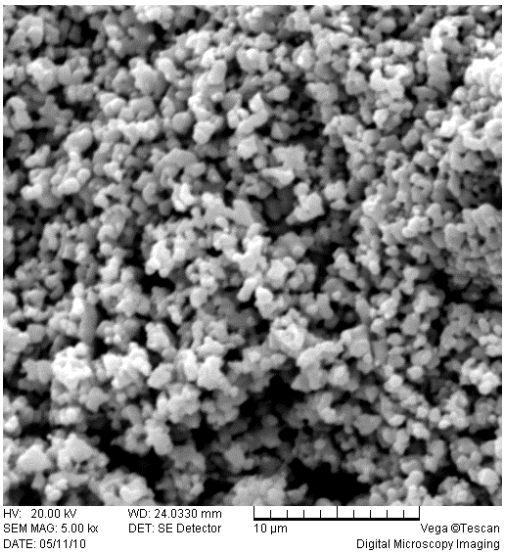
a_1



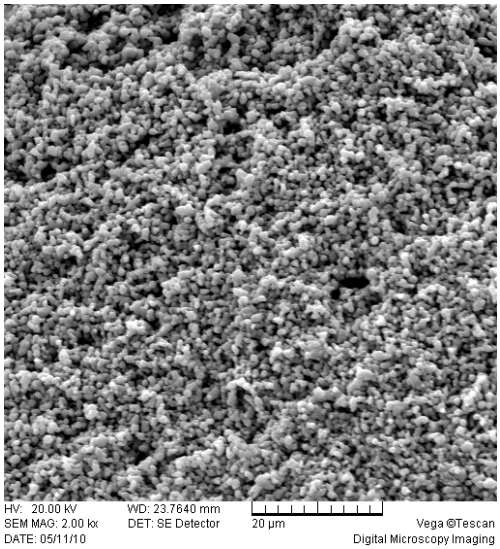
a_2



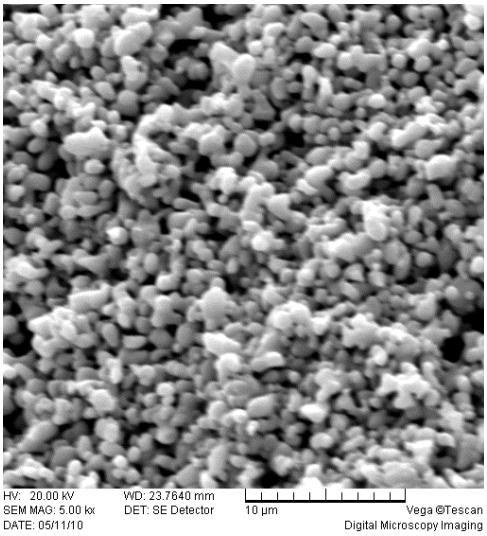
b_1



b_2

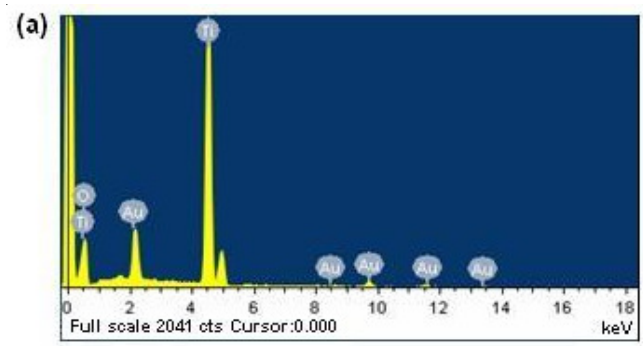


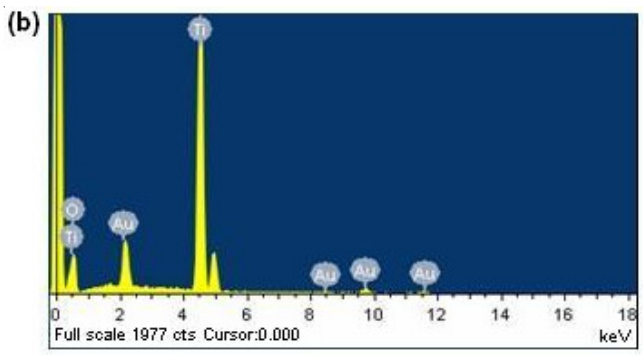
c_1



c_2

Fig. 2. SEM morphologies of TiO_2 cathode sintered for the same reaction time of 5 h at (a) 700 °C (b) 850 °C and (c) 950 °C





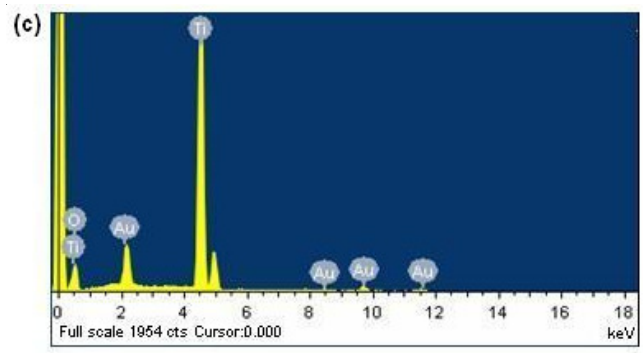
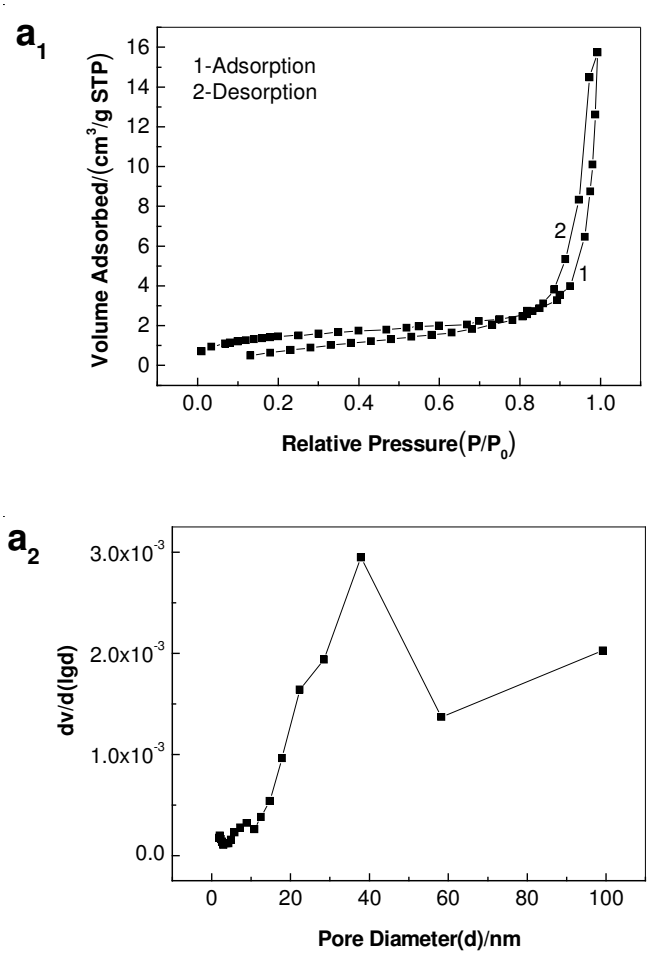


Fig. 3. EDX photographs and chemical composition of TiO_2 cathode sintered for the same reaction time of 5 h at (a) 700 °C (b) 850 °C and (c) 950 °C

Effect of sintering temperatures on the suface areas and pore-size distribution: The surface parameters of surface area and the data calculated from the *t*-plot were estimated by the low-temperature nitrogen adsorption at relative pressures (P/P_0) in the range of 0.0-1.0. The BET surface areas of TiO_2 cathode sintered at 700, 850 and 950 ºC are 4.9327, 2.4437 and 1.6419 m^2/g, respectively. With the increase of temperature, the specific surface areas of TiO_2 cathode decrease.

The textural parameters of TiO_2 cathode were obtained by nitrogen adsorption-desorption experiment at 77 K. Fig. 4 shows the nitrogen adsorption-desorption isotherms and the corresponding pore size distributions of the TiO_2 cathode sintered at different temperatures. As shown in Fig. 4(a_1), (b_1), (c_1), the similar nitrogen adsorption-desorption isotherms of all samples can be classified as a type IV isotherm, each hysteresis loop is type H_2 and a steep increase in nitrogen volume adsorbed at higher P/P_o (by the mechanism of capillary condensation) indicate a typical of a mesoporous material[14-17]. Furthermore, the pore size distributions are reported in Fig. 4(a_2), (b_2), (c_2) for TiO_2 sintered at various temperatures and concentrate below 50 nm. According to IUPAC classification, pores within porous materials can be divided into micropore (width less than 2 nm), mesopore (width between 2 and 50 nm) and macropore (width greater than 50 nm)[18-20]. From above analysis, we can obtain that the samples sintered at 700, 850 and 950 ºC are mesoporous structure.



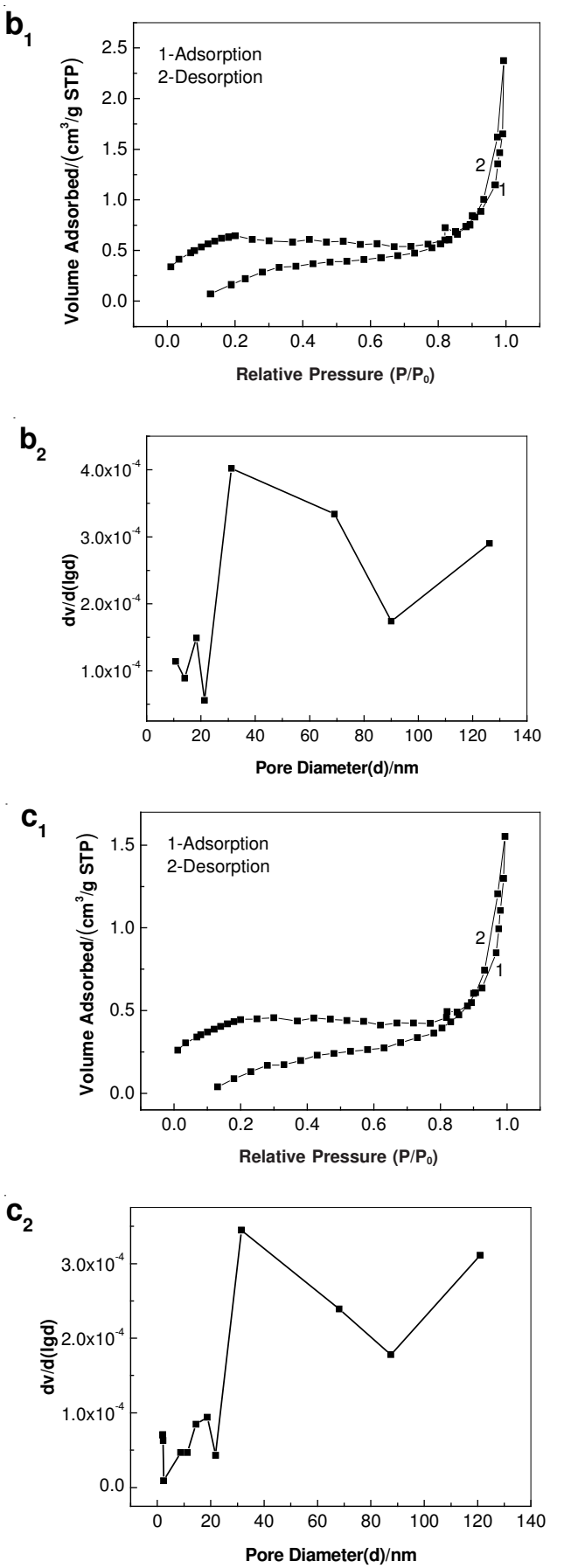


Fig. 4. Nitrogen curves and pore-size distribution of the TiO_2 sintered for the same reaction time of 5 h at (a) 700 °C (b) 850 °C and (c) 950 °C

Effect of sintering temperatures on the electrical conductivity of TiO_2 cathode: In general, electrical conductivity of TiO_2 can be enhanced by doping. For instance, da Silva *et al.*[21] studied the electrical conductivity of TiO_2 single crystals doping of chromium ions implanted with 140 keV at room temperature. It changed from variable to fixed range hopping. Patil *et al.*[22] investigated the electrical resistivity of TiO_2 doped WO_3 thin films. It decreased with the increase of temperature. Karthik *et al.*[23] reported nickel-doped anatase TiO_2 nanoparticles by sol-gel method, the conductivity of which decreases with increasing Ni-dopant concentration. Holt *et al.*[24], demonstrated the electrical conductivity of Cr_2O_3 doped with TiO_2. It decreased with TiO_2 concentration higher than 10 mol %. However, not only doping but also sintering can be changed the electrical conductivity of TiO_2 cathode. In present investigation, the electrical conductivity of the as-prepared TiO_2 pellets is shown in Fig. 5. With the increase of temperature from 700-950 ºC, the electrical conductivity of the TiO_2 pellets slightly increased, indicating the semiconductor behaviour of TiO_2 cathode. The electrical conductivity of the samples may be analyzed by the well-known Arrhenius relation[10]:

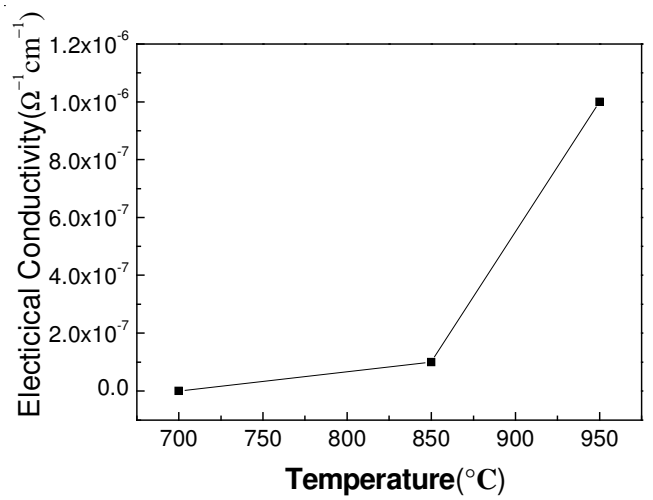


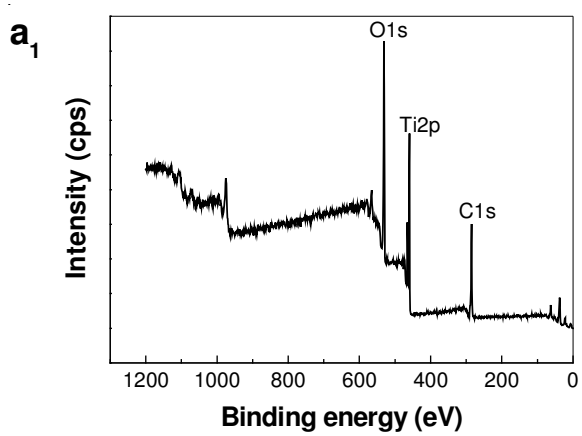
Fig. 5. Electrical conductivity of TiO_2 cathodes sintered at different temperatures

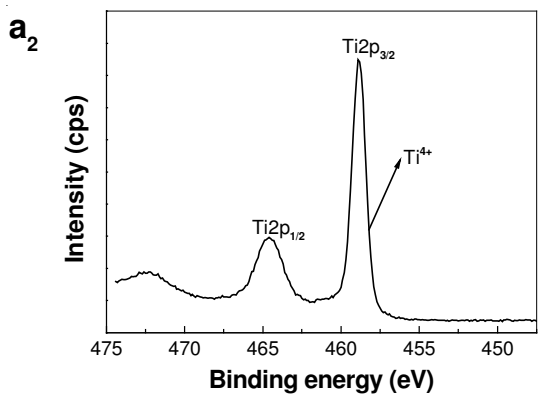
$$\sigma = \sigma_o \exp\left[-\frac{\Delta E}{KT}\right]$$

where σ_0 is the pre-exponential factor, ΔE is the activation energy for conduction and k is the Boltzmann constant. In this formula, it is assumed that the activation energy (ΔE) is independent of temperature (T). As can be seen, the electrical conductivity of TiO_2 cathode increases with the increasing temperature.

The possible reason may be explained by considering various effects. Firstly, the $TiO_{1.95}$ phase may increase the electron concentration of the system for the electric charge balance, which results in the increase of the electrical conductivity of the obtained TiO_2 cathode. Furthermore, under the low oxygen and high temperature conditions, different oxygen atoms in TiO_2 crystal get different force in which some oxygen atoms with small force obtain enough energy, which leave the equilibrium position to generate oxygen vacancies and an increase of deviation of stoichiometric ratio. It also increases the electrical conductivity of TiO_2 cathode. From above analysis, the increase of the electrical conductivity is mainly due to the increase in the electron concentration of the system. Therefore, it is believed that $TiO_{1.95}$ generation and oxygen vacancies are fairly effective in achieving high conductivity of TiO_2 cathode. Furtherwork concerning about investigation of detailed mechanism is in progress.

Effect of sintering temperature on oxygen vacancies of TiO_2 cathode: The composition of the titania pellets was measured by XPS. XPS survey spectra of the TiO_2 pellets sintered in argon at 700, 850 and 950 ºC are shown in Fig. 6(a_1), (b_1) and (c_1). Ti and O are detected at the surface for all of the samples. Fig. 6(a_2), (b_2) and (c_2) shows Deconvolute XPS $Ti2p_{3/2}$ peak of TiO_2 sintered for the same reaction time of 5 h. If TiO_2 has perfect stoichiometry, then the $Ti2p_{3/2}$ peak should be fitted with only TiO_2 species with a binding energy of about 458.8 eV[25-27]. Fig. 6 (a_2) shows the Ti2p region of the stoichiometric TiO_2 surface. However, curve-fitting of $Ti2p_{3/2}$ of the surface of the TiO_2 pallets sintered in argon at 850 and 950 ºC using only TiO_2 species did not give a satisfying result. Some deviations were evident in the range of 456.3-457.5 eV. The lower the number of oxygen atoms bound to Ti in a given species, the lower the binding energy of this species. Therefore, the $Ti2p_{3/2}$ peaks at 456.3 and 457.5 eV *i.e.*, lower than 458.8 eV of TiO_2 species, could best be deconvoluted by invoking the presence of another species. The newly added species is considered to be Ti^{3+}, namely TiO_{2-x} as a non-stoichiometric oxide. This result indicates TiO_2 cathode sintered at 850 and 950 ºC forms oxygen vacancies,which lead to TiO_{2-x} formation. The defect reaction can be represented as follows[28]:





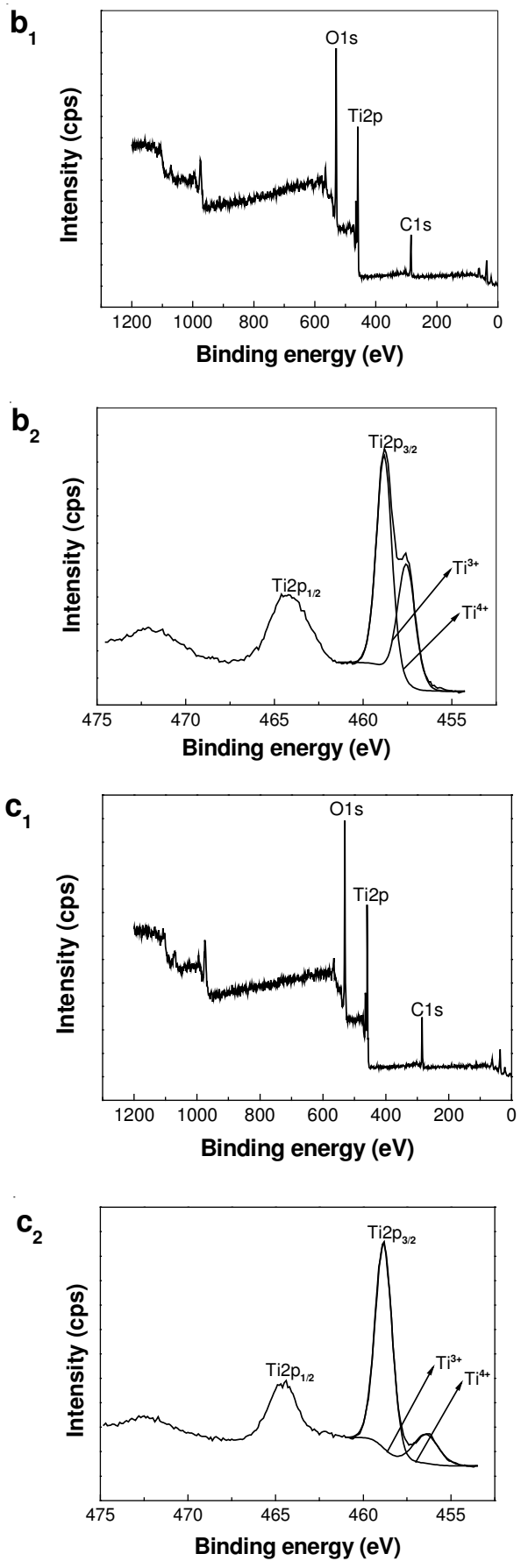


Fig. 6. XPS survey spectra and deconvolute XPS $Ti2p_{3/2}$ peak of TiO_2 sintered for the same reaction time of 5 h at (a) 700 °C (b) 850 °C and (c) 950 °C

$$O_o^x = V_o^x + O \quad (1)$$

$$V_o^x = V_o^{\cdot} + e^- \quad (2)$$

$$V_o^{\cdot} = V_o^{\cdot\cdot} + e^- \quad (3)$$

The overall reaction formula is:

$$O_o^x = V_o^{\cdot\cdot} + O + 2e^- \quad (4)$$

or

$$O_o^x = V_o^{\cdot} + O^{2-} \quad (5)$$

Table-2 shows the areas and binding energies of the deconvoluted peaks of $Ti2p_{3/2}$ for the TiO_2 samples, along with the TiO_{2-x}/TiO_2 ratios calculated from the areas, which give an indication of the degree of non-stoichiometry. The TiO_{2-x}/TiO_2 ratios of the surfaces of the TiO_2 pallets sintered in argon at 850 and 950 ºC were 0.656 and 0.208.

TABLE-1
AREAS AND BINDING ENERGIES OF DECONVOLUTED PEAKS OF $Ti2p_{3/2}$ OF XPS OF TiO_2 AND ARGON ION SPUTTERING SAMPLES AND CALCULATED TiO_{2-x}/TiO_2 AND RELATIVE ATOMIC MOLE RATIOS OF TiO_2

T (ºC)	$Ti2p_{3/2}$				Ti^{3+}/Ti^{4+}
	$Ti^{4+}(TiO_2)$		$Ti^{3+}(TiO_{2-x})$		
	BE (eV)	Area	BE (eV)	Area	
700	458.8	29010.24	—	—	0
850	458.8	22114.56	457.5	14500.51	0.656
950	458.8	25939.08	456.3	5398.42	0.208

Conclusion

In summary, the influence of sintering temperatures structure and electrical conductivity of TiO_2 was studied. According to the research, we can obtain the following results. First, TiO_2 can be transformed from A→R with the increase of the temperature. And the oxygen vacancies in TiO_2 crystal lead to the formation of low-valence titanium oxide (TiO_{2-x}) at high temperature. Second, the specific surface areas of TiO_2 cathode decrease with the increase of the temperature and adsorption-desorption isotherms and pore size distribution indicate TiO_2 cathode is mesoporous structure. The TiO_2 particle grows larger and tends to be homogenized, the porosity decreases and overall structure tends to be more densification. Finally, the electrical conductivity of TiO_2 increase with the rise of the temperature.

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