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Electro-oxidation of coal on NiO and/or Co_3O_4 modified TiO_2/Pt electrodes

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ABSTRACT

A TiO_2/Pt based electrode exhibited better activity for the oxidation of coal in a basic system compared to Ti/Pt, TiO_2–Cu/Pt and pure metal electrodes. The surface morphologies and composition of the electrodes were studied by SEM and XRD, respectively. Linear sweep voltammetry was employed to investigate the catalytic effects of electrodes, and the product of coal oxidization was determined by a gas collection test. The TiO_2/Pt electrodes that were modified with NiO and/or Co_3O_4 exhibited higher average currents and a lower decrease in mass during electrolysis compared to the other electrodes; this finding indicated that NiO and Co_3O_4 play important roles as catalysts.

1. Introduction

Electro-oxidation of coal is considered a highly efficient way to utilize fossil fuel, namely clean coal technology (CCT) [1]. The electrolysis of coal, which can be used as a depolarization agent [2], is an alternative for hydrogen production. At 25 °C, the theoretical potential of coal electrolysis is 0.21 V [3], which is much lower than the water electrolysis potential (1.23 V) [4]. The actual energy consumption for coal electrolysis is only one-third to one-half of the energy for water electrolysis. CO_2 and H_2, collected at the anode and cathode, respectively, are pure enough for use without further purification.

The catalytic effect of various electrodes has been investigated, and Pt is commonly used as a working electrode [3–6]. Sathe and Botte plated noble metals (Pt, Rh, Pt–Rh, Pt–Ir, and Pt–Ir–Rh) on carbon fibers and investigated their electrolytic efficiency of producing CO_2 from coal; they found that Pt–Ir showed the best resistance to erosion and weight loss consisted of only 1%. All the electrodes exhibited a similar performance, and the energy consumption was 50% lower compared to hydrogen production by the electrolysis of water under similar operating conditions [7]. Our group investigated Ti/Pt–Fe [8], Ti/TiO_2–Pt and Ti/TiO_2–Pt–Ru [9] electrodes for the electro-oxidation of coal in sulphuric acid, and we found that Ti/Pt–Fe exhibited the best activity. A less expensive Pt–Fe alloy was generated on the Ti sheet surface. The metal oxide modified electrodes (Ti/IrO_2–RuO_2, Ti/IrO_2) also perform well because 99.98% of anode gas consists of CO_2 [10]. The mechanism of coal oxidation has been proposed as follows [11–13]:

$$\text{Anode}: \ C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^- \tag{1}$$

$$\text{Cathode}: \ 4H^+ + 4e^- \rightarrow 2H_2 \tag{2}$$

$$\text{Total}: \ C + 2H_2O \rightarrow CO_2 + 2H_2 \tag{3}$$

Thus far, most work has focused on the electro-oxidation in acidic systems. However, the oxidation in a basic system could liquefy coal in high efficiency. Humic acid, traditionally produced by an electrical method, is the main product in basic systems [14–16]. It is different from the oxidization in acidic systems, in which coal is used as a depolarization agent. Senftle et al. reported that the oxidative consumption of coal to produce alkali-soluble compounds was found to proceed preferentially at the edges of aromatic planes [17]. Organic sulfur removal from coal by electrolysis is also performed in alkaline media [18]. A basic system enables the utilization of electrodes modified with metal oxides, which have shown their catalytic activity in organic electrochemistry because metal oxides may dissolve in acidic systems [19].

In the present work, several electrodes were investigated for the electro-oxidation of coal. We determined that TiO_2/Pt based electrodes modified by NiO and/or Co_3O_4 showed the best catalytic effect.

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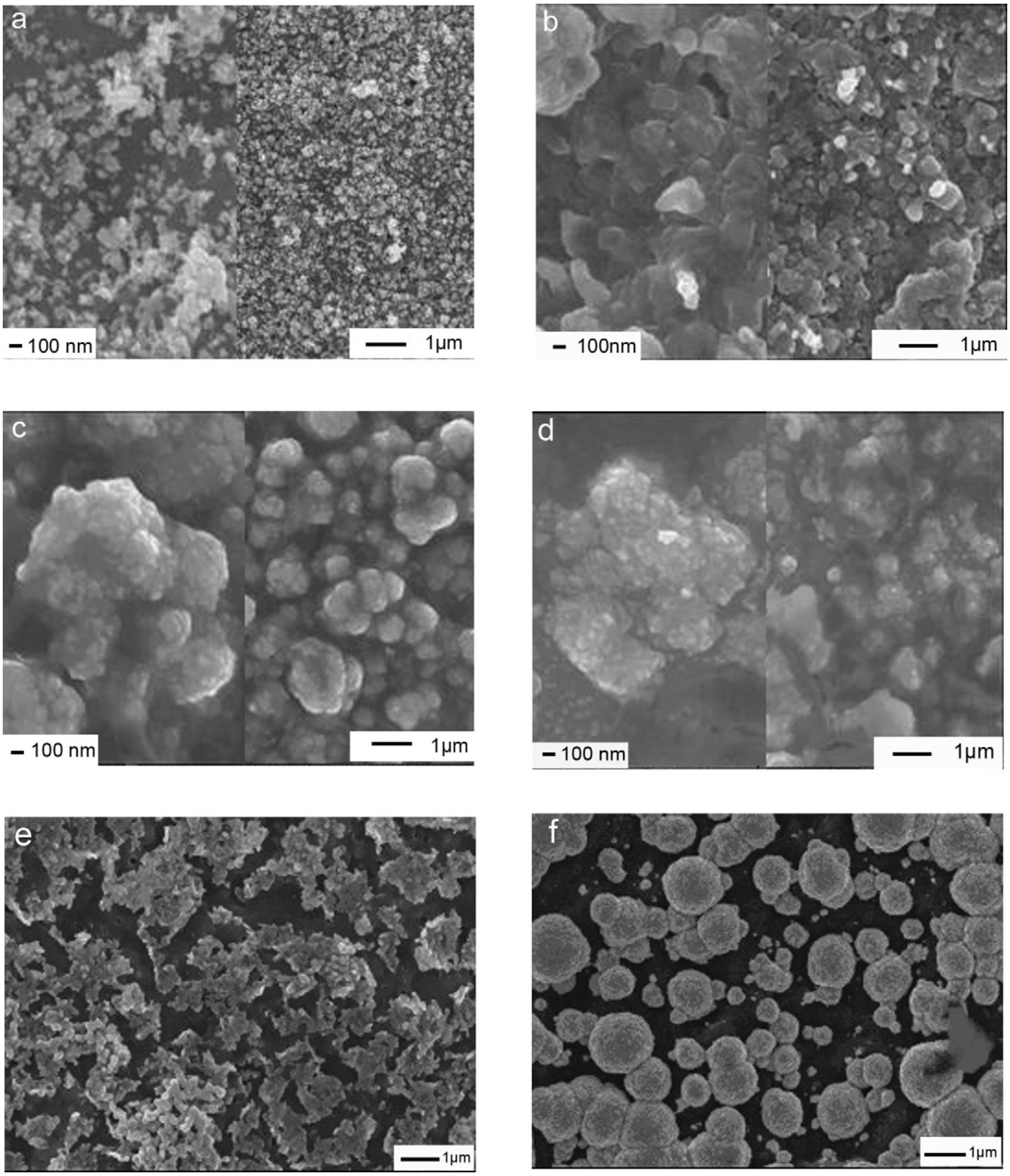

Fig. 1. SEM images of the electrodes: (a) TiO_2/Pt; (b) TiO_2/Pt–Co_3O_4; (c) TiO_2/Pt–NiO; (d) TiO_2/Pt–Co_3O_4–NiO; (e) TiO_2/Pt; and (f) TiO_2–Cu/Pt. Co_3O_4 and NiO were electrodeposited; (a–d) Pt was electrolessly deposited onto TiO_2 and (e and f) Pt and Cu were electrodeposited.

2. Experimental

2.1. Preparation of electrodes

Ti substrates (2 cm × 2 cm) modified by porous TiO_2 layers were obtained as previously described [9]. Pt particles were electrolessly plated in a plating solution (0.2 g/L of $H_2PtCl_6{\cdot}6H_2O$, 12 g/L of hydrazine hydrate, 5 g/L of hydroxylamine hydrochloride, pH = 4.5, T = 45 °C). The substrate was covered by Pt particles in 10 min. Under a constant current density of 2.1 mA/cm^2 and pH = 4.5, the TiO_2/Pt electrodes were electroplated with a different metal oxide catalyst and in different electroplate solutions in 5 min as shown in Table 1. Finally, the prepared electrodes were heated to 500 °C to form the dense phase and then cooled to room temperature.

2.2. Electro-oxidation of coal

A potentiostat (CHI660B, Shanghai Chenhua Instrument Company) was used for the electrolysis experiments. The cell consisted of an H-type cell, whose compartment was separated by a porosity

Table 1
Electroplating solutions for different electrodes. X denotes the agent used in preparation.

	$CoSO_4{\cdot}7H_2O$ (20 g/L)	$NiSO_4{\cdot}6H_2O$ (200 g/L)	H_3BO_3 (30 g/L)	NaCl (15 g/L)
TiO_2/Pt–Co_3O_4	X		X	X
TiO_2/Pt–NiO		X	X	X
TiO_2/Pt–Co_3O_4–NiO	X	X	X	X

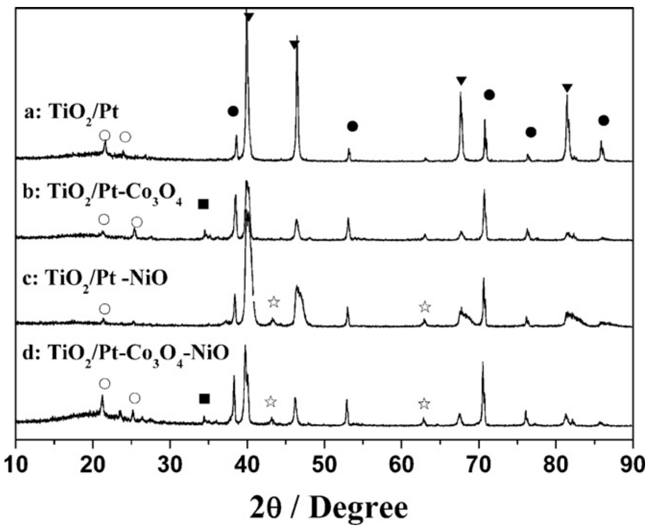

Fig. 2. XRD analysis of the electrodes: (a) TiO_2/Pt; (b) TiO_2/Pt–Co_3O_4; (c) TiO_2/Pt–NiO; (d) TiO_2/Pt–Co_3O_4–NiO; (●) Ti; (○) TiO_2; (▼) Pt; (■) Co_3O_4; and (☆) NiO.

frit. The solution used for the cathode was 1 M NaOH, and the anode solution consisted of 6 g of coal suspended in 100 mL of NaOH (1 M), which was stirred at a constant rate. Pt was used as a counter electrode, while a saturated calomel electrode (SCE) was used as the reference electrode.

2.3. SEM, XRD and ICP analyses

Scanning electron microscopic (SEM) images were taken with a JSM-6700F microscope (Shimadzu Ltd.). X-ray diffraction (XRD) measurements were performed with a DLMAX-2200 diffractometer (JEOL Ltd.), and an IRIS Advantage 1000 Atomic Emission Spectrometer (Thermo Elemental Ltd.) was used for Inductive Coupled Plasma Emission Spectrometer (ICP) measurements.

3. Results and discussion

3.1. Morphology and composition analysis

Fig. 1 shows the SEM images of the electrodes modified by nanoparticles of different catalysts. Compared to the TiO_2 with electrodeposited Pt (Fig. 1(e)), TiO_2 with electrolessly deposited Pt showed a homogenous surface consisted of nano-Pt particles (Fig. 1(a)). The difference was due to the low conductivity of the TiO_2 substrate. When Cu was electroplated to enhance the conductivity of the substrate, relatively homogenous Pt particles could be electrodeposited onto the TiO_2–Cu substrate, as shown in Fig. 1(f).

Particles on the surface of the TiO_2/Pt–Co_3O_4 electrode consisted of small pieces, while those on the TiO_2/Pt–Co_3O_4–NiO and TiO_2/Pt–NiO electrodes consisted of small balls. After the electrolysis of coal (120 h), 11.6% of the Co_3O_4 was lost on the TiO_2/Pt–Co_3O_4, while only 6.4% of the NiO on the TiO_2/Pt–NiO was lost, which will be discussed in Section 3.4. These secondary units (small balls and pieces) that constituted particles were responsible for the mass decrease of the electrodes. The balls reinforced particles on the surface.

The compositions of deposited catalysts on the electrode surfaces were confirmed by XRD analysis (Fig. 2). The XRD spectra of TiO_2/Pt–Co_3O_4–NiO showed peaks of Co_3O_4 (2 2 0) and NiO (0 1 2, 1 0 4 and 1 1 0). There were no peaks found for the alloy phases of Co_3O_4 and NiO. According to the ICP results, the mass density of Co_3O_4 on TiO_2/Pt–Co_3O_4 was 1.86 mg/cm^2, which was almost the same as Pt (1.90 mg/cm^2). However, the XRD peaks of Co_3O_4 were quite weak (Fig. 2(b) and (d)), indicating that most of the Co_3O_4 existed in an amorphous phase.

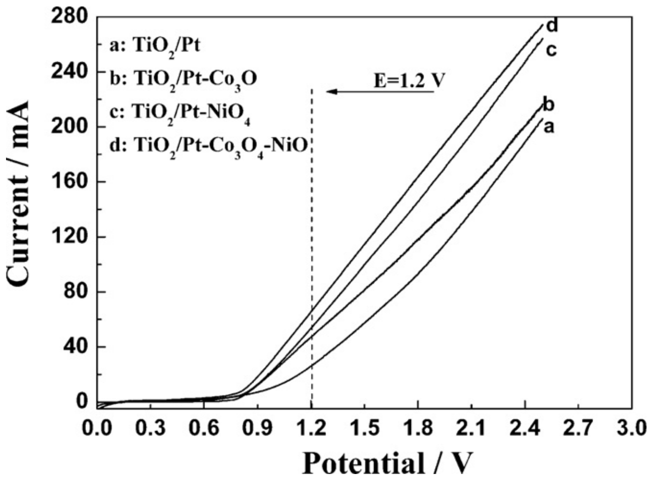

Fig. 3. LSV results of TiO_2 based electrodes: (a) TiO_2/Pt; (b) TiO_2/Pt–Co_3O_4; (c) TiO_2/Pt–NiO; and (d) TiO_2/Pt–Co_3O_4–NiO.

3.2. Linear-sweep voltammetry (LSV) and chronoamperometry (i–t curve) analysis

The LSV results of different electrodes are shown in Fig. 3. An increase of current from 0.7 V indicated that the coal electro-oxidation occurred. We performed the electrolysis study at 1.2 V for the gas-collection test and determined the existence of the reaction.

At 0.8 V, the modified TiO_2/Pt electrodes showed a higher current compared to the TiO_2/Pt electrode, and the TiO_2/Pt–Co_3O_4–NiO electrode performed the best. Its average current was 16.20 mA during the electrolysis study at 1.2 V for 1 h (Table 2). The good performance should be ascribed to the high content of catalyst on the TiO_2/Pt–Co_3O_4–NiO electrode. According to the ICP analysis, 3.42 mg/cm^2 of catalyst (1.86 mg/cm^2 Co_3O_4 and 1.56 mg/cm^2 NiO) was modified on the substrate. The catalyst contents for TiO_2/Pt–Co_3O_4 and TiO_2/Pt–NiO were 1.46 mg/cm^2 (Co_3O_4) and 1.72 mg/cm^2 (NiO), respectively. Under the same conditions (0.21 mA/cm^2, 5 min), a high efficiency (3.42 mg/cm^2) for the deposition of catalyst could be achieved if the active metals were codeposited.

The current contribution per gram (CCG) of these catalysts was calculated to evaluate the catalytic efficiency. Values of the CCG for TiO_2/Pt–Co_3O_4, TiO_2/Pt–NiO and TiO_2/Pt–Co_3O_4–NiO, were 2.1 A/g, 2.3 A/g and 1.2 A/g, respectively. Both NiO and Co_3O_4 exhibited high catalytic activities. A low CCG for TiO_2/Pt–Co_3O_4–NiO could possibly be due to its relatively low surface area.

Fig. 4 shows the *i*–*t* curves of different electrodes. The TiO_2/Pt electrode showed a much higher current compared to the pure metal electrodes, suggesting that the porous surface of TiO_2 should be responsible for the current enhancement. However, due to the low conductivity of the TiO_2, Pt cannot be electrodeposited firmly and homogeneously on TiO_2, as shown in Fig. 1(e), while the electroless plated Pt performed much better (Fig. 1(a)).

3.3. Gas collection

Due to its complexity, the reaction of coal is usually investigated by indirect methods, e.g., as a gas collection test. We collected gas generated from both the anode and cathode, and the gas volume after 0.5 h was calculated as shown in Fig. 5; the main gas products consisted of O_2 and H_2. A NaOH solution was used for the blank test,

Table 2
Catalytic activity of prepared electrodes (electrolyzed for 1 h).

	TiO_2/Pt	TiO_2/Pt–Co_3O_4	TiO_2/Pt–NiO	TiO_2/Pt–Co_3O_4–NiO
Current density (A/g)	1.2	2.1	2.3	1.2
Total current (mA)	9.12	12.44	15.72	16.20
H_2 (L/(g h))	0.54	0.95	1.02	0.53
Electrolytic efficiency of H_2 (%)	97.93	98.21	98.13	98.57
Gas from anode (L/(g h))	0	0	0	0

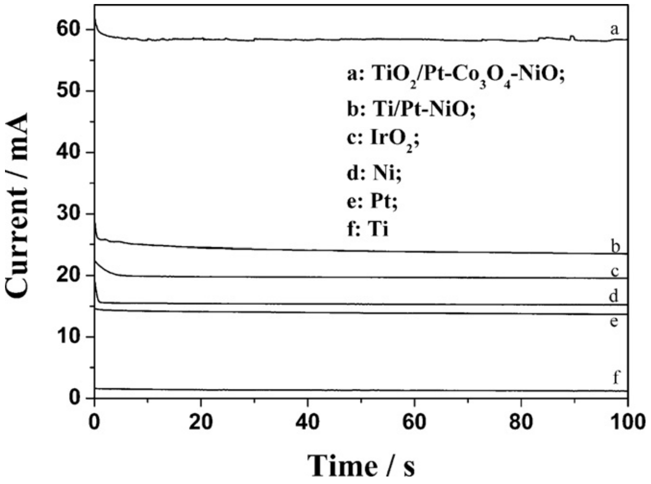

Fig. 4. *i*–*t* curves of different electrodes in the coal slurry at 1.2 V.

and a gas volume ratio of H_2 (cathode) to O_2 (anode) was constant at 2:1 as shown in Fig. 5; the gas was due to water splitting. However, the situation with the coal slurry was quite different. First, little gas was collected on the anode because the overpotential of the O_2 generation was increased by the coal that was oxidized instead of OH^-. Thus, different from reaction (1), the half reaction on the anode could be described as follows:

$$\text{Coal} + OH^- \rightarrow \text{oxidized coal} + H_2O \tag{4}$$

In addition, the coal particles enhanced the resistance of the solution, leading to a decrease in the total current. Therefore, less H_2 was obtained from the cathode compared to the blank test.

The activities of H_2 production on different electrodes are listed in Table 2. The TiO_2/Pt–Co_3O_4–NiO electrode showed the best performance with a high columbic efficiency (98.57%) of H_2 production. The amount of generated H_2 per gram from TiO_2/Pt–NiO (1.02 L/(g h)) was two times more than from TiO_2/Pt and TiO_2/Pt–Co_3O_4–NiO, which confirmed the CCG results.

3.4. ICP analysis of the electrodes

The ICP analysis was used to examine the mass decrease of metal oxides modified on the electrodes and to investigate the stability of different morphologies (Fig. 6). The catalysts were more stably attached on the TiO_2 substrate compared to the Ti substrate. A loss of 54.2% Pt was determined for the Ti/Pt–Co_3O_4 electrode after 120 h of electrolysis, while 8.1% Pt was lost on a TiO_2/Pt–Co_3O_4. As shown in Fig. 6(a), all the TiO_2 based electrodes show a smaller

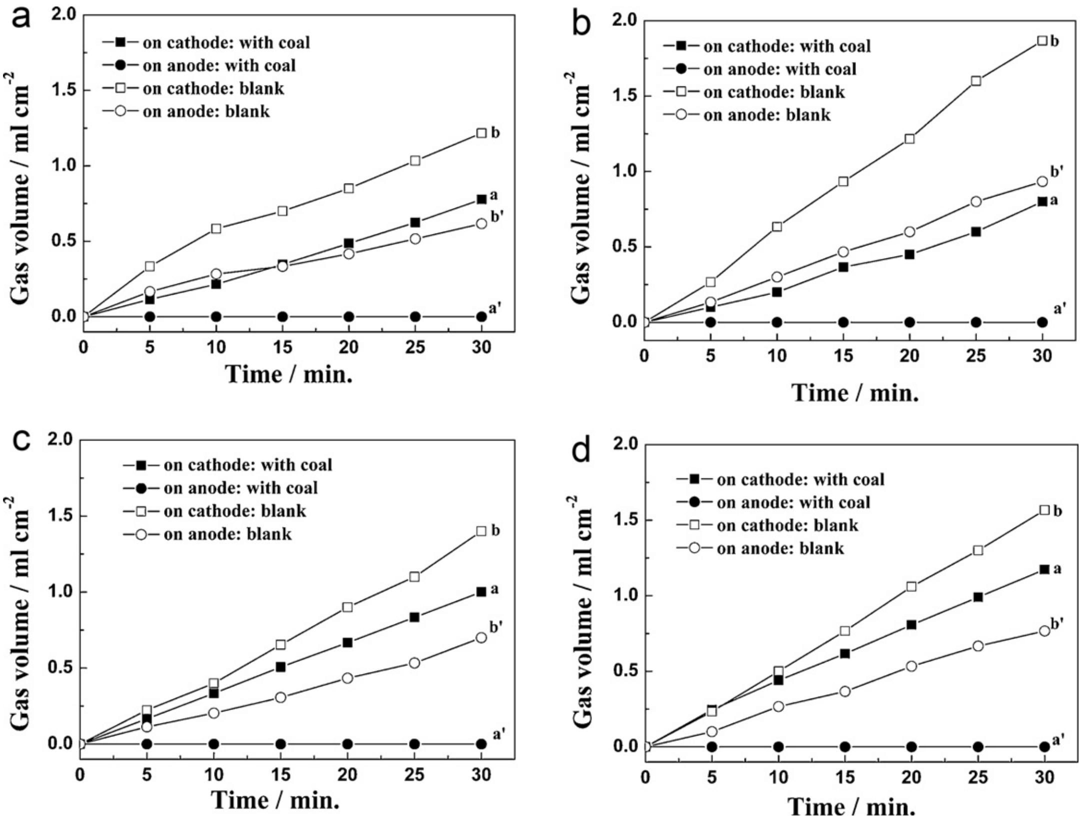

Fig. 5. Volume of collected gas at 1.2 V: (a) TiO_2/Pt; (b) TiO_2/Pt–Co_3O_4; (c) TiO_2/Pt–NiO; and (d) TiO_2/Pt–Co_3O_4–NiO.

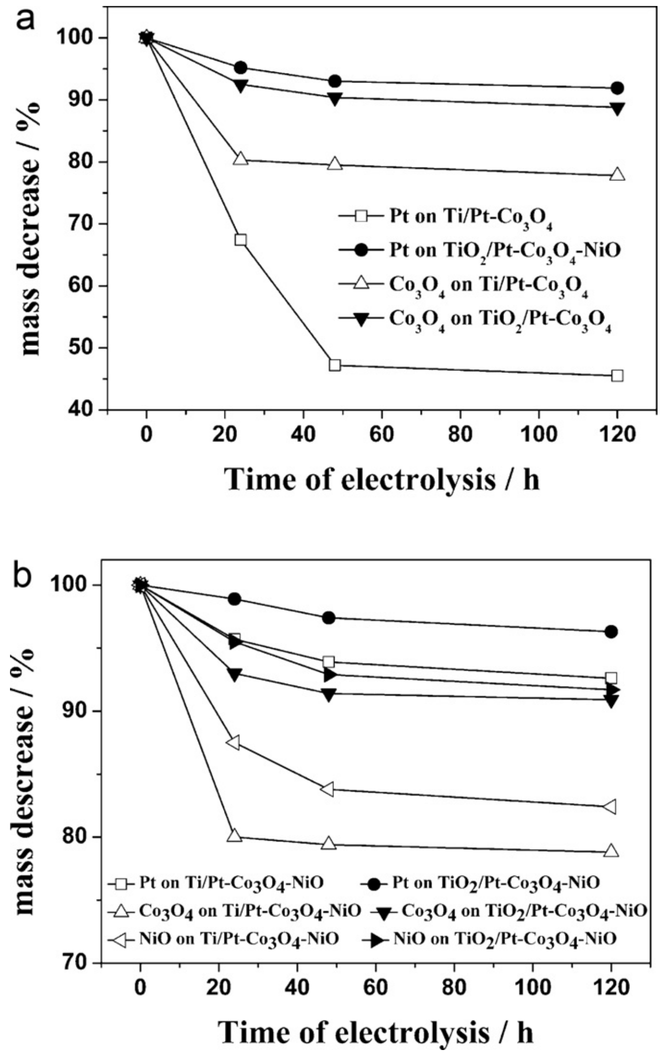

Fig. 6. Mass decrease of catalyst on the following: (a) $TiO_2/Pt–Co_3O_4$, $Ti/Pt–Co_3O_4$ and (b) $TiO_2/Pt–Co_3O_4–NiO$, $Ti/Pt–Co_3O_4–NiO$.

mass decrease. The porous surface of the TiO_2 substrate was greatly responsible for the high stability of the modified catalyst because the catalysts could insert themselves into the porous surface.

The NiO enhanced the adhesion of Pt and Co_3O_4 on both Ti and TiO_2. Compared to $Ti/Pt–Co_3O_4$, on which 54.2% Pt was lost, $Ti/Pt–Co_3O_4–NiO$ had 92.6% Pt remaining on the substrate after electrolysis for 120 h. With the addition of NiO, the mass loss of Co_3O_4 decreased from 11.6% to 9.1%. According to the SEM results, $TiO_2/Pt–Co_3O_4–NiO$ and $TiO_2/Pt–NiO$ almost had the same morphology, suggesting that NiO was responsible for the formation of the ball-like secondary units that enhanced the stability of the electrodes.

3.5. Mechanism

Ni and Co metal oxides have been reported to possess superior activity in catalytic oxidations [20] and pseudo-capacitor applications [21]. As shown in the LSV results (Fig. 3), the gas collection test (Fig. 5) and the ICP test (Fig. 6), the modified electrode had the best performance. Both catalysts were active because of the metal oxide hydroxide generated during electrolysis [22,23]:

$$\mathrm{NiO} + \mathrm{OH^-} \rightarrow \mathrm{NiOOH} + \mathrm{e^-} \quad (5)$$

$$\mathrm{Co_3O_4} + \mathrm{H_2O} + \mathrm{OH^-} \rightarrow 3\mathrm{CoOOH} + \mathrm{e^-} \quad (6)$$

As p-type semiconductors, both NiO and Co_3O_4 can produce hydroxyl radical to oxidize the coal at a high enough potential [24,25]. Metal oxide hydroxide undergoes the following process when used as an anode material:

$$\mathrm{OH^-} \xrightarrow{\mathrm{MOOH}} {}^{\bullet}\mathrm{OH} + \mathrm{e^-} \quad (7)$$

It was reasonable to assume that MOOH (M = Ni, Co) was responsible for the oxidization of coal. The reaction of coal can be started by hydroxyl radicals as shown in reaction (8). Reaction (9) could occur in the blank solution, in which oxygen is obtained from hydroxyl radicals.

$$\text{With coal}: {}^{\bullet}\mathrm{OH} + \text{coal} \xrightarrow{\mathrm{MOOH}} \text{oxidized coal} \quad (8)$$

$$\text{Blank}: {}^{\bullet}\mathrm{OH} + {}^{\bullet}\mathrm{OH} \rightarrow (1/2)\mathrm{O_2} + \mathrm{H_2O} \quad (9)$$

The effect of Co_3O_4 was determined by gas collection curves in the blank test. Comparing the results from Fig. 5(b) and (c), more gas was generated on $TiO_2/Pt–Co_3O_4$ compared to $TiO_2/Pt–NiO$. This finding indicated that the overpotential of oxygen evolution could be decreased by Co_3O_4 in a basic system [19]. Co_3O_4, which competed with coal in affecting the overpotential of O_2, facilitated reaction (9) because of its high ability to generate the hydroxyl radical. However, curve a in Fig. 5(b) indicated its lower activity for coal oxidation compared to $TiO_2/Pt–NiO$, and it could be attributed to the relatively low ability of Co_3O_4 to introduce the hydroxyl radical into coal (reaction (8)).

An interesting phenomenon is that $TiO_2/Pt–Co_3O_4–NiO$ had the highest current density (4.05 mA/cm^2) despite its low CCG value. There could be a possible cooperation effect on the surface of NiO and Co_3O_4, which is currently under further investigation.

4. Conclusion

A thin layer of porous TiO_2 could be used as an electrode substrate for coal electrolysis because its conductivity can be enhanced by metal deposition. An electroless deposit of Pt nanoparticles onto a TiO_2 substrate showed a homogeneous, stable surface. A NiO or Co_3O_4 modified TiO_2/Pt electrode showed the highest activity for the oxidization of coal, which was confirmed by both gas collection and an LSV test. Both metal oxides could generate hydroxyl radicals, which enhance the electro-oxidation of coal.

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