

Effect of third metal on the electrocatalytic activity of PtRu/Vulcan for methanol electro-oxidation

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Abstract The effect of a third metal on the activity of PtRu/Vulcan toward methanol oxidation reaction (MOR) is studied. An efficient method to prepare ternary catalysts was used, which allows the introduction of the third metal to PtRu/Vulcan without altering its particle size or dispersion. Ni, Mo, Co, and Ir were chosen and added to PtRu/Vulcan, based on theoretical and experimental literature results, anticipating enhancement in the catalytic activity of PtRu/Vulcan. The composition of the third metal can be varied from trace to considerable amounts. Transmission electron microscopy and energy-dispersive X-ray analysis were used to determine the particle size, dispersion, and the composition of the ternary catalysts. Cyclic voltammetry, chronoamperometry, and CO-stripping voltammetry were used to analyze and compare the activities of the catalysts at 25 °C. It has been found that the addition of even trace amounts of third metal significantly affects the catalytic activity of PtRu toward MOR.

Keywords Methanol electro-oxidation · PtRu/Vulcan · Ternary catalysts · Catalytic activity

Introduction

Development of the direct methanol fuel cell (DMFC) has been an objective of several prominent research groups for

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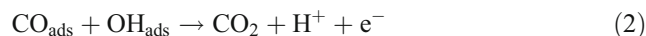
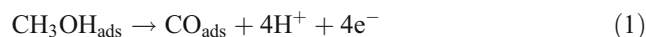
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more than 30 years and is now in the verge of commercialization [1, 2]. The commercialization of DMFCs can be further facilitated by overcoming a few fundamental problems. One main problem is the crossover of methanol from the anode to the cathode through the membrane. Another problem is the deficient activity of the anode catalysts leading to slow kinetics of methanol oxidation [1–3]. Both contribute to reduced output cell voltage. Many researchers committed their efforts to reduce methanol crossover by developing new membranes or modifying state of art Nafion[®] membranes [4]. Several others devote their attention to improve the kinetics of methanol oxidation by modifying the preparation conditions of catalysts or by introducing additional metals.

To date, PtRu/Vulcan remains to be the best binary catalyst for the oxidation of methanol [3, 5]. Several ternary and quaternary catalysts based on PtRu were prepared and tested so far and some have shown improvement in their catalytic activity toward methanol oxidation when compared with PtRu [6–18]. Some of the catalyst formulations tested up to now to improve the activity of PtRu include PtRuPd [6], PtRuW [6, 7], PtRuOs [8, 9], PtRuSn [10], PtRuMo [11], PtRuNi [12], PtRuCo [13], PtRuMeO_x [14, 15], PtRuOsIr [16], PtRuSnW [17], and PtRuMoW [18].

The ordinary mechanism of methanol oxidation is believed to involve two basic steps as follows (subscript “ads” stands for “adsorbed at the catalyst surface”) [19, 20]:



Step 1 involves progressive dehydrogenation of adsorbed methanol molecule. Step 2 is the oxidation of adsorbed CO ensued from the dehydrogenation process. It is widely

believed for binary PtRu catalysts that at low temperature, platinum adsorbs and dehydrogenates methanol, whereas ruthenium provides OH_{ads} at low potentials to oxidize CO. At elevated temperature (above 60 °C), it has been reported that Ru can also adsorb methanol, thereby contributing to its dehydrogenation [21]. Therefore, the third metal added to PtRu should be either active toward dehydrogenation of methanol or toward the oxidation of adsorbed species (mainly CO). Actually, it has been reported that partially oxidized products such as formaldehyde and formic acid can also be formed in addition to CO_2 [22, 23].

Most studies reported so far on PtRu-based ternary catalysts used transition metals as cocatalysts for the oxidation of methanol [6–18]. Mostly, the third metal used to alloy with PtRu was chosen under the condition that it should provide oxygen-containing species at low potentials to oxidize adsorbed CO, thereby decreasing catalytic poisoning ([24] and references therein). We choose a purely experimental approach to identify a PtRu-based ternary catalyst that shows significant improvement over PtRu for the oxidation of methanol. Recently, we have shown that a considerable enhancement of methanol oxidation reaction (MOR) activity was noted for PtRu when doped with trace amounts of Ir [25]. We attributed the improvement in performance to the ability of Ir to dehydrogenate methanol coupled with formation of oxygen-containing species helping CO electro-oxidation. In this article, we discuss the activities of metals capable of forming oxygen-containing species at low potentials or affecting the electronic properties of the base PtRu alloy. Further, comparing the activities of such catalysts with our past results on PtRuIr [25] will hopefully help understanding the role of the third metal in MOR.

We have prepared Vulcan-supported PtRu-based ternary nanoparticles with Ni, Mo, or Co as the third metal. Quantum chemistry calculation studies by Anderson et al. [26–28] showed that Co and Mo should be more active toward adsorption of H_2O molecules, whereas Ni is expected to be more resistant to adsorb water. Therefore, alloying PtRu with Mo or Co might decrease the catalyst poisoning by oxidizing adsorbed CO at low potentials. On the other hand, it is reported in the literature that Ni induces changes in the electronic properties of PtRu and thereby increases its activity [12]. The present work evaluated the effect of Ni, Mo, and Co as cocatalysts on PtRu/Vulcan and compared their activities with that of PtRuIr/Vulcan for the oxidation of methanol at 25 °C. Ternary catalysts were prepared using a procedure developed in our laboratory [29]. This method allows controlled variation of ternary catalysts compositions. Transmission electron microscopy (TEM) along with energy-dispersive X-ray (EDX) analysis was utilized to determine particle size and composition of the catalysts, respectively. Catalytic activity of the ternary

nanoparticles toward methanol oxidation was screened using electrochemical methods in half-cell experiments. It was found that the activities of the ternary catalysts are sensitive to type and amount of the third metal. Possible reasons for the observed effect of the third metal on electrocatalytic activities toward MOR are discussed.

Materials and methods

Acetyl acetonates of the metals were used as precursors except for molybdenum, where molybdenum (II) acetate was used. All the precursors were purchased from Alfa Aesar GmbH, Germany. Vulcan® XC72R (Cabot) carbon powder was utilized as the catalyst substrate. The catalysts PtRuX/Vulcan (X=Ni, Mo, Co) were prepared starting from PtRu/Vulcan because this method allowed controlled deposition of the third metal. First, the base PtRu/Vulcan catalyst was prepared with an optimal 68:32 Pt/Ru atomic ratio following the method developed in our laboratory and described in detail in Sivakumar and Tricoli [25] and Sivakumar et al. [29]. Then, appropriate amounts of “X” precursors were sublimed under vacuum (10^{-2} mbar) at fixed temperatures in a flask also containing the binary PtRu/Vulcan catalyst. Subsequent cooling of the flask allowed the precursor vapors to deposit on PtRu/Vulcan, which were then decomposed in nitrogen atmosphere at 320 °C for 3 h to obtain PtRuX/Vulcan catalysts. Altering the sublimation temperature of precursors controlled the amount of X deposited on PtRu/Vulcan. The precursors were sublimed at 170 and 220 °C in this study. Hereafter, the samples prepared at 170 °C are referred as PtRuX-I and the samples prepared at 220 °C as PtRuX-II.

Particle size and dispersion were characterized by using TEM (JEOL 2010 microscope operating at 20 kV). EDX analysis (Oxford-Pentafet instrument) was performed to determine the composition of the catalysts. Electrochemical experiments were performed on a personal computer-controlled Solartron SI 1287 Electrochemical Interface. Ag/AgCl was used as the reference electrode, but all the potentials referred in this paper are vs the standard hydrogen electrode (SHE). Cyclic voltammetry (CV), Chronoamperometry (CA) at a constant potential of 600 mV, and CO-stripping voltammetry were performed to evaluate the activity of the catalysts. All the experiments were carried out at 25 °C. Details of the experimental setup and preparation of the working electrodes are similar to those given in our earlier paper [30]. In brief, 1 M methanol in 0.5N H_2SO_4 was used in all the electrochemical experiments except for CO-stripping voltammetry where no methanol was present in the solution. The CV experiment was run at a scan rate of 10 mV/s. For CO-stripping voltammetry, CO was adsorbed onto the electrode

surface by bubbling a CO/N₂ gas mixture (12.5 vol.% CO) into the solution at a low flow rate for 15 min. The working electrode was held at 75 mV during this process. Afterward, the dissolved CO in the solution was removed by bubbling nitrogen, and the electrode was cycled twice between 0 and 800 mV at a scan rate of 5 mV/s to obtain CO-stripping characteristics.

Anodic dissolution of the less noble component of the catalyst can in principle occur at high potential, thereby affecting the observed Faradaic current and also altering the catalyst composition and activity. Therefore, it is recommendable to keep the potential within certain limits. In an earlier study, Paffett et al. [31] noted appreciable depletion of chromium in a PtCr catalyst only above 1,250 mV (vs SHE). Accordingly, to avoid anodic dissolution, we have chosen to keep the potential always below 800 mV throughout this work.

Results and discussion

Changing the sublimation temperature of precursors during their preparation altered the composition of catalysts. From trace to considerable amounts of the third metal can be introduced without altering the morphology of the catalysts. Table 1 gives the composition of all the ternary catalysts studied, as determined by EDX analysis. It should be pointed out, however, that the reported compositional values refer to the catalyst mass as a whole. These values could significantly deviate from composition at the catalyst surface. TEM analysis was carried out on ternary catalysts to determine the particle size and distribution over the support and their uniformity. The analysis was performed over several zones, and all the images were similar. Most of the studies so far on ternary catalysts failed to keep the morphology of particles constant, which does not allow a direct comparison of the activities. There are several reports studying the effect of particle size on the activity of

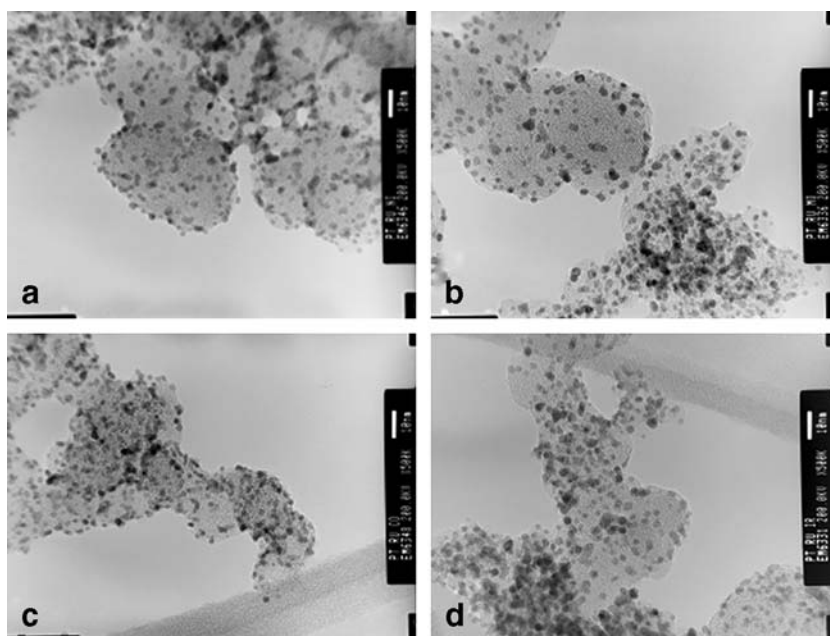
catalysts for methanol oxidation, and the results show a strong dependence of activity on the particle size of catalysts [32]. This recommends the importance of maintaining the particle size of ternary catalysts to compare the activity of different third metals and their compositions with respect to the binary catalyst. Figure 1 shows representative TEM micrographs of PtRuX-I catalysts. The particles were evenly dispersed over the support for all catalysts. The histogram of the particle size distribution (not shown) gives a narrow range with the average particle size being 2 nm. The size and distribution of the particles were similar to PtRu/Vulcan [29]. Therefore, the preparation method used in our studies allowed us to compare their activities with PtRu/Vulcan, without compromising on the morphological aspects, i.e., without altering the particle size or distribution. The activities of the ternary catalysts with different compositions as compared to PtRu/Vulcan are discussed one by one. 68-Pt:32-Ru atomic was the chosen composition of the reference PtRu/Vulcan catalyst. Such composition was chosen because it corresponds to the maximum activity of PtRu/Vulcan nanoparticles prepared according to our method [30]. In fact, it was shown earlier that the methanol oxidation current was about 50% lower for a 50:50 Pt/Ru composition [30]. Thus, comparison with the optimized PtRu/Vulcan gives a meaningful measure of the influence of the third metal on catalytic activity.

PtRuNi/Vulcan catalysts Figure 2a shows the cyclic voltammograms of PtRuNi-I and PtRuNi-II. For comparison, CV of in-house prepared PtRu/Vulcan recorded under the same conditions is shown. It is clear from the figure that incorporating nickel decreases the activity of PtRu toward methanol oxidation. Even trace amounts of nickel added to PtRu have been found to have an adverse effect on the latter's catalytic activity for methanol oxidation. PtRuNi-I with a composition of 62:36:2 (atomic ratio) was found to decrease the activity of PtRu/Vulcan by about 20%; a further increase in the nickel content (PtRuNi-II, 55:36:9) decreases the catalytic activity further. The steady-state catalytic activity of PtRuNi as compared to PtRu is shown in Fig. 2b. CA experiments reflected the conclusions drawn from CV experiments: the addition of even trace amounts of Ni to PtRu/Vulcan decreases its catalytic activity toward methanol oxidation. Earlier studies indicated that the addition of Ni to PtRu brings an electronic interaction of Ni with Pt, thereby inducing an increase in the catalytic activity of PtRu toward MOR [33]. However, the results presented above indicate the opposite, where the introduction of Ni decreases the catalytic activity of PtRu. CO-stripping voltammetry was performed over PtRuNi-I/Vulcan to get some insight on its catalytic activity with respect to PtRu/Vulcan. During the first anodic scan, the characteristic current peak was observed corresponding to CO electro-

Table 1 Composition of PtRuX/Vulcan catalysts (X=Ni, Mo, Co, and Ir)

Catalysts	Composition (atomic ratio)
PtRu/Vulcan	68:32
PtRuNi-I/Vulcan	62:36:2
PtRuNi-II/Vulcan	55:36:9
PtRuMo-I/Vulcan	54:32:14
PtRuMo-II/Vulcan	50:25:25
PtRuCo-I/Vulcan	60:38:2
PtRuCo-II/Vulcan	50:30:20
PtRuIr-I/Vulcan	63:35:2
PtRuIr-II/Vulcan	54:30:16

Fig. 1 TEM micrographs of **a** PtRuNi/Vulcan, **b** PtRuMo/Vulcan, **c** PtRuCo/Vulcan, and **d** PtRuIr/Vulcan



oxidation and CO_2 liberation. This feature was always absent during the second cycle, which proves complete removal of dissolved CO upon purging the solution with nitrogen. Figure 3 shows the CO-stripping voltammogram of PtRuNi-I/Vulcan along with that of PtRu/Vulcan for comparison. The peak potentials for CO stripping were found to be same for both PtRu and PtRuNi-I/Vulcan, which indicates similar intrinsic activity for the catalysts to oxidize CO. The CO-stripping area for PtRuNi was found to be smaller than that of PtRu. The stripping area is proportional to the number of active sites on the catalyst surface for CO adsorption. Because the physical surface area of the PtRu and the PtRuNi catalysts is likely to be the same (PtRuNi has been prepared by Ni-precursor vapor deposition onto the PtRu catalyst), the decrease in the stripping area points out that the addition of nickel diminishes the number of active surface sites for CO adsorption. This is not surprising, as Ni deposition on the PtRu surface, in fact, buries part of the Pt sites, which are highly active for CO adsorption. It is interesting to note that Pt sites are also active for methanol adsorption and electrochemical dehydrogenation according to step 1 shown above. In the light of these considerations, the CO-stripping results can give a reasonable account for the adverse effect of Ni addition on the apparent electrocatalytic activity of PtRu toward MOR as evicted from Fig. 2. In fact, on the one hand, CO stripping shows that Ni does not promote intrinsic activity of the catalyst toward CO electro-oxidation (no shift of the ignition potential and of the peak potential). On the other hand, the diminished CO-stripping area for PtRuNi is indicative of a reduced number density of surface sites active for methanol adsorption/dehydrogenation.

PtRuMo/Vulcan catalysts Figure 4 shows the cyclic voltammogram (a) and current vs. time graph at steady potential (b) of PtRuMo/Vulcan with different concentrations of Mo. Both CV and CA curves show that adding Mo to PtRu decreases the catalytic activity of the latter toward methanol oxidation with the decrease being more marked when a larger amount of Mo is added. The results obtained were quite similar to those of PtRuNi/Vulcan. Theoretical studies [26, 27] suggested that the addition of molybdenum to PtRu might promote water adsorption. Water adsorption at low potentials is an important step in methanol oxidation because it provides oxygen-containing species at low potentials required for oxidizing CO (step 2). In fact, CO-stripping experiments on PtRuMo-I/Vulcan (Fig. 5) confirmed the above hypothesis, where the CO-stripping peak was generally shifted to a lower potential when compared to PtRu. A clear negative shift can be noted for the CO ignition potential. A less remarkable negative shift of the peak potential is also observed. However, the peak was broader as compared to PtRu, whereas a narrow stripping peak indicates a stronger catalyst activity. This makes it difficult to conclude from CO-stripping results whether the addition of Mo to PtRu increases its catalytic activity for CO oxidation. Nevertheless, methanol oxidation on PtRuMo/Vulcan, evaluated using CV and steady-state CA measurements, did not show an increase in their activity when compared with PtRu. Ordonez et al. [34] reported enhancement in the MOR upon addition of small amounts of Mo to Pt, which he attributed to the promotional effect of Mo on Pt for CO oxidation. The noted promotional effect of Mo was for the binary PtMo catalyst, but in the case of ternary PtRuMo, Ru might provide the required OH_{ads}

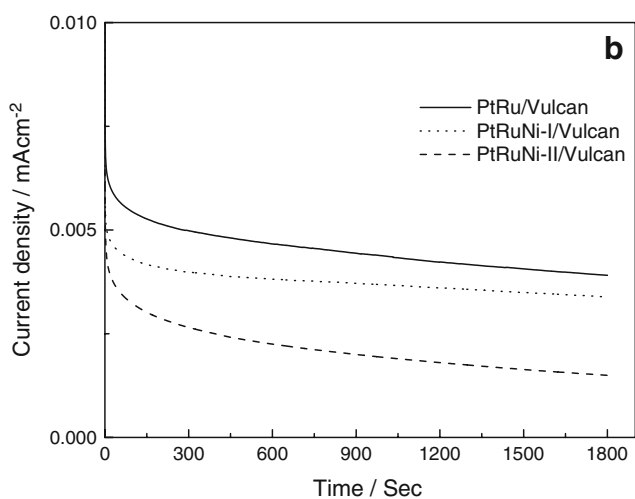
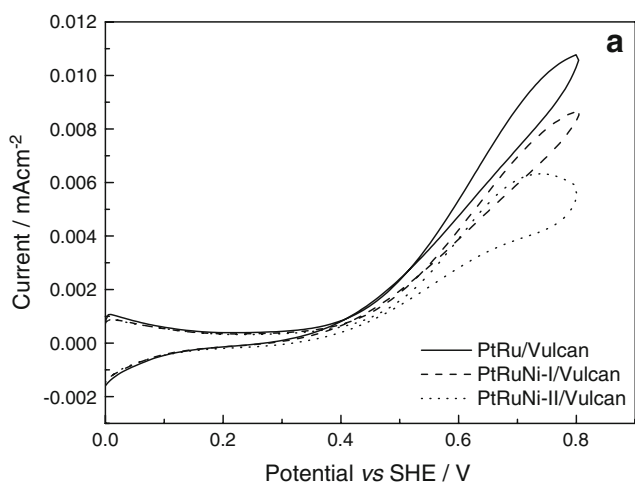


Fig. 2 **a** Cyclic voltammograms at (scan rate of 10 mV/s) and **b** chronoamperometry measurements (potential 600 mV, SHE) of PtRuNi/Vulcan with different compositions for the oxidation of 1 M methanol

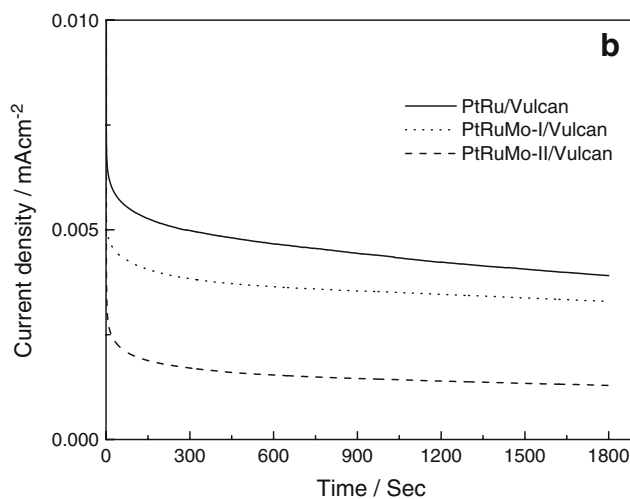
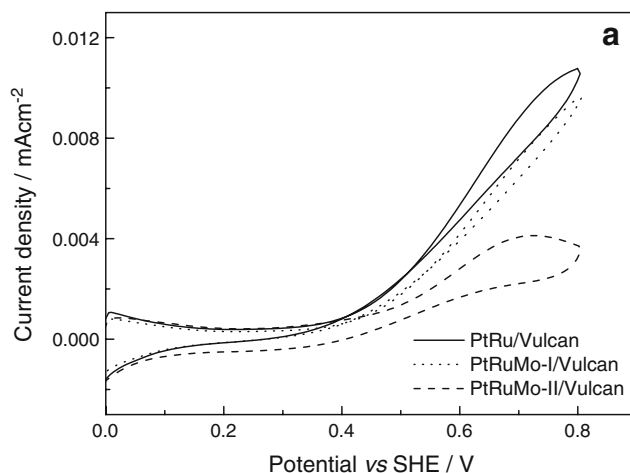


Fig. 4 **a** Cyclic voltammograms at (scan rate of 10 mV/s) and **b** chronoamperometry measurements (potential 600 mV, SHE) of PtRuMo/Vulcan with different compositions for the oxidation of 1 M methanol

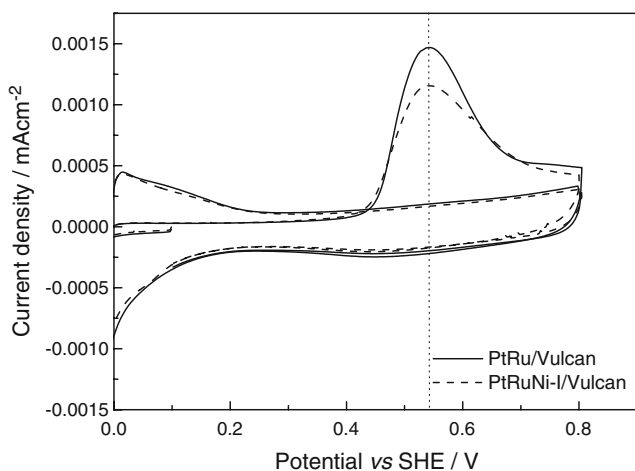


Fig. 3 CO-stripping voltammograms for PtRu/Vulcan and PtRuNi-I/Vulcan

species thereby concealing the effect of Mo. Lima et al. [35] observed a significant increase in the MOR activity for the PtRuMo catalyst as compared to PtRu at 400–450 mV and suggested that the improvement might be due to the oxidation of CO at low potentials. Those observations are apparently in disagreement with the CV and CA results from Fig. 4. We can think of three possible reasons for this disagreement. One could be the consistently higher Mo content in our PtRuMo catalysts (Table 1) as compared to those of Lima et al. [35] where Mo content was 4% atomic. Another reason could be related to substantial difference in the preparation method. In fact, it should be stressed that Lima's catalysts were obtained by simultaneous electro-reduction of the various salt precursors from solutions, whereas ours were formed by vapor deposition of a Mo precursor on the surface of pre-existing PtRu nanoparticles. The third possible reason could be ascribed to the significantly higher potential (600 mV) utilized in our CA

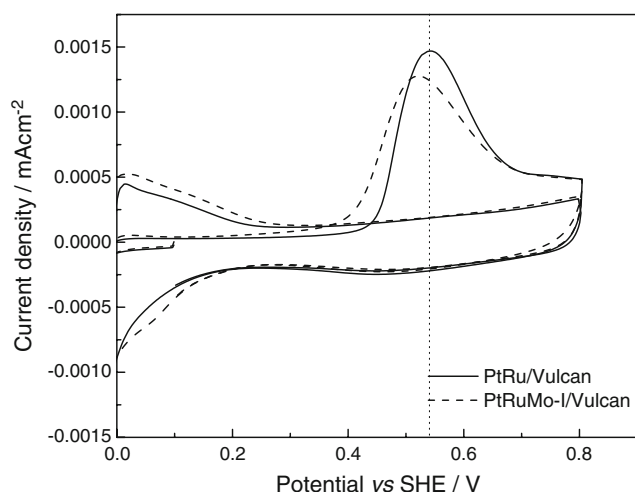


Fig. 5 CO-stripping voltammograms for PtRu/Vulcan and PtRuMo-I/Vulcan

experiment with respect to tests carried out by Lima et al. (400–450 mV).

PtRuCo/Vulcan catalysts Figure 6a shows the CVs for methanol oxidation for PtRuCo/Vulcan with different compositions, as compared to PtRu. Unlike PtRuNi/Vulcan and PtRuMo/Vulcan, addition of trace amounts of Co was found to increase the catalytic activity of PtRu toward methanol oxidation. At 550 mV, the increase in the catalytic activity of PtRuCo-I/Vulcan (60:38:2) with respect to PtRu was found to be 11%. However, adding more cobalt proved futile, with PtRuCo-II/Vulcan (50:30:20) giving a much lower catalytic activity than PtRu. Figure 6b displays the CA curves for PtRuCo/Vulcan as compared to PtRu at a constant potential of 600 mV. All three catalysts showed an initial steep decrease in current density, but the decrease was more significant for PtRuCo-II/Vulcan, the catalyst identified by CV studies to have the lowest activity. It is interesting to note that there seems to be a correspondence between the more pronounced initial decrease in the current in the CA plot for PtRuCo-II, and the current decrease in the CV plot noted at potential positive of 700 mV with marked loop hysteresis. This correspondence is observable also for the PtRuNi-II catalyst (Fig. 3). Previous works suggested that the initial decrease in the current in CA experiments is related to CO poisoning of the catalyst [36]. PtRuCo-I/Vulcan showed good catalytic activity for the oxidation of methanol. When compared to PtRu, an increase of 25% is noted for PtRuCo-I after 10 min from the start of the experiment. Figure 7 shows the CO-stripping voltammogram of PtRuCo-I/Vulcan together with that of PtRu. A shift of 30 mV toward low potentials was noted for PtRuCo-I/Vulcan. Differently from PtRuMo, this shift is not accompanied by peak broadening with respect to PtRu. This suggests that PtRuCo-I/Vulcan is more active

toward the oxidation of CO than PtRu/Vulcan. These results also confirm the theoretical studies by Anderson et al. [26, 27]. Thus, the improved catalytic activity of PtRuCo-I/Vulcan for the oxidation of methanol can be attributed to the improvement in its catalytic activity toward the oxidation of adsorbed species (mainly CO) formed by methanol dehydrogenation.

PtRuIr/Vulcan catalysts We have shown in an earlier investigation that the addition of trace amounts of iridium increases the activity of PtRu significantly for MOR [25]. Because we are comparing the activities of ternary catalysts, it is apt to briefly discuss some of those results here about the effect of iridium as the third metal for MOR. Figure 8 shows the CVs (a) and the CA curves (b) for PtRuIr/Vulcan with two different compositions as compared to PtRu. The CVs shows that the addition of iridium

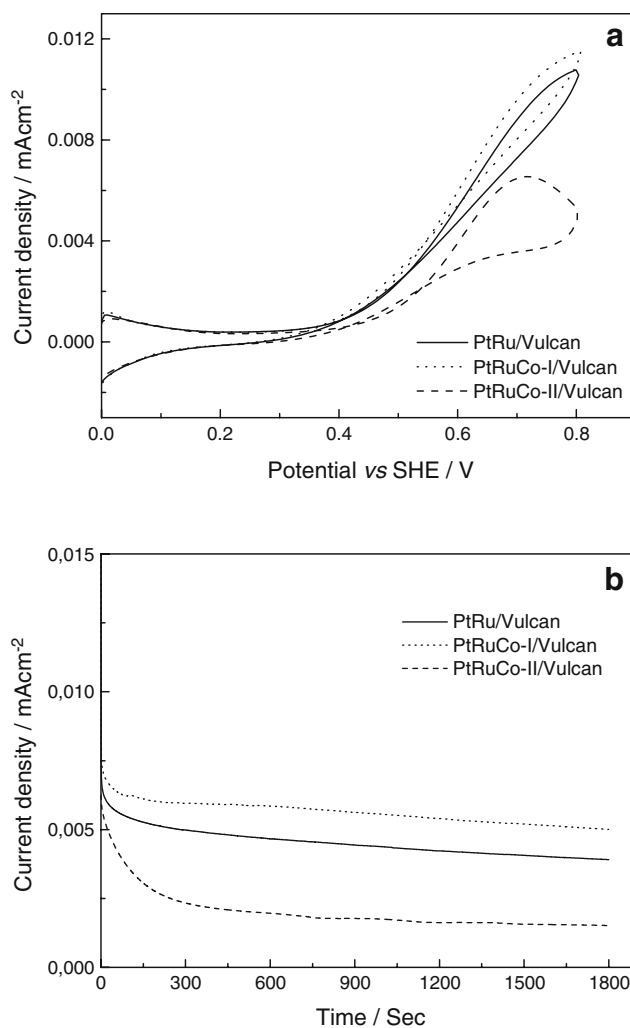


Fig. 6 **a** Cyclic voltammograms (at scan rate of 10 mV/s) and **b** chronoamperometry measurements (potential 600 mV, SHE) of PtRuCo/Vulcan with different compositions for the oxidation of 1 M methanol

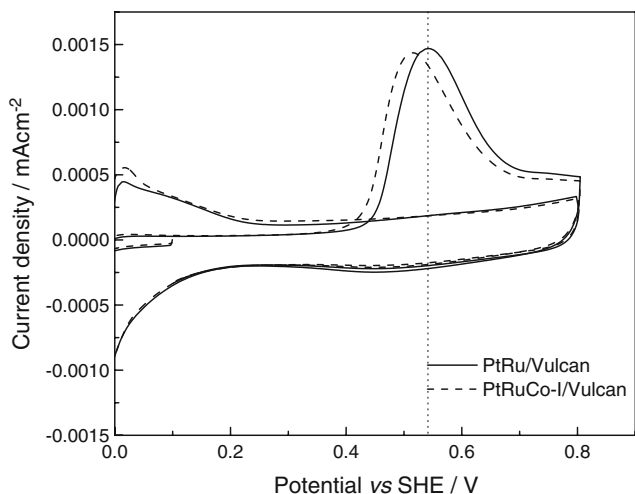


Fig. 7 CO-stripping voltammograms for PtRu/Vulcan and PtRuCo-I/Vulcan

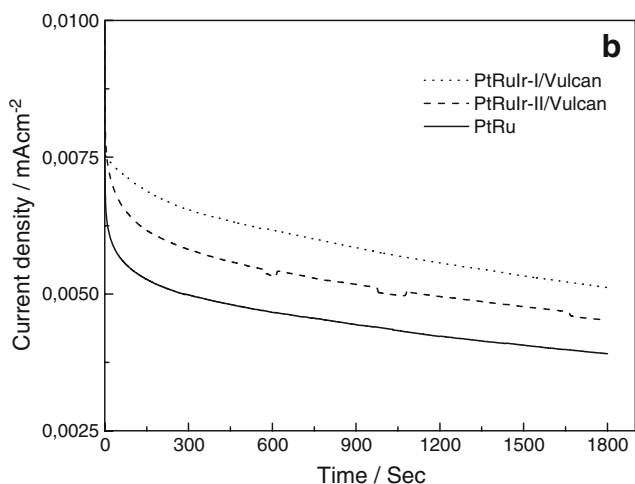
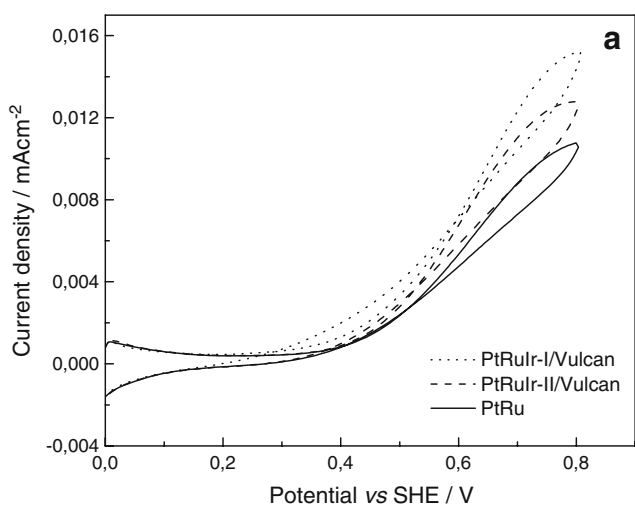


Fig. 8 **a** Cyclic voltammograms at (scan rate of 10 mV/s) and **b** chronoamperometry measurements (potential 600 mV, SHE) of PtRuIr/Vulcan with different compositions for the oxidation of 1 M methanol

to PtRu has a positive impact on the catalytic activity of the latter toward methanol oxidation. PtRuIr-I/Vulcan with atomic composition of 63:35:2 was more active (by about 40%) than PtRu at 550 mV. An increase in the iridium composition (PtRuIr-II) decreased the activity of the catalyst. Although the activity of PtRuIr/Vulcan decreased on increasing the composition of Ir, PtRuIr-II yet performed better than PtRu for MOR. CA plots shown in Fig. 8b reflect the findings of CV studies, with PtRuIr-I/Vulcan giving higher current densities than PtRuIr-II/Vulcan and PtRu. After 10 min from the start of the CA experiment, PtRuIr-I/Vulcan showed an increase of 32% with respect to PtRu for the oxidation of 1 M methanol. An insight into the increased catalytic activity of PtRuIr-I over PtRu can be obtained from CO-stripping studies. Figure 9 gives the CO-stripping curves for PtRuIr-I as compared to PtRu. The stripping areas for both the catalysts are similar, indicating similar number density of surface sites active for CO adsorption. The peak potential of PtRuIr-I was shifted by 35 mV to lower potentials and appeared somewhat narrower as compared to PtRu. This suggests that addition of Ir to PtRu increases its CO oxidation activity.

In our studies above, it is evident that the third metal added to PtRu should have both methanol dehydrogenation and CO oxidation ability to significantly improve catalyst activity for MOR. Our findings also highlight the reasons for the fact that in spite of considerable amounts of research on ternary catalysts, only a few have shown better activity for MOR when compared to PtRu. This is because most of the metals that are active for water adsorption and splitting turn to be poorly active for methanol dehydrogenation or vice versa.

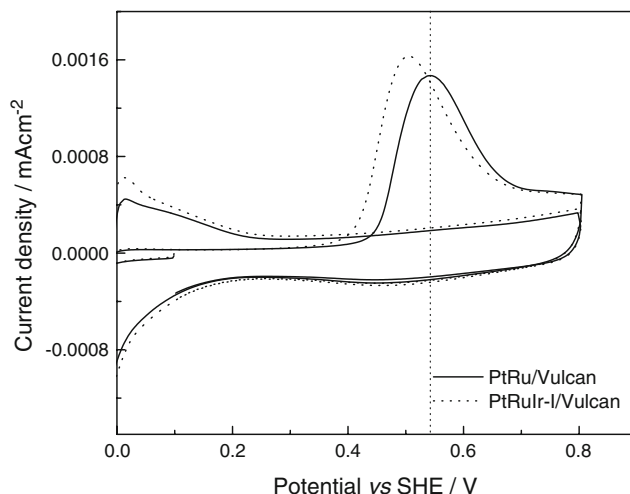


Fig. 9 CO-stripping voltammograms for PtRu/Vulcan and PtRuIr-I/Vulcan

Conclusion

The effect of the third metal (Ni, Mo, Co, and Ir) added to PtRu/Vulcan catalysts on the methanol electro-oxidation activity was studied. The investigated catalysts were prepared using an in-house developed method, which allowed good control over the composition and particle size. It was found that even trace amounts of the third metal on PtRu largely affect its catalytic activity toward MOR. Iridium and cobalt were found to promote the activity of PtRu, whereas nickel and molybdenum decrease the activity of PtRu for MOR. Furthermore, it is evident from comparing the results with literature that the effect of the third metal on PtRu activity depends notably on the preparation procedure. The results show that the activity of PtRu for MOR can be improved significantly by adding trace amounts of third metals, especially those active for not only CO oxidation but also methanol dehydrogenation.

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