

Galvanostatic Pulse Plating of PtRu Nanoparticles for Direct Methanol Fuel Cells

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A galvanostatic pulse electrodeposition technique of preparing nanoparticulate PtRu electrocatalyst for direct methanol fuel cells has been demonstrated. After extensive cyclic voltammetric analysis, we determined the optimized parameters for the methanol oxidation to be current on-time on 50 ms, current off-time of 400 ms, current density of 50 mA/cm², and total charge of 8.0 C/cm². In addition, the catalyst loading was measured at 68 μg/cm², resulting in a mass activity of 213 mA/Pt . mg. The composition for the nanoparticles was confirmed as Pt₆₅Ru₃₅. High-magnification images on the specimen indicated fine particles in 4-20 nm with uniform distributions.

PtRu has attracted considerable attention as an anode electrocatalyst for direct methanol fuel cells [1]. Recently, the research objective for the PtRu has concentrated on the synthesis in nanoparticulate form with desirable atomic distributions in both bulk and surface states. Conventional synthetic route involves chemical reduction techniques which unfortunately require post-treatments to remove surfactants and reaction products. This engenders results in some difficulties in precise composition control [2,3]. In contrast, electrodeposition is recognized to produce PtRu directly, albeit with a reduced coulombic efficiency [3-6]. In this work, we adopt a pulse galvanostatic deposition technique to fabricate the PtRu nanoparticles on carbon clothes and evaluate their methanol oxidation abilities. In addition, morphologies, compositions, and phase analysis of the as-prepared PtRu particles were conducted using Transmission Electron Microscope (TEM), Inductively Coupled Plasma Mass Spectrometry (ICP-MS), and X-ray Diffraction (XRD).

A carbon cloth was used as the starting substrate in this study. Prior to the electrodeposition, the carbon cloth was coated with an ink dispersion which was prepared

by mixing 5.0 mg Nafion solution (5.0 wt%) and 8.0 mg commercial carbon powders (Vulcan XC-72R) in 5.0 ml 99.5 wt% ethanol for 30 min. The ink dispersion was deposited carefully on a $2 \times 2 \text{ cm}^2$ carbon cloth which was kept at 80°C atop a hotplate to evaporate the residual ethanol. The coating of the ink dispersion effectively reduced the surface area, porosity, and capacitance of the carbon cloth. Afterwards, an electrochemical treatment was adopted by imposing multiple voltammetric cyclings on the carbon cloth at potential between -0.2 and $+1.1 \text{ V}$ (vs. Ag/AgCl) at a scan rate of 50 mV/s in an electrolyte of 0.5 M sulfuric acid. The purpose for this step was to homogenize the pretreated carbon cloth and expose a larger surface area. For subsequent pulse electrodeposition, the electrolyte was prepared by mixing proper amounts of RuCl_3 and NaNO_2 (1:10 molar ratio) in aqueous solution at 100°C for 1 hour, followed by addition of H_2PtCl_6 and cooled to room temperature. Then, the H_2SO_4 was added to increase the conductivity of the plating bath. The resulting concentrations for the Pt, Ru, and H_2SO_4 are 5.0 mM , 5.0 mM , and 0.25 M , respectively. Figure 1 provides the illustration for the pulse parameters including $T_{\text{on}}=50 \text{ ms}$, $T_{\text{off}}=200\sim 500 \text{ ms}$, $J_A=50 \text{ mA/cm}^2$, and total coulomb charge of 8.0 C/cm^2 .

Electrochemical measurements were conducted at room temperature in a three-electrode arrangement using an EG&G 263A. Cyclic voltammetric analysis (CV) was taken in a potential range of -0.2 and 0.9 V at a scan rate of 20 mV/s in solutions of 0.5 M H_2SO_4 (for hydrogen absorption/desorption), as well as 0.5 M H_2SO_4 and 1 M CH_3OH (for methanol oxidation).

Figure 2 exhibits the XRD pattern for the as-deposited PtRu where a single diffraction peak at 41° was present. From the JCPDS data, the Pt exists in a fcc phase with the (111) peak at 39.8° . Since the atomic size of Ru is smaller than that of Pt, alloying of Ru into the Pt lattice is expected to reduce the latter's lattice parameter. This explains the observed slight shift of the diffraction peak (111) into higher angles. The XRD result suggested alloying of Pt and Ru was achieved successfully.

Figure 3(A) provides the CV scans for the as-prepared PtRu nanoparticles in 0.5 M H_2SO_4 electrolyte at T_{off} of 200, 300, 400, and 500 ms, respectively. Earlier, it was established that the characteristic peak for the hydrogen adsorption and desorption at Pt surface appeared in the potential range of $-0.12\text{--}0.02 \text{ V}$ [7-10]. However, in the case of PtRu, the oxidation of Ru into RuO_xH_y was taking place concurrently and thus the CV responses became rather broad. As expected, we observed broad CV profiles from all samples. In particular, the curve from T_{off} of 400 ms exhibited the largest current value.

Since the area underneath the CV scans also reflects the effective electrochemical surface area, we surmised T_{off} of 400 ms to be of great interest among all our samples.

Figure 3(B) demonstrates the CV curves in 0.5 M H_2SO_4 and 1 M CH_3OH . These CV profiles provide critical information including the onset potentials, forward/backward peak current (i_f), and the ratio of forward peak current to backward peak current (i_f/i_b). These values are listed in Table I along with the information on particle sizes (from TEM) and Pt ratios (from ICP-MS). In methanol oxidation, these recorded CV curves demonstrated typical characteristics of PtRu, i.e., they were consistent with what have been reported in literature [11-13]. Interestingly, the sample for T_{off} of 400 ms revealed the highest ability for the methanol oxidation. For the onset potentials, samples with higher Ru ratios exhibited lower values. This behavior is understandable because the Ru atom not only is prone to oxidation in the electrolyte itself but also promotes oxidation of CO at Pt surface. Thus excess presence of Ru produces lower onset potentials for oxidation signals. Figure 4(a) exhibits the effect of T_{off} over the resulting Pt amount and specific i_b (defined as the absolute value of the cathodic peak current) in the PtRu nanoparticles. It can be seen that the amount of Pt and specific i_b increased with larger T_{off} . The values for mass activity and i_f/i_b are also provided in Fig. 5(b). In literature, the mass activity reflects the intrinsic catalytic ability of an electrocatalyst while the ratio of i_f/i_b indicates the tendency of efficient removal of adsorbed CO at the Pt sites [12,13]. Once again, we observed the highest values for samples with T_{off} of 400 ms, indicating the highest catalytic ability for the methanol oxidation. Our results were consistent and reliable confirming the superiority of samples with T_{off} of 400 ms.

The images from samples with T_{off} of 200 and 400 ms are shown in Fig. 5. Apparently, the sample with T_{off} of 400 ms demonstrated better distributions of fine PtRu particles. In contrast, there was moderate aggregation occurring for sample with T_{off} of 200 ms. The difference in the PtRu sizes and distribution might explain the observed superiority in samples with T_{off} of 400 ms.

In summary, we successfully demonstrated the growth of PtRu nanoparticles on carbon clothes by a pulse electrodeposition technique. By varying the durations for T_{off} , we were able to produce PtRu in various compositions and particle sizes. We determined that a T_{off} of 400 ms produced nanoparticles with the highest catalytic ability for the methanol oxidation. The sizes for the PtRu was in 4-20 nm range while its composition was $\text{Pt}_{64}\text{Ru}_{36}$. In addition, the measured mass activity was approximately 213 mA/mg. We also observed that a shorter T_{off} resulted in lower catalytic abilities.

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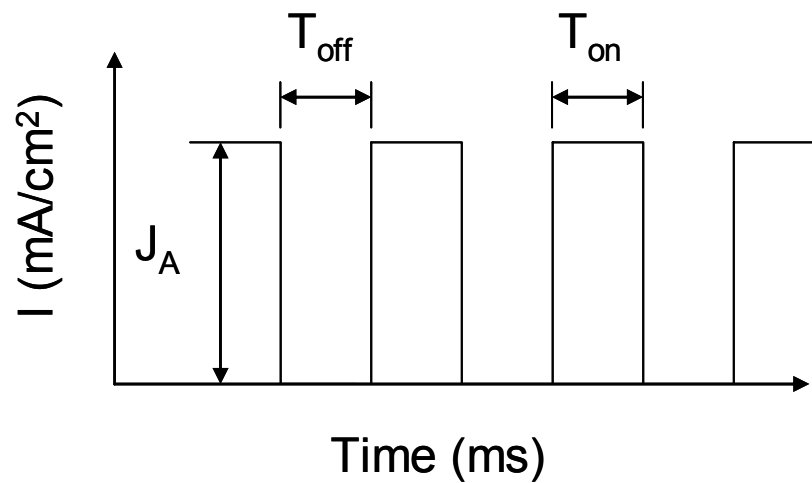


Figure 1: Illustration of parameters used in the pulse galvanostatic electrodeposition.

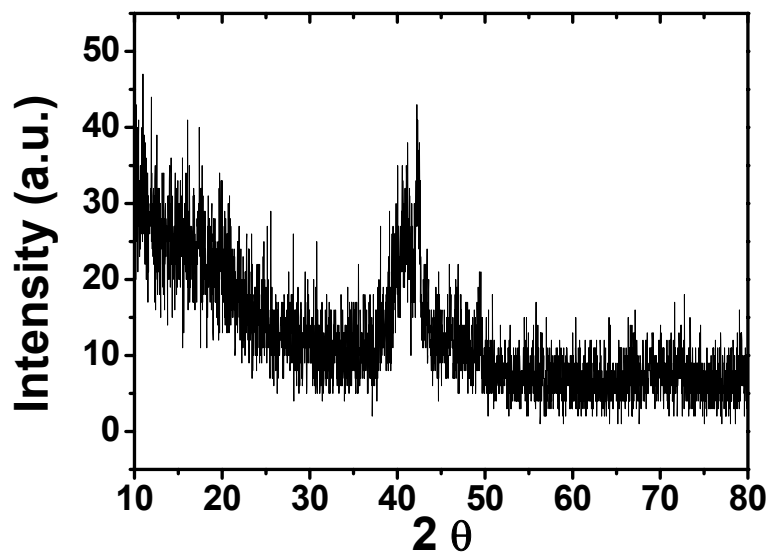


Figure 2: The XRD pattern of electrodeposited PtRu on a Cu substrate.

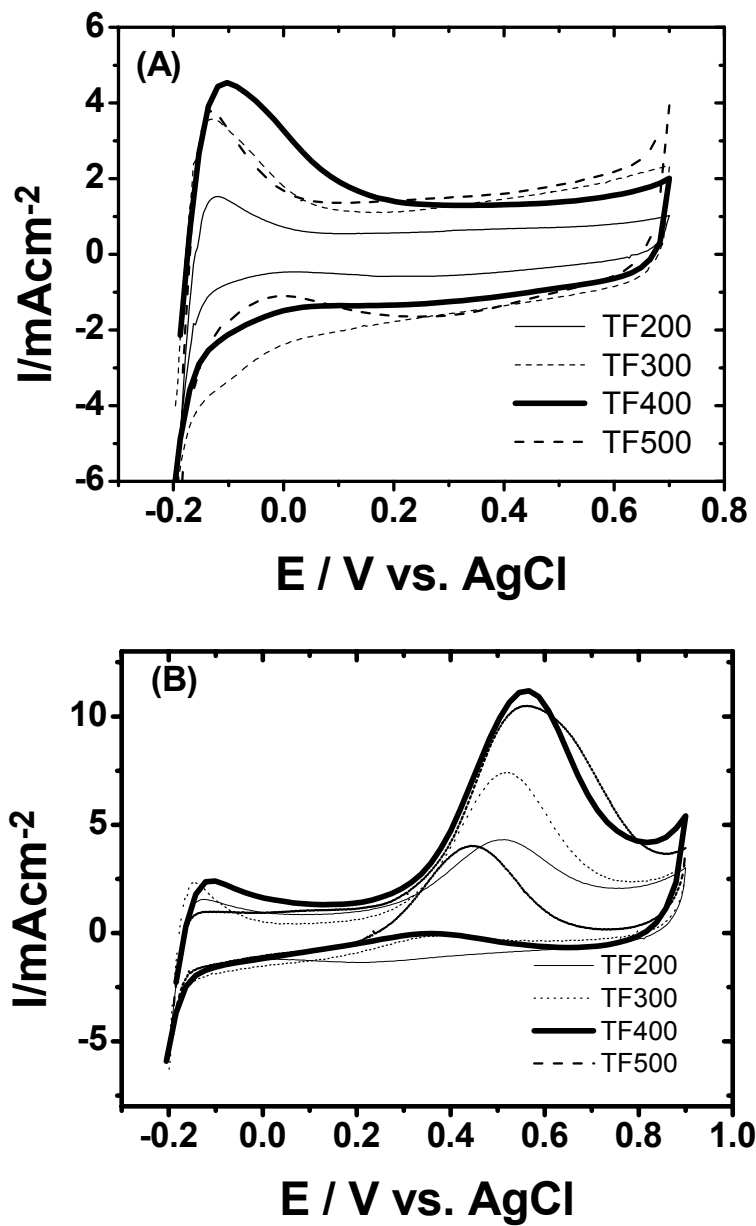


Figure 3: Cyclic voltammograms of PtRu electrocatalysts deposited with various T_{off} (labeled as TF in the diagrams, unit in ms) in electrolyte of (A) 0.5 M H_2SO_4 , as well as (B) 0.5 M H_2SO_4 and 1.0 M CH_3OH .

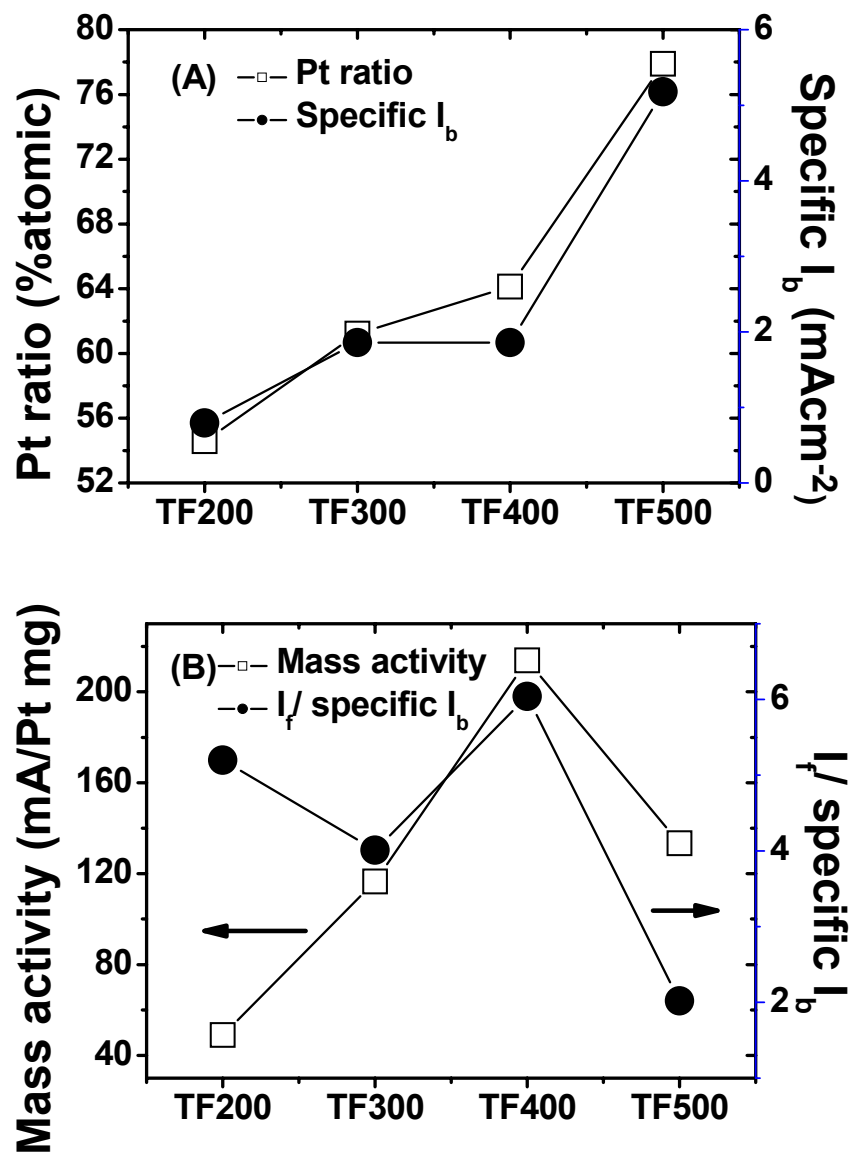


Figure 4: Relations of CV parameters with various T_{off} (labeled as TF, unit in ms); (A) specific I_b and Pt ratio, as well as (B) mass activity and I_f/I_b .

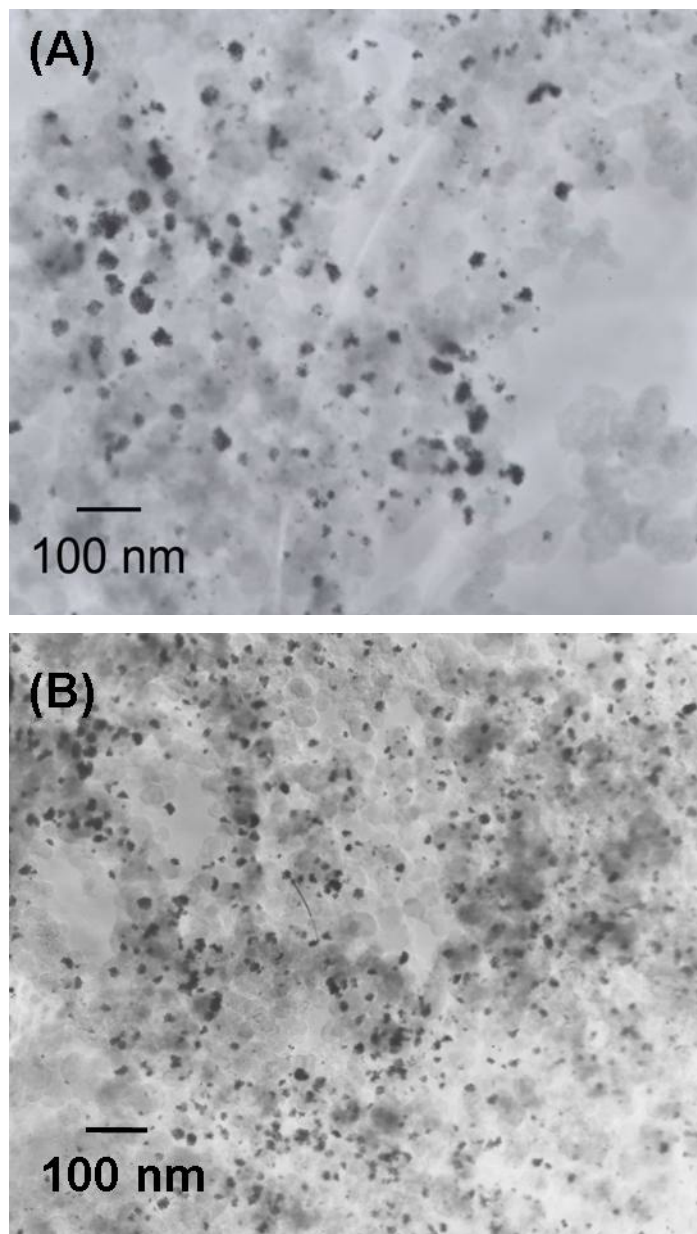


Figure 5: The TEM images for PtRu nanoparticles prepared with (a) T_{off} of 200 ms, and (b) T_{off} of 400 ms, respectively.

Table I. Materials information of PtRu from various T_{off} (labeled as TF).

Parameter (in ms)	Pt Atomic %	Total weight (mgcm^{-2})	Onset potential (V vs. AgCl)	Mass activity		Particle size(nm)	i/i_b
				mA/Pt	mA/PtRu		
				mg	mg		
TF200	54.6	0.129	0.106	48.9	34.2	8-32	5.20
TF300	61.2	0.085	0.135	116.5	87.7	na	4.01
TF400	64.1	0.068	0.167	213.8	165.8	4-20	6.04
TF500	77.9	0.091	0.217	133.4	116.3	na	2.02