

The study of oxygen spillover and back spillover on Pt/TiO₂ by a potential dynamic sweep method

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Abstract

Oxygen spillover and back spillover on Pt/TiO₂ catalysts have been studied by a potential dynamic sweep method. The characteristics of *I*–*V* profiles of Pt/TiO₂ electrodes in the three potential sweep regions are different from those of Pt and TiO₂ electrodes. The catalytic role of Pt/TiO₂ in oxygen spillover and back spillover is identified. It decreases, and the electrochemical oxygen adsorption (or desorption) increases with elevating temperature of hydrogen post-treatment of Pt/TiO₂; to a certain extent (hydrogen post-treatment of Pt/TiO₂ at 700°C), the control step of oxygen electrode process (anodic oxidation or cathodic reduction) changes from oxygen diffusion to electrochemical oxygen adsorption or desorption, respectively. Increasing the amount of Pt supported on TiO₂ enhances the processes of oxygen spillover and back spillover. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Oxygen spillover and back spillover; Catalytic role of Pt/TiO₂; Potential dynamic sweep; Control step of oxygen electrode process

1. Introduction

Pt/TiO₂, as a redox type of catalyst [1], has been widely used in oxidations and reductions, and also in semiconductor sensors. As a gas-sensing material, it shows a reliable and reversible response to the environment with combustible gas and air, respectively; its performance relates to hydrogen and oxygen spillover and back spillover [2].

In heterogeneous catalysis, hydrogen spillover and back spillover as well as oxygen spillover and back spillover are important catalytic behaviors which have studied and verified for a long time. Hydrogen spillover, brought about on Pt/TiO₂ [3,4,6] and the gate (–Pt supported on TiO₂) mechanism, was proposed [4,5] to explain the processes of hydrogen spillover in which active hydrogen was inserted in TiO₂ solid and moved out of it. Electrical conductivity of TiO₂ was increased by spillover hydrogen species from Pt/TiO₂ to transfer electrons to TiO₂ [6]. It was investigated further by means of Fourier transform near infrared (FT-NIR) Raman spectroscopy [7].

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As the results of hydrogen spillover on Pt/TiO₂, the ‘strong metal–support interaction’ (SMSI) [8–10] or the ‘strong metal–semiconductor interaction’ (SMSi) [1] were brought about at high temperatures and at same time, the morphology and adsorption property of Pt/TiO₂ catalysts were changed.

But until now, oxygen spillover and back spillover have not been identified so definitely as hydrogen spillover and back spillover. People designed catalysts carefully and set up experimental equipments skillfully. With the help of electron spectroscopy, some careful studies of oxygen spillover on Pb/Cu and Ag/SiO₂ were carried out, but only preliminary verification was obtained [11,12].

However, for explanation of the excellent oxidation performance of Pt/TiO₂ and other catalysts [13,14], scientists frequently imputed that to oxygen spillover and back spillover, so people are interested in and pay more attention to oxygen spillover and back spillover than before. Later in propylene oxidation to acrolein, active oxygen migrates through the bulk diffusion in tetra-component bismuth molybdate catalysts by ¹⁸O tracer and using a water tank model for functional metal catalysts [15]. Recently, Li et al. [16] and Jiang et al. [17] proved oxygen spillover on Pt/CeO₂ and Mn₂O₃–Na₂WO₄/SiO₂ catalysts by FT-Raman and electron spin resonance spectroscopy (ESR), electron paramagnetic resonance (EPR) and X-ray absorption near edge structure (XANES), respectively. They showed oxygen spillover brought about in the surface lattice on the supports.

The results in this paper demonstrate that oxygen spillover and back spillover are brought about not only on the surface of Pt/TiO₂ catalysts, but also significantly in TiO₂ crystal lattice. Discussion about catalytic behavior of oxygen spillover and back spillover on Pt/TiO₂ has been given in this paper.

2. Experimental method

TiO₂ (anatase; commercial product; BET area, about 10 M²/g; AR) powder was supported with 1.5 wt.% and 4.5 wt.% Pt, respectively, by chemical impregnation with H₂PtCl₆ solution (10 mg Pt/ml). The water used for solution was distilled for three times.

Pt/TiO₂ and TiO₂ powder was pressed into disks of 0.5 cm² in area and 0.5 mm in thickness was used as electrodes which were treated under the conditions listed in Table 1.

Gold was evaporated onto back surface of Pt/TiO₂ and TiO₂ electrodes for Ohmic contact where leads were fixed. The experiments of potential dynamic sweep were conducted in the cell with three compartments in which reference and counter-electrodes were RHE and Pt electrodes, respectively.

Table 1
Series of Pt/TiO₂ electrodes and their treatment conditions

Electrodes	Code name	Symbols	Treatment conditions		
			Pre-treatment of TiO ₂	Supported with Pt	Post-treatment of Pt/TiO ₂
Pt		a			
TiO ₂	TD-23	b	500°C, H ₂ , 2 h		
Pt/TiO ₂	Te	c	500°C, H ₂ , 2 h	1.5 wt.%	200°C, H ₂ , 2 h
Pt/TiO ₂	TD-27	d	500°C, H ₂ , 2 h	1.5 wt.%	500°C, H ₂ , 2 h
Pt/TiO ₂	TD-31	e	500°C, H ₂ , 2 h	4.5 wt.%	500°C, H ₂ , 2 h
Pt/TiO ₂	TD-33	f	500°C, H ₂ , 2 h	1.5 wt.%	700°C, H ₂ , 2 h

The working electrodes were Pt/TiO₂, TiO₂ or Pt electrodes, respectively. High pure nitrogen was purged through the compartments of working and counter-electrodes before and during measurement. The surface of every working electrode was cleaned by pre-sweep for more than 200 times in 1 M NaOH solution before measurement. The experimental devices included potentiostat, function generator and so on [4].

3. Results and discussion

3.1. Oxygen spillover and back spillover on Pt/TiO₂

In Fig. 1, the peak currents of oxygen anodic oxidation and cathodic reduction for Pt electrode are distinct on the anodic and cathodic branches of its I - V profile, respectively, under oxygen region. An apparent oxygen evolution peak is located at ca. 1.6 V. OH⁻ radical (water) is adsorbed and oxidized, creating the current of electrochemical oxygen adsorption. Being reduced, oxygen adsorbed on the surface of Pt electrode is reduced to OH⁻ radical (water), creating the current of electrochemical oxygen desorption. When the potential sweep region was extended positively, adsorbed oxygen increased and oxygen adsorption layer thickened, the current of oxygen cathodic reduction consequently followed larger, in company with the negative shifting of peak current-potential of oxygen cathodic reduction. In the three potential sweep regions, the relative increasing values of N of current of oxygen cathodic reduction are 1, 1.8 and 1.9, respectively, reaching saturation state in Fig. 3. As shown in Fig. 2, the peak current-potential of oxygen anodic oxidation stays stable, while those of oxygen cathodic reduction are 0.75, 0.71 and 0.70 V, respectively, shifting negatively only a small potential range, 50 mV. The results above illustrate that the amount of oxygen adsorbed on the

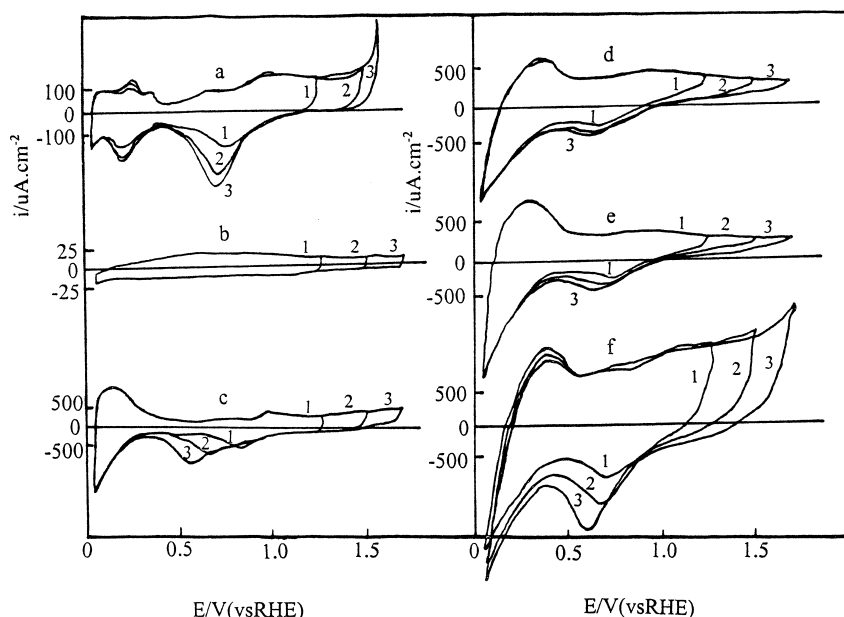


Fig. 1. The I - V profiles of Pt, TiO₂ and Pt/TiO₂ electrodes in the three potential sweep regions at 16 mV s⁻¹ in 1 M NaOH at 30°C. Note that (1) the symbols of the electrodes are the same in this paper as shown in Table 1. (2) 1. The sweep region is 0.04–1.24 V. 2. The sweep region is 0.04–1.49 V. 3. The sweep region is 0.04–1.69 V (0.04–1.60 V for Pt electrode).

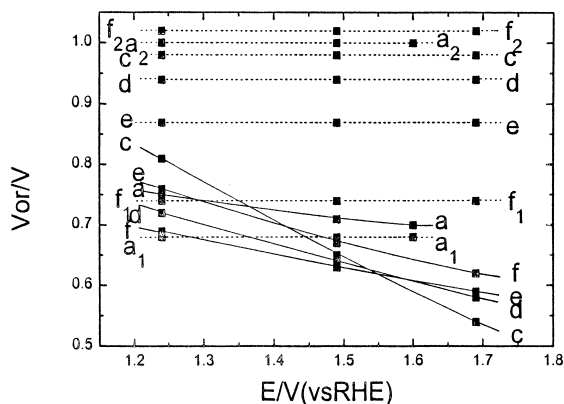


Fig. 2. The peak current–potential (V_{or}) of oxygen electrode processes shifting with the positive extending of potential sweep region for Pt/TiO₂ and Pt electrodes at 16 mV s^{-1} in 1 M NaOH at 30°C: (---) anodic oxidation, (—) cathodic reduction. Note: (1) a_1 , f_1 —the weak peak current of oxygen anodic oxidation for Pt and Pt/TiO₂ (TD-33) electrodes, respectively. (2) a_2 , f_2 —the strong peak current of oxygen anodic oxidation for Pt and Pt/TiO₂ (TD-33) electrodes, respectively.

surface of Pt electrode and its peak current–potential of oxygen electrode processes (anodic oxidation and cathodic reduction) are all comparatively definite [18,19]. As known in Figs. 6 and 7, the peak current of oxygen electrode processes is proportional to the sweep speed, S . In Figs. 8 and 9, the peak current–potential of oxygen electrode processes shifts only a small potential range with sweep speed, S (10 mV positively and 30 mV negatively, respectively). The results further illustrate that oxygen electrode processes of Pt electrode are the electrode surface processes; electrochemical oxygen adsorption or desorption is the control step of the oxygen electrode process (anodic oxidation or cathodic reduction, respectively).

There is nonselective current over a wide potential range and no oxygen evolution peak at ca. 1.60 V on the I – V profile of TiO₂ electrode. It is revealed that there is no additional surface energy state in semiconductor forbidden band and there is no obvious electrochemical oxygen adsorption (or desorption) on TiO₂ electrode.

The peak current of oxygen electrode processes is clearly exhibiting on the anodic and cathodic branches of the I – V profile for Pt/TiO₂ (Te) electrode, respectively. It indicates that the rate of

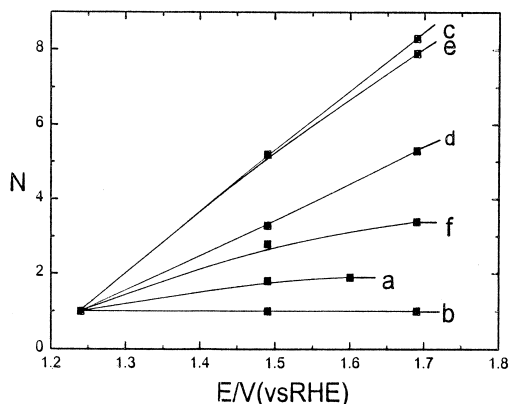


Fig. 3. The relative increasing value, N of current of oxygen cathodic reduction in the three potential sweep regions for Pt, TiO₂ and Pt/TiO₂ electrodes at 16 mV s^{-1} in 1 M NaOH at 30°C. Note: the current in the sweep region 0.04–1.24 V as 1 for Pt, TiO₂ and Pt/TiO₂ electrodes.

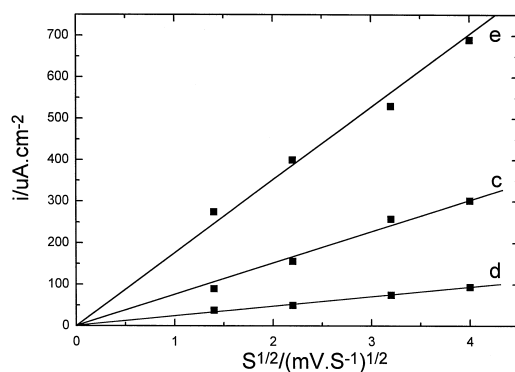


Fig. 4. The peak current of oxygen anodic oxidation plotted against the square root of sweep speed, $S^{1/2}$, for Pt/TiO₂ (Te, TD-27 and TD-31) electrodes in the sweep region (0.04–1.50 V) in 1 M NaOH at 30°C.

oxygen redox reaction on Pt/TiO₂ is amplified by supporting Pt on TiO₂ powder. In the three potential sweep regions, the relative increasing values of N of current of oxygen cathodic reduction are 1, 5.2 and 8.3, respectively, and does not get saturation state far away in Fig. 3. The peak current–potential of oxygen anodic oxidation remains unchanged, while those of oxygen cathodic reduction are 0.81, 0.65 and 0.54 V, respectively, shifting negatively a large potential range, 270 mV in Fig. 2. In Figs. 4 and 5, the peak current of oxygen electrode processes for Pt/TiO₂ (Te) is proportional to the square root of sweep speed, $S^{1/2}$. It is indicated in Figs. 8 and 9 that the peak current–potential of oxygen electrode processes for Pt/TiO₂ (Te) shifts more positively and negatively, respectively, than those of Pt electrode with sweep speed S . The same results for Pt/TiO₂ (TD-27 and TD-31) electrodes could be achieved by comparing their I – V profiles with those of Pt and TiO₂ electrodes. The results demonstrate that oxygen electrode processes for Pt/TiO₂ (Te, TD-27 and TD-31) electrodes are not as pure as the electrode surface processes, concerning the property of crystal lattice of Pt/TiO₂ electrodes (TiO₂). Oxygen diffusion is the control step of oxygen electrode processes for them. Being oxidized, electrochemical oxygen adsorption brings about on Pt over the surface of Pt/TiO₂ electrodes; active oxygen species shifts directly fast from Pt into TiO₂ crystal lattice, or shifts fast from Pt to zone of the surface of Pt/TiO₂ electrodes (no Pt supported), then straight soon passes in TiO₂ crystal lattice [20] to be interstitial oxygen. This process

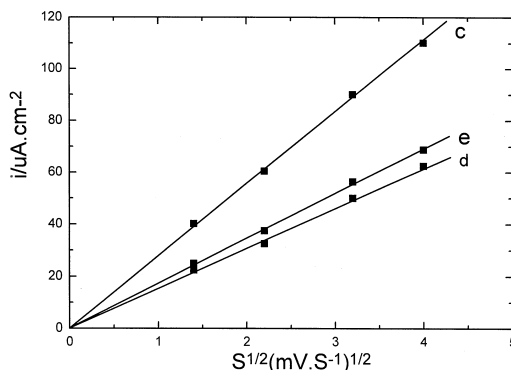
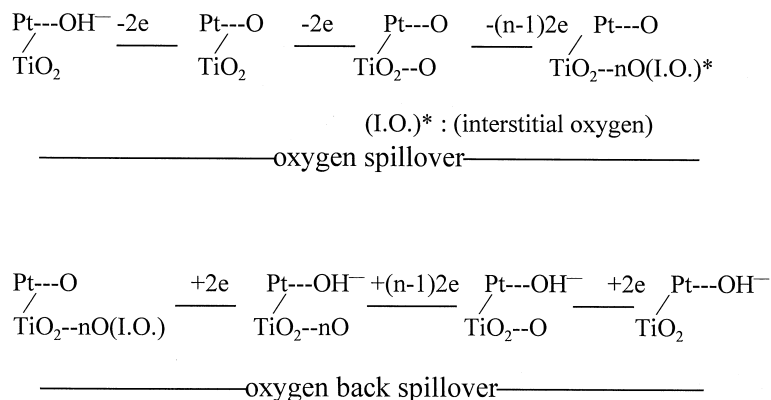


Fig. 5. The peak current of oxygen cathodic reduction plotted against the square root of sweep speed, $S^{1/2}$, for Pt/TiO₂ (Te, TD-27 and TD-31) electrodes in the sweep region (0.04–1.50 V) in 1 M NaOH at 30°C. Note: the peak current of oxygen cathodic reduction for Pt/TiO₂ (Te) is multiplied by 5.5. That for Pt/TiO₂(TD-31) is multiplied by 4. That for Pt/TiO₂(TD-27) is multiplied by 10.

displays oxygen spillover. Interstitial oxygen is an identical substance with active oxygen species. Being reduced, interstitial oxygen moves out of inner TiO_2 crystal lattice fast to the surface of Pt/TiO_2 electrodes, takes part in cathodic reduction through or on Pt over the surface of Pt/TiO_2 electrodes. This process displays oxygen back spillover. The roads of oxygen transfer in oxygen back spillover could be contrary entirely to that in oxygen spillover. Being the same as the catalytic role of Pt/TiO_2 in hydrogen spillover and back spillover [4,5], the Pt on the surface of Pt/TiO_2 electrodes is also the ‘gate’ for active oxygen species passing in and moving out of TiO_2 crystal lattice:



Following the potential sweep region extending positively, interstitial oxygen passing in the TiO_2 crystal lattice is getting increased due to oxygen spillover in oxygen anodic oxidation process. The current of oxygen cathodic reduction is getting increased and showing unsaturation state in Fig. 3 due to oxygen back spillover in oxygen cathodic reduction process. As mentioned above, oxygen diffusion is the control step of the oxygen electrode processes for them, so the peak current–potential of oxygen cathodic reduction shifts more negatively than those of Pt electrode in the three potential sweep regions, being undefined. The relationship between the peak current or peak current–potential of oxygen electrode processes, and sweep speed, S for them are all different from those for Pt electrode.

3.2. The temperature effect of hydrogen post-treatment of Pt/TiO_2 on oxygen spillover and back spillover

Pt/TiO_2 (Te, TD-27 and TD-33) electrodes were all supported with 1.5 wt.% Pt. They were post-treated with hydrogen at temperatures 200, 500 and 700°C, respectively. In the three potential sweep regions, their maximal relative increasing values, N , of current of oxygen cathodic reduction are 8.3, 5.3 and 3.4, respectively, the latest is going to emerge a tendency of saturation state in Fig. 3. Their peak current–potential of oxygen cathodic reduction shifts negatively, maximally 270, 140 and 100 mV as shown in Fig. 2 wherein the peak current–potential of oxygen anodic oxidation for them stays at the potential stably in the three potential sweep regions. In Fig. 8, the peak current–potential of oxygen anodic oxidation for $\text{Pt}/\text{TiO}_2(\text{Te})$ shifts positively larger, for Pt/TiO_2 (TD-27) mild, for $\text{Pt}/\text{TiO}_2(\text{TD-33})$ less, with sweep speed S among them. In Fig. 9, the peak current–potential of oxygen cathodic reduction for Pt/TiO_2 (Te) shifts negatively larger, for Pt/TiO_2 (TD-27) mild, for $\text{Pt}/\text{TiO}_2(\text{TD-33})$ less with sweep speed S among them. These comparisons could illustrate that the catalytic role of Pt/TiO_2 in oxygen spillover and back spillover decreases with elevating temperature of hydrogen post-treatment of Pt/TiO_2 .

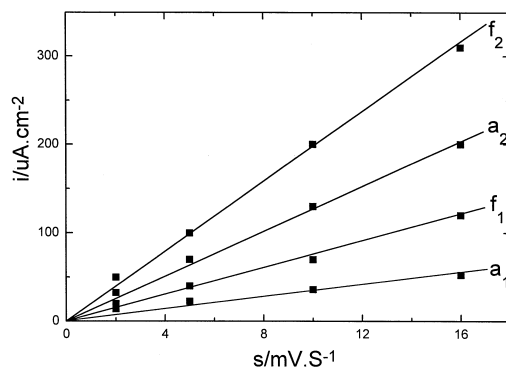


Fig. 6. The peak current of oxygen anodic oxidation plotted against sweep speed, S , for Pt/TiO₂ (TD-33) and Pt electrodes in the sweep region (0.04–1.50 V) in 1 M NaOH at 30°C.

In Figs. 4 and 5, the peak current of oxygen electrode processes for Pt/TiO₂ (Te and TD-27) electrodes is proportional to the square root of sweep speed, $S^{1/2}$. Oxygen diffusion is the control step of their oxygen electrode processes. Owing to the catalytic role of Pt/TiO₂ in oxygen spillover and back spillover bringing about on Pt/TiO₂ (Te and TD-27) electrodes, active oxygen species shifts through Pt on the surface of the Pt/TiO₂ electrodes passing in and moving out of TiO₂ crystal lattice, producing a diffusion role. Oxygen diffusion is the control step of oxygen electrode processes reasonably.

In Figs. 6 and 7, the peak current of oxygen electrode processes for Pt/TiO₂ (TD-33) and Pt electrodes is proportional to the sweep speed, S . Electrochemical oxygen adsorption (or desorption) is the control step of their oxygen electrode processes. With Pt/TiO₂ being post-treated with hydrogen at 700°C, and a large amount of active hydrogen entering TiO₂ crystal lattice, simultaneously a great deal of bonded hydrogen is produced [21]. So the catalytic role of Pt/TiO₂ in oxygen spillover and back spillover is decreasing, correspondingly, electrochemical oxygen adsorption (or desorption) is increasing. It becomes the control step of oxygen electrode process. Briefly, the catalytic role of Pt/TiO₂ in oxygen spillover and back spillover decreases and electrochemical oxygen adsorption (or desorption) increases with elevating temperature of hydrogen post-treatment of Pt/TiO₂. To a certain extent (hydrogen post-treatment at 700°C), the control step of oxygen electrode process changes from oxygen diffusion to electrochemical oxygen adsorption (or desorption).

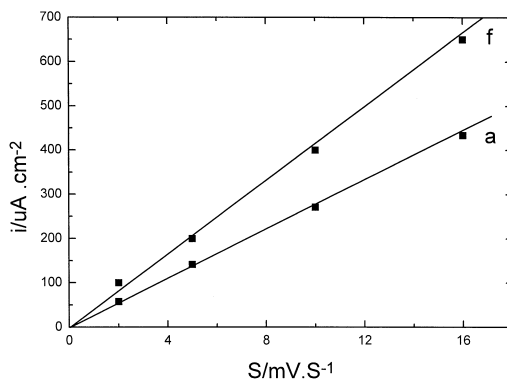


Fig. 7. The peak current of oxygen cathodic reduction plotted against sweep speed, S , for Pt/TiO₂ (TD-33) and Pt electrodes in the sweep region (0.04–1.50 V) in 1 M NaOH at 30°C.

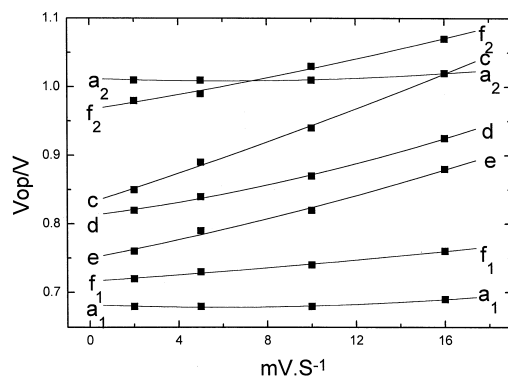


Fig. 8. The peak current–potential of oxygen anodic oxidation (V_{op}) for Pt/TiO₂ and Pt electrodes shifting positively with sweep speed, S in the sweep region (0.04–1.50 V) in 1 M NaOH at 30°C.

3.3. The effect of supported Pt amount on oxygen spillover and back spillover

Compare the I – V profile of Pt/TiO₂ (TD-31) electrode with that of Pt/TiO₂ (TD-27) electrode. Temperatures of hydrogen pre-treatment of TiO₂ and post-treatment of Pt/TiO₂ for them were all 500°C. They were supported with 4.5 wt.% and 1.5 wt.% Pt, respectively. In the three potential sweep regions, relative increasing values, N of current of oxygen cathodic reduction for the former are 1.0, 5.2 and 7.9, for the latter are 1.0, 3.3 and 5.3, respectively. The current of oxygen anodic oxidation for the former is 1.6 times as large as that for the latter in 0.04–1.49 and 0.04–1.69 V sweep regions, respectively. In Figs. 8 and 9, the peak current–potential of oxygen electrode processes for the former shifts more positively and negatively, respectively, than those for the latter with sweep speed S . These results imply that the catalytic role of Pt/TiO₂ in oxygen spillover and back spillover on the former is more prosperous than that on the latter. As mentioned above, Pt is not only the ‘gate’ for active oxygen species in oxygen spillover and back spillover, but also the place where electrochemical oxygen adsorption (or desorption) is brought about.

The amount of supported Pt being increased, electrochemical oxygen adsorption is increased, and active oxygen species passing in TiO₂ crystal lattice is increased correspondingly through Pt, the ‘gate’ which is more present on TiO₂. Being reduced, interstitial oxygen moving out of inner TiO₂ crystal lattice to the surface of Pt/TiO₂ electrode through Pt, the ‘gate’ which is more present on

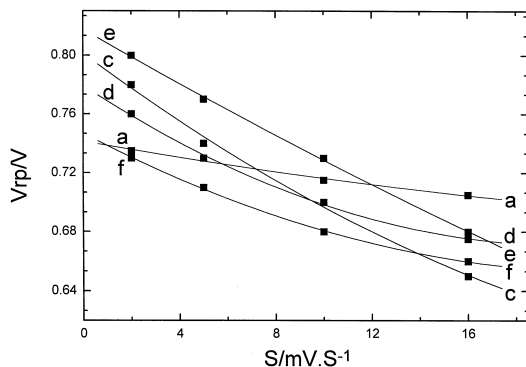


Fig. 9. The peak current–potential of oxygen cathodic reduction (V_{rp}) for Pt/TiO₂ and Pt electrodes shifting negatively with sweep speed, S , in the sweep region (0.04–1.50 V) in 1 M NaOH at 30°C.

TiO₂ too, taking part in cathodic reduction is enhanced, and the produced current of oxygen cathodic reduction is getting large in sequence. So increasing the amount of supported Pt appropriately enhances the processes of oxygen spillover and back spillover.

4. Conclusions

The characteristics of the $I-V$ profiles of Pt/TiO₂ electrodes (except TD-33) in the three potential sweep regions and their relationship between the peak current of oxygen electrode processes and sweep speed S , etc., are obviously different from those of Pt and TiO₂ electrodes, identifying the catalytic role of Pt/TiO₂ in oxygen spillover and back spillover so it could be studied by a potential dynamic sweep method.

It decreases and the electrochemical oxygen adsorption (or desorption) increases with elevating temperature of hydrogen post-treatment of Pt/TiO₂. To a certain extent (hydrogen post-treatment of Pt/TiO₂ at 700°C), the control step of oxygen electrode process changes from oxygen diffusion to electrochemical oxygen adsorption (or desorption). Increasing the amount of Pt supported on TiO₂ appropriately enhances the processes of oxygen spillover and back spillover.

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