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ARTICLE

Effect of IrO_2 Content on Microstructure and Capacitance of IrO_2-CeO_2-G/Ti Electrode

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Abstract: The novel IrO_2-CeO_2-G/Ti composite electrodes were prepared by thermal decomposition method. The synthesized electrodes with different IrO_2 content were characterized by scanning electron microscope (SEM), transmission electron microscope (TEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The electrochemical performances of the electrodes were investigated by cyclic voltammetry, galvanostatic charge–discharge and electrochemical impedance spectroscopy in 0.5 mol/L H_2SO_4 solution. The results show that the electrode with 2.5 mg/cm^2 IrO_2 exhibits an excellent specific capacitance value of 459.5 F/g, and maintains the specific capacitance at about 97.8% after 5000 charge-discharge cycles at 5 mA/cm^2 current density. The electrode with 2.5 mg/cm^2 IrO_2 is an ideal electrode for supercapacitor due to its unique composition proportion and the excellent pseudocapacitance property.

Key words: supercapacitor; IrO_2-CeO_2-G/Ti composite electrode; IrO_2 content; specific capacitance

With the development of economy, the problems such as depletion of oil resources, environmental pollution, and greenhouse effect are getting severer year by year[1]. To solve these problems, new energy technology and comprehensive and efficient utilization of environmental resources have become the focus of scientific research[2]. In recent years, electrochemical capacitors (ECs), also called pseudo-capacitors (PCs), have attracted more and more attention due to their high power density, environmental friendly and other advantages[3]. Design and preparation of high electrochemical active electrode materials has also become an important study area[4].

With good corrosion resistance and pseudo capacitance, IrO_2 electrode has higher specific capacitance than double layer capacitors. However, high cost and small specific surface area limit its application[5,6]. Adding non-noble metal oxides (such as Ce, Mn, Zr), plays a synergistic effect with IrO_2, which can inhibit IrO_2 crystallization so as to improve pseudocapacitive performance and reduce the cost of electrode[7]. Graphene is a great supercapacitor electrode material because of its high specific surface area, and excellent thermal and electrical conductivity[8]. However, graphene is exceedingly easy to agglomerate[9], which reduces the specific surface area of the electrode and may lead to a decrease in electrical capacity[10]. One of the effective solutions is to combine graphene with metal oxide. Therefore, in this research, we prepared the IrO_2-CeO_2-G/Ti electrodes, focusing on the influence of precious metal content on the microstructure and capacitance of the electrodes. It was desirable to find a low-cost electrode with high electrochemical performance.

1 Experiment

Commercial chloroiridic acid (H_2IrCl_6, containing 35% Ir by mass) and cerium trichloride were used as the precursor materials. Then they were mixed separately with ethanol. Subsequently, the two solutions were mixed (the mole ratio of Ir^{4+} and Ce^{3+} was 7:3) together into 1 mL solution under ultrasonic agitation for 2 h. Finally, 2 mg acidified graphene was added to 1 mL mixture solution prepared above

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(all reagents used in this study were analytical grade, purchased from Sinopharm Chemical Reagent Co., Ltd, and used without further purification). The resultant solutions were coated onto the titanium substrate. The coatings were dried at 90 °C for 10 min under infrared light and then sintered in a furnace at 380 °C for 15 min each. The above-mentioned steps were repeated several times until the content of IrO_2 was 0.5, 1, 1.5, 2.0, 2.5, 3.0 mg/cm^2. Finally, all samples were annealed at 380 °C for 1 h to obtain IrO_2-CeO_2-G electrodes.

The morphologies of the surfaces of the coatings were observed using a SEM system (Supra 55, Carl Zeiss, Oberkochen, Germany). X-ray diffraction (XRD) patterns were collected on an X-ray Single Crystal Diffractometer (Rigaku, Miniflex600, Japan). X-ray photoelectron spectra (XPS) were recorded on a Thermofish K-Alpha Scientific apparatus. The electrochemical measurements were carried out in a standard three-electrode system on a AUTOLAB (PGSTAT302N, Switzerland) working station. A saturated calomel electrode (SCE) was used as the reference electrode and a Ti strip as the counter electrode. 1 cm×1 cm IrO_2-CeO_2-G/Ti composite electrode was used as the working electrode and 0.5 mol/L H_2SO_4 aqueous solution was used as the electrolyte. The cyclic voltammetry (CV) measurements were performed within the potential window of −0.1~1.2 V. Galvanostatic charge–discharge (GCD) tests were taken under the potential window of 0~1.1 V with electric current density of 2, 5 and 10 mA/cm^2. Electrochemical impedance spectroscopy (EIS) measurements were performed within the frequency range of 10^5~0.05 Hz at open circuit potential. The amplitude of the AC voltage was kept at 5.0 mV, whereas the electrodes were subjected to DC potentials of 1.0 V during the EIS.

2 Results and Discussion

Fig.1 shows the morphologies of IrO_2-CeO_2-G/Ti composite electrodes with different contents of IrO_2. The surfaces all presented the typical “mud-crack” morphology. When the content of IrO_2 was less, the coating surface was discontinuous and more cracks could be seen. With the increase of IrO_2 content, more and more white crystals precipitated out on the surface. It was worth noting that when the content of IrO_2 exceeded 2 mg/cm^2, the roughness of electrode surface increased with uneven distribution and a small part of the external coating may fall off, causing lower coating quality than the calculation. The coatings with excessive IrO_2 content did not exhibit the capacitance performance, but had a high cost. Thus, appropriate content of IrO_2 is crucial.

Fig.2 shows the XRD patterns of the IrO_2-CeO_2-G/Ti electrodes with different IrO_2 content. The diffraction peaks of the titanium substrate were indexed undisputedly to 2θ angles of 35.6°, 38.4°and 40.2°. It could be noticed that as the IrO_2 content increased, the relative intensities of the titanium peaks decreased rapidly. The diffraction peaks of rutile were at 27.64° and 34.49°, and they correspond to the (110) and (101) crystal faces (JCPDS card PDF #88-0288), respectively. The diffraction peak of CeO_2 was not observed in the XRD pattern, suggesting that CeO_2 might exist in an amorphous form. Research illuminated amorphous structure was an indispensable condition for application to supercapacitors by increasing the coating defects and the active sites[11]. The existing state of graphene in the composite electrode could be observed in Fig.3a and 3b. The morphology

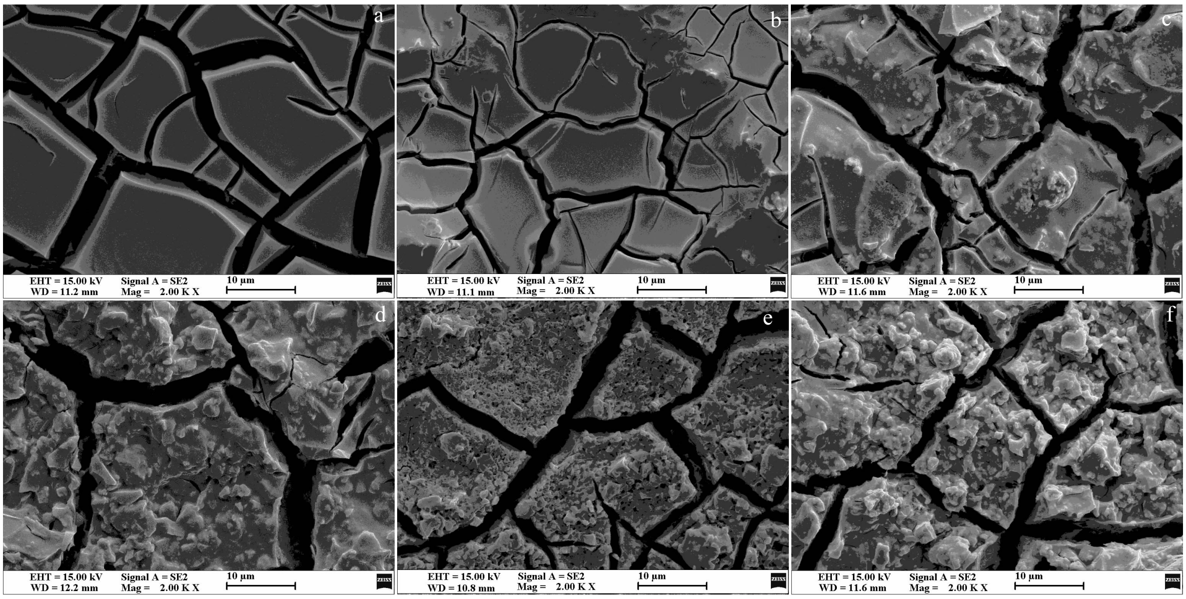

Fig.1 Morphologies of IrO_2-CeO_2-G/Ti composite electrodes with different IrO_2 content: (a) 0.5 mg/cm^2, (b) 1.0 mg/cm^2, (c) 1.5 mg/cm^2, (d) 2.0 mg/cm^2, (e) 2.5 mg/cm^2, and (f) 3.0 mg/cm^2

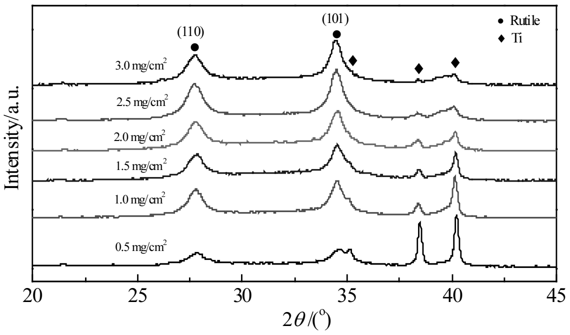

Fig.2 XRD patterns of IrO_2-CeO_2-G/Ti with different IrO_2 contents

of electrode coating was stereoscopic, and this porous laminated structure may make a more even distribution of IrO_2. Fig.3c shows a selected area electron diffraction pattern, which correspond to the crystal surface of $(101)_{d=0.25863\ \mathrm{nm}}$ and $(110)_{d=0.3185\ \mathrm{nm}}$ of IrO_2 in PDF#88-0288 card.

Fig.4 is the XPS spectra of IrO_2-CeO_2-G/Ti electrode. Ce 3d spectrum (Fig.4b) was decomposed into several peaks related to the spin orbital dipole. Calibration was performed by U and V, which were related to the spin orbital components of Ce $3d_{3/2}$ and Ce $3d_{5/2}$. High binding energy peaks were located in U (901.9 eV) and U'' (916.7 eV) with Ce $3d_{3/2}$, and V (883.4 eV) and V''(899.2 eV) belonging to the Ce $3d_{5/2}$. Ce$3d_{3/2}$ and Ce $3d_{5/2}$ showed that Ce mainly exists in Ce^{4+}. Besides, the couple (U',V') at 904.3 and 885.8 eV were the characteristic of the Ce^{3+}. The narrow-scan of Ir 4f orbital is shown in Fig.4a. The Ir 4f orbital was mainly composed of two main peaks (Ir $4f_{7/2}$ and Ir $4f_{5/2}$), and the corresponding binding energy were 62.00 and 64.90 eV, respectively. This proved that Ir mainly existed in Ir^{IV} oxidation state, which was consistent with previous literature reports[12,13]. Meanwhile, the peak of 63.5 eV may correspond to Ir^{III}. And the peak of the satellite forming at the higher binding energy position might be IrO_{2+x} (x >0)[14]. It has been reported that the existence of Ce^{3+} could enhance the interaction between ceria and the surrounding atoms[15]. And then, this might generate a transformation of the lattice oxygen in ceria into the lattice of IrO_2, keeping Ir at the higher valence state.

The CV (scan rate 25 mV/s) curves are shown in Fig.5. In the positive potential range of 0.6~0.7 V, there was a pair of significant redox peaks that corresponded to the transformation between Ir(III) and Ir(IV), which also matched the XPS results. It was shown that the electrodes had good charge storage and pseudocapacitance performance. And the potential values E_{pa}, E_{pc} and $\Delta E_p=E_{pa}-E_{pc}$ did not change along with the change of the content of IrO_2, which expressed their good reversibility.

Fig.6 shows the galvanostatic charge-discharge and the C_s curves of the IrO_2-CeO_2-G/Ti electrodes under 5 mA/cm² current density. The specific capacitance of the electrodes were calculated by the following equations[16]:

$$C_s = it/(\Delta Vm) \tag{1}$$

Where, C_s is the specific capacitance, i is the current density (5 mA/cm²); t is the time for discharging, $\triangle V$ is the voltage interval of the discharge, m is the total mass of active materials[17]. As we know from Eq. (1), the results of current density (i) and time (t) was the electric quantity (q^*), so q^*/m was the main factor affecting the C_s. As the content of IrO_2 increased, the specific capacitance increased first and then decreased. The specific capacitance reached a maximum of 459.5 F/g when the content was 2.5 mg/cm². Compared to the content of 2.5 mg/cm², the specific capacitance decreased by 19.85% when the content was 3 mg/cm². There may be two reasons why the best content was 2.5 mg/cm². On the one hand, when the content of IrO_2 is less

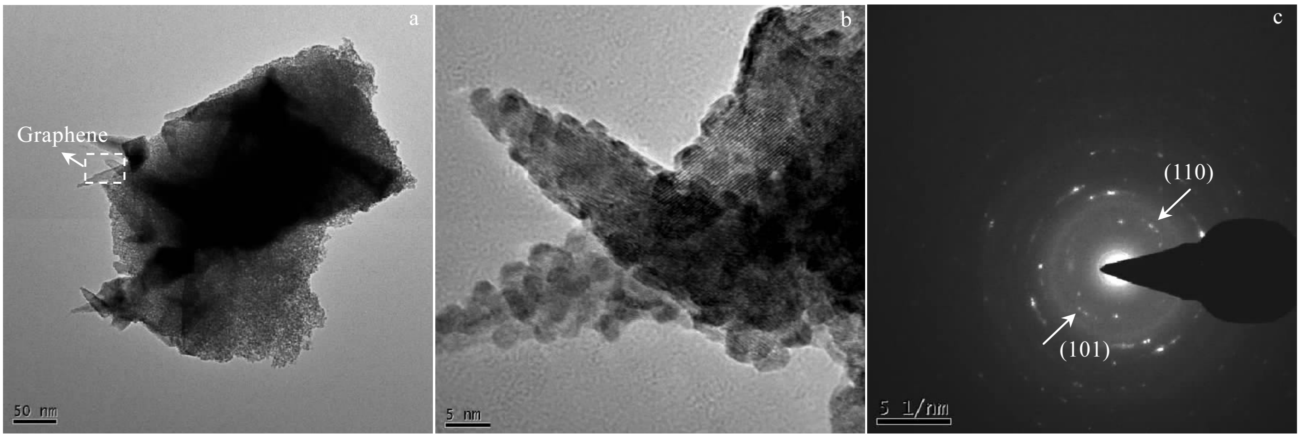

Fig.3 TEM (a, b) images of IrO_2-CeO_2-G and selected area electron diffraction pattern (c) (M_{IrO_2}=2.5 mg/cm²)

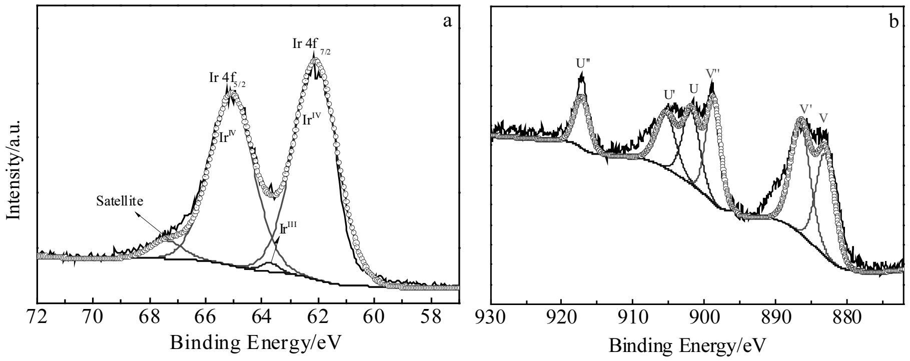

Fig.4 XPS spectra of IrO_2-CeO_2-G/Ti (M_{IrO_2}=2.5 mg/cm^2): (a) Ir 4f and (b) Ce 3d

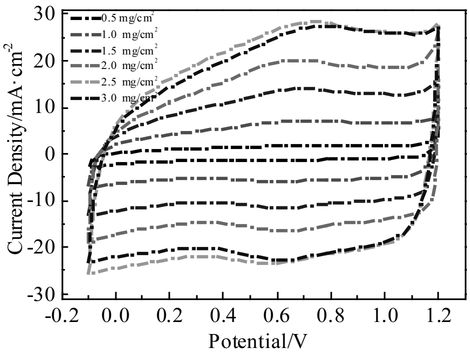

Fig.5 Cyclic voltammetry curves of IrO_2-CeO_2-G/Ti electrodes with different contents of IrO_2

than 2.5 mg/cm^2, the coating fails to cover the matrix and the active materials involved in the REDOX reaction is insufficient, resulting in fewer active sites. On the other hand, when the content is too much, the binding force between the electrode outer layer and the substrate decreases, resulting in partial shedding. Moreover, some internal oxide may not participate in the REDOX reaction in time, resulting in that q^* cannot increase with the content (m) year on year, and then q^*/m decreases. Therefore, a moderate content IrO_2 is very important.

It is critical for supercapacitors to maintain large capacitances under high charge/discharge current densities because it directly determines their application prospect. Fig.7 shows the charge-discharge curves of electrodes (M_{IrO_2}=2.5 mg/cm^2) at various galvanostatic current densities. It is worth mentioning that the specific capacitance was not changing noticeably with the increase of current density (The C_s were 424, 395 and 374 F/g under 2, 5 and 10 mA/cm^2, respectively). At low current density, the ohmic drop was low and the inner active sites could be sufficiently contacted with electrolyte[18], which contributed to achieve high specific capacitance. On the other hand, the internal electrode material could not fully participate in the electrode reaction due to the control of electron conduction and ion diffusion rate at high current density. Importantly, compared to the specific capacitance at 2 mA/cm^2, the value of the electrode at 10 mA/cm^2 only decreased by 11.8%. The little capacitance fading at a very high current density demonstrates that the electrode material has a high rate capability and could allow for a rapid redox reaction at high current charging-discharging.

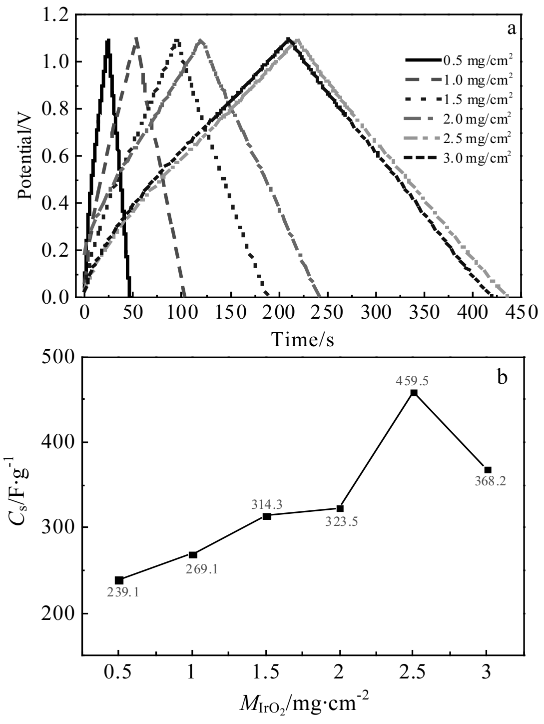

Fig.6 Galvanostatic charge-discharge (a) and C_s curves (b) of IrO_2-CeO_2-G/Ti with different IrO_2 contents (5 mA/cm^2)

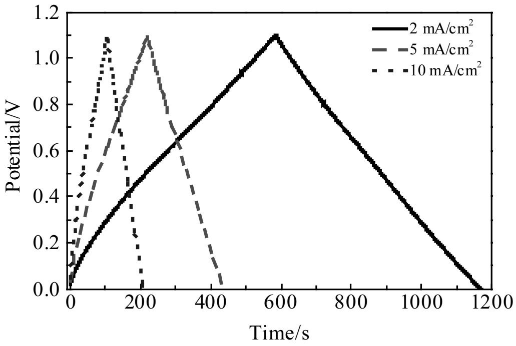

Fig.7 Charge-discharge curves of different current density (M_{IrO_2} =2.5 mg/cm^2)

Fig.8 shows the AC impedance spectra. The fitting diagram of equivalent circuit of components is shown in Fig 8b, including R_s, R_{ct}, C_{dl}, Z_W, and C_F. The R_s is bulk resistance of the electrochemical system, which reflects electric conductivity of the electrolyte and electrodes; R_{ct} is faradic charge-transfer resistance; C_F is the pseudocapacitance and C_{dl} is the double-layer capacitance; Z_W is the Warburg impedance related to a combination of the diffusion effects of ion on the interface between the active material particles and electrolyte, which is generally indicated by a straight loping line at low frequency end. The combination of R_{ct} and Z_W is called faradic impedance, which reflects kinetics of the electrochemical reactions[17]. Semicircular in the high frequency region could be seen from Fig.8c. The diameter of the semicircle represented the R_{ct}, which indicated that the electrode reaction was controlled by charge diffusion[19]. As the content of IrO_2 increased, the radius of the semicircle gradually decreased. This meant that the adding of active material had a certain promoting effect on the charge transferring. Intermediate frequency area has an angle of 45°, called the Warburg impedance, which were the characteristics of the porous electrode. The low-frequency region was approximately parallel to the line of virtual axis to characterize the capacitive resistance. Fig.8a shows that the capacitive reactance was minimal when the IrO_2 content was 2.5 mg/cm^2. The capacitance of the electrode was inversely proportional to the capacitive $Z_{im}(Z_{im}=-1/(2\pi fC))$[20]. It can be observed that with the content increasing, the charge storage capacity of the electrode increased first and then decreased.

The cycling stability of electrodes were examined by Galvanostatic charge–discharge at a current density of 5 mA/cm^2. Fig.9 shows that the C_s of IrO_2-CeO_2-G/Ti electrodes first increased (first 500 cycles) and then declined after 5000 cycles. Initially, the diffusion and reaction were unstable due to defects and impurities on the surface. Moreover, the internal activating oxide was less reactive. As the number of cycles increased, the active substances continuously participated in the reaction. These were the reasons why the C_s first increased. The capacitance holding rate of electrodes were all above 90% after 5000 cycles, which showed the electrodes have excellent cyclic stability. And the electrode with content of 2.5 mg/cm^2 IrO_2 remained 97.8% capacitance after 5000 cycles.

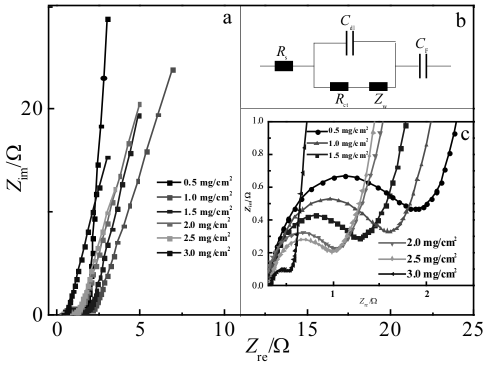

Fig.8 EIS of different IrO_2 content IrO_2-CeO_2-G/Ti: (a) Nyquist diagram, (b) equivalent circuit diagram, and (c) amplification of high frequency area

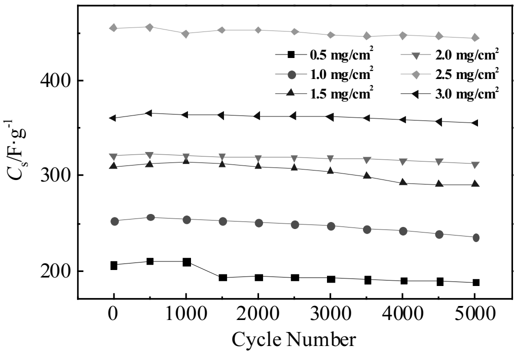

Fig.9 Cyclic numbers curves of IrO_2-CeO_2-G/Ti with different IrO_2 contents

3 Conclusions

1) IrO_2-CeO_2-G/Ti electrodes with nanoscale prepared by thermal decomposition are suitable for supercapacitor.

2) The as-prepared electrode with 2.5 mg/cm^2 IrO_2 can deliver a maximum specific capacitance of 459.5 F/g and has outstanding stability (remaining 97.8% C_s) over 5000 cycles.

3) Furthermore, high specific capacitance is maintained (87.2% C_s) at high charge-discharge current densities due to the unique structure and proportion.

4) The excellent electrochemical performance coupled

with the relatively low cost and simple preparation process renders electrode with 2.5 mg/cm^2 IrO_2 very potential alternative electrode for practical application in supercapacitors.

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IrO_2涂覆载量对IrO_2-CeO_2-G/Ti电极组织结构和电容性能的影响

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摘 要：采用热分解法制备了新型IrO_2-CeO_2-G/Ti复合电极。采用SEM、TEM、XRD和XPS等测试手段分别对不同IrO_2含量的电极进行表征。采用循环伏安法、恒流充放电法和电化学阻抗谱法对电极的电化学行为进行研究。结果表明，IrO_2涂覆载量为2.5 mg/cm^{2}的电极具有最大的比电容值459.5 F/g。在5 mA/cm^{2}电流密度下，经5000次充放电循环后IrO_2涂覆载量为2.5 mg/cm^{2}电极比电容仍能保持97.8%。该种复合电极材料因其独特的元素组成和良好的赝电容性能，是一种理想的超级电容器电极材料。

关键词：超级电容器；IrO_2-CeO_2-G/Ti复合电极；IrO_2涂覆载量；比电容

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