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Complex SrRuO₃−Pt and LaRuO₃−Pt Catalysts for Direct Alcohol Fuel Cells

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Using energy efficient and rapid solution combustion synthesis technique, a variety of complex, i.e., perovskites/ platinum (ABO_3/Pt), catalysts were synthesized. A high-throughput NuVant system was used for testing these compositions as an anode catalyst for electrooxidation of methanol and ethanol in the conditions close to those for direct alcohol fuel cells. It was found that a variety of ABO_3/Pt compositions with Ru at B-site, prepared directly in the combustion wave, exhibit comparable performance with Pt−Ru alloy. It is important that these bifunctional catalysts contain much less platinum than that used in standard ones.

1. Introduction

Direct alcohol fuel cells (DAFCs) are considered as advanced sources of energy for a variety of applications, particularly for the portable electronics.[1,2] Among different compounds methanol is examined as a primary fuel for DAFC because of its low cost and easy storage.[3,4] However, the aspect of the methanol toxicity remains crucial.[5] Thus, although having higher cost, ethanol is also considered an attractive alternative fuel because it has low toxicity and can be produced from a broad variety of biomass products.

It is well-recognized that during low-temperature electrochemical oxidation of such fuels at anode different intermediate chemisorbed species are produced, including carbon monoxide, which blocks the electrocatalytic active sites and hence reduces the overall performance of the cell.[6,7] Thus, primarily the platinum-based alloys have been studied as catalysts for DAFC application. Indeed, Pt is the only known active noble metal in acid environment (proton exchange membrane) and the platinum alloys (e.g., Pt−Ru and Pt−Sn) are believed to be effective electrocatalysts for methanol/ ethanol oxidation.[5,8]

Recently we suggested a different approach for developing the effective multifunctional catalysts for DAFCs.[9,10] It was proposed that mixed conductive complex oxides, which are known as excellent water adsorbents and catalysts for CO oxidation, could be the alternative materials for considered application. Specifically, we explored a variety of electronically conductive perovskites (ABO_3), which have an excellent proton transport property, as basic elements for design of anode catalyst for methanol and ethanol electrooxidation. Moreover, we used a combinatorial-type methodology for finding the effective perovskite-based catalysts, which includes energy efficient rapid solution combustion (SC) synthesis technique for catalyst preparation in combination with a throughput catalyst activity testing method. It was shown that $LaRuO_3$ and $SrRuO_3$ compositions possess sizable activity for methanol electrooxidation in the conditions similar to those for DMFC. It was also revealed that direct incorporation (during combustion reaction) of a small amount of platinum on the perovskite surface leads to a significant enhance of its catalytic performance.

In this work, a library of $LaRuO_3$- and $SrRuO_3$-based perovskites with different amounts of loaded platinum was synthesized and tested for both methanol and ethanol electrooxidation. It was proved that optimum compositions show close apparent catalytic activities to standard platinum alloy. However the perovskite-based materials involve 4−6 times less platinum than the standard. These results suggest that such multifunctional catalysts prepared by combustion technique may hold a key for low-cost solution of effective catalyst for DAFCs.

2. Experimental Procedure

2.1. Catalysts Synthesis. A combination of combustion and reactive solution approaches leads to so-called *solution (aqueous) combustion (SC) synthesis* method.[11,12] Typically SC involves a self-sustained reaction in solutions of metal nitrates and different fuels, which can be classified on the basis of their chemical structure, i.e., the type of reactive groups (e.g., amino, hydroxyl, carboxyl) bonded to the hydrocarbon chain.[13] While SC can be performed in different reaction modes, including volume combustion synthesis (VCS),[11] self-propagating sol−gel combustion (SGC),[12] impregnated combustion (IC)[13] and impregnated active combustion,[14] in this work we used conventional VCS approach, which is described in detail in our previous work.[12]

The metal nitrates $Me(NO_3)_x$ (where Me = Sr, La), ruthenium nitrosyl nitrate solution, and glycine $C_2H_5NO_2$ (all Alfa Aesar) were used to synthesize different catalysts. First, reactants are dissolved in water and obtained solution is thoroughly mixed to reach an essential molecular level of homogenization for the reaction medium. After homogeneous solution preheating (temperature variation less than ±1 °C) to the water boiling point (100 °C), it starts to evaporate. At some specific temperature (T_{ig}), which varies for different systems (e.g., ∼130 °C for $LaRuO_3$ and 250 °C for $SrRuO_3$), the solution self-ignites essentially uniformly all over the reaction volume. After ignition the temperature rises rapidly to values in the range of 300−1000 °C as a function of solution composition. High temperature being accompanied by intensive gasification (CO_2, N_2, steam) in a short time period (0.1−1 s) converts the initial solution to a fine (specific surface area from 6 to 17 m²/g) well-crystallized powder with the desired phase composition. The latter was confirmed by X-ray diffraction (XRD) analysis (see also Table 1).

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In general, in such systems the reactions under equilibrium conditions can be represented as follows:

$$Me^{\nu}(NO_3)_{\nu} + \left(\frac{5}{9}\nu\phi\right)CH_2NH_2CO_2H + \frac{5}{4}\nu(\phi-1)O_2 \Longrightarrow$$
$$MeO_{\nu/2}(s) + \left(\frac{10}{9}\nu\phi\right)CO_2(g) + \frac{25}{18}\nu\phi H_2O(g) +$$
$$\left[\nu\left(\frac{5}{9}\phi+1\right)/2\right]N_2(g)$$
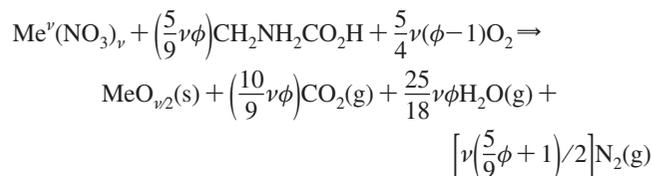
where Me^{ν} is a metal with $\nu = $ valence; ϕ is a fuel to oxidizer ratio, $\phi = 1$ means that the initial mixture does not require atmospheric oxygen for complete oxidation of fuel, while $\phi > 1$ (<1) implies fuel-rich (-lean) conditions.

Besides pure perovskites the design of multifunctional catalyst involves preparation of perovskite−platinum composites. These complex oxide−metal powders were synthesized by adding a Pt containing reagent, i.e., tetraammine−platinum nitrate into the initial metal nitrate + glycine solution, followed by direct SC synthesis of the catalysts. The product phase composition and crystallinity were determined by using an X_1 advanced diffraction system (Scintag Inc.). The BET specific surface area of powders was measured by Autosorb 1C (Quantchrome Instruments, USA) apparatus.

2.2. Catalysts Screening. Electrochemical screening system NuVant 100P was used to define the apparel catalytic activities of the prepared materials in conditions similar to those in DAFCs.[15] The details on the experimental setup can be found elsewhere,[9,10] Briefly, the device consists of electroinsulating ceramic block with an array of 25 fuel cells and corresponding independent graphite sensor electrodes for each cell. Serial flow fields machined on the surface of the ceramic block permit delivery of fuel (liquid or gas) to the cells. Anode and cathode catalyst inks are prepared by dispersion of the corresponding powders in solubilized Nafion solution (Aldrich, Milwaukee, WI). Gas diffusion layers (GDLs) for each anode catalyst candidates are prepared by uniform coating of carbon fiber paper (Toray paper, E-TEK, TGPH-60) with the ink and then punching out 0.713 cm² disks. Typically six replicate samples for each of the four catalyst compositions (total 24) and one blank sample disk were prepared and then randomly positioned in the array. The loading for perovskite-based catalysts was ∼6 mg/cm², while for standard Pt or Pt−Ru catalysts ∼4 mg/cm². In turn, the Pt loading for the cathode, which was used as common counter/reference electrode, was 1 mg/cm². The 25 working anode electrodes were hot-pressed (160 °C at 1000 lb-force for 5 min) with the Nafion 17 (DuPont Nafion Products, Fayetteville, NC) sheet. In turn, the counter/reference electrode was hot-pressed (160 °C at 1800 lb-force for 5 min) onto the other side of the same polymer membrane, making a membrane electrode assembly (MEA).

Thus-prepared MEA was installed in the NuVant systems. The array fuel cell was conditioned by passing wet hydrogen through both sides of the MEA at 60 °C for 12 h while cycling between 0 and 0.2 V vs the counter hydrogen electrode. The anode stream was then switched to the corresponding fuel, i.e., methanol or ethanol (1 M concentration—8 mL/min), and the array of fuel cells was conditioned by cycling between 0 and 0.7 V until reaching steady-state performance. A computer-controlled potentiostat is used to condition the array and acquire the polarization curves from each cell (see ref Fifteen for details).

The set of polarization curves were then simultaneously obtained by potential sweeps (cyclic voltammetry) from 0 to 0.8 V. To study the long-term catalysts activity the potentiostatic (Chronoamperometry) measurements were also conducted

Table 1. Selected Characteristics of As-Synthesized Catalysts

sample phase composition	catalyst loading (mg/cm²)	actual Pt loading (mg/cm²)	BET surface area (m²/g)
LaRuO₃	6.0	0	17
LaRuO₃ + 1 wt % Pt	5.9	0.06	9.7
LaRuO₃ +5 wt % Pt	6.9	0.34	6.8
LaRuO₃ + 10 wt % Pt	6.8	0.68	7.0
LaRuO₃ + 15 wt % Pt	6.5	0.97	6.4
SrRuO₃	6.0	0	9.1
SrRuO₃ + 1 wt % Pt	6.2	0.06	8.8
SrRuO₃ + 5 wt % Pt	5.8	0.29	7.8
SrRuO₃ + 10 wt % Pt	6.1	0.61	7.3
SrRuO₃ + 15 wt.% Pt	6.2	0.92	6.8
Pt-black	3.0	3.00	30
Pt−Ru	4.7	3.10	62

for the duration of several hours. In this case, the electrode is poised at low potential (0.05 V), followed by an instant step of potential to a value where the reaction occurs and the current is measured as a function of time. Note, that potential values in this study were measured with respect to dynamic hydrogen electrode (DHE).[16]

3. Results and Discussions

A library of SrRuO₃ and LaRuO₃-based perovskites was synthesized in VSC mode. Some of their characteristics are presented in Table 1. While perovskites with relatively high surface area (6−17 m²/g) were synthesized, these values are below of those for standard catalysts (i.e., Pt-black and Pt−Ru). It is interesting that specific surface areas of the pure oxide powders are typically higher than for oxide-metal composition. The latter is related to the larger amount of gas-phase products during combustion of non diluted solutions.[17] As it was discussed in ref 10 as-synthesized products involve desired perovskites, as well as some amounts of La₂O₃ and Sr(NO₃)₂. Calcination for 2 h at 800 °C leads to pure perovskite structures. However, in this paper we present data obtained by using as-synthesized (AS) powders. Finally, it is worth noting that from the synthesis standpoint the La-based system appears to be the most convenient. Indeed, for this system, the as-synthesized product contains a large amount (>80%) of the desired phase (LaRuO₃) and the specific surface areas of this perovskite before (17 m²/g) and after (8.5 m²/g) calcination are the highest one among all produced compositions.

Typical polarization curves of methanol electrooxidation by various catalysts obtained at a sweeping rate of 20 mV/s, flow rate of 8 mL/min, and different temperatures are presented in Figure 1. As could be expected the maximum current density for all catalysts drops as temperature decreases, indicating that the electrocatalytic reaction is a thermally activated process. It can be also seen (Figure 1a) that in the investigated potential range (0−0.8 V) the onset potential for Pt-black is much higher (∼0.6 V) as compared to Pt−Ru alloys (∼0.25 V). This effect is typically explained by the role of ruthenium on preventing catalyst poisoning by the CO species. Note, that for both perovskite-based catalysts onset potentials are similar to those for the Pt−Ru standard (compare Figure 1a and Figure 1b,c). However, it is noteworthy that LaRuO₃ + Pt exhibits more negative onset potential (ca. 0.26 V) than that of SrRuO₃ + Pt (ca. 0.30 V). It is more important that oxide compositions with 15 wt % of loaded Pt possess maximum current densities comparable with Pt-based composition. Again as-synthesized compositions of La-based catalysts have advantages as compared to Sr-based ones.

Similar trends are observed in the case of ethanol electrooxidation by the same catalysts. Figure 2 shows the linear scan
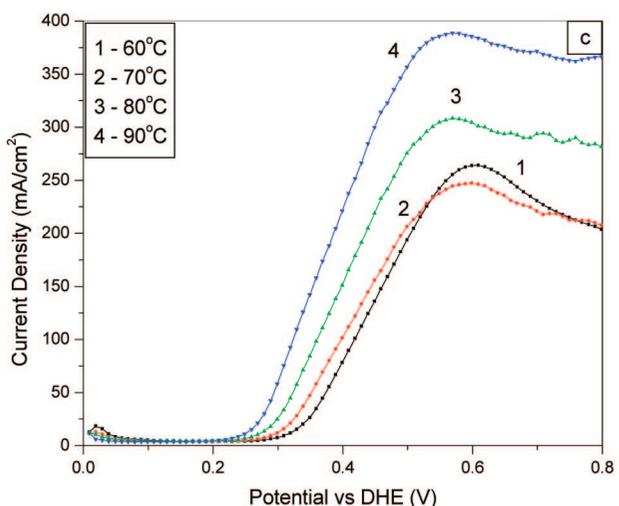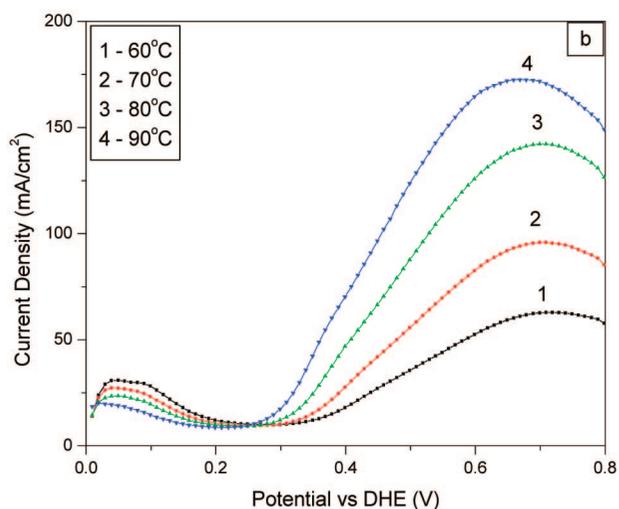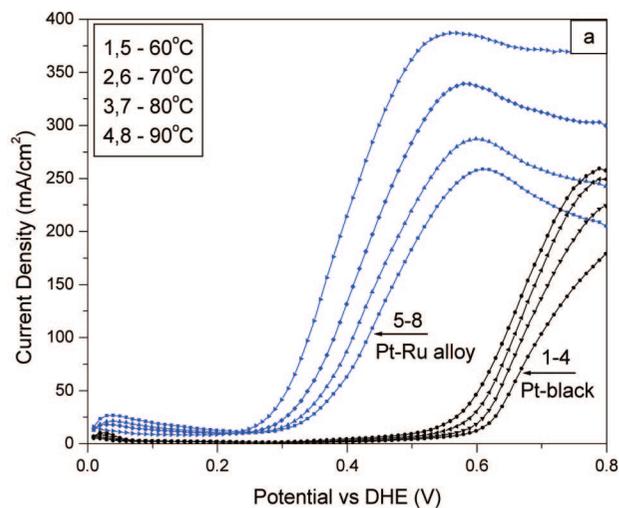
Figure 1. Temperature dependence of electrooxidation of methanol by different catalysts: (a) Pt-black and Pt−Ru alloy; (b) SrRuO$_3$ + 15 wt % Pt; (c) LaRuO$_3$ + 15 wt % Pt.

Figure 2. Temperature dependence of electrooxidation of ethanol by different catalysts: (a) Pt-black and Pt−Ru alloy; (b) SrRuO$_3$ + 15 wt % Pt; (c) LaRuO$_3$ + 15 wt % Pt.

voltammetries of ethanol oxidation for standard Pt- and perovskite-based compositions. The only difference that can be outlined is slightly lower values of maximum current density for all investigated catalysts. Note, that the complete electrooxidation of ethanol at anode involves 12 electrons/molecule (6e in the case of methanol) and requires the cleavage of the C−C bond, which makes ethanol oxidation more difficult than that of methanol.[5]

The question is: how does the amount of loaded platinum influence the catalyst activity? Figures 3 and 4 present the typical polarization curves for two families of complex oxide-based catalyst with different amounts of noble metal for electrooxidation of methanol and ethanol, respectively. It can be seen that in both cases Pt enhances catalyst performance. But this effect being pronounced when Pt is introduced in the range of 1−5 wt %, diminishes at higher loads. In the potential range of
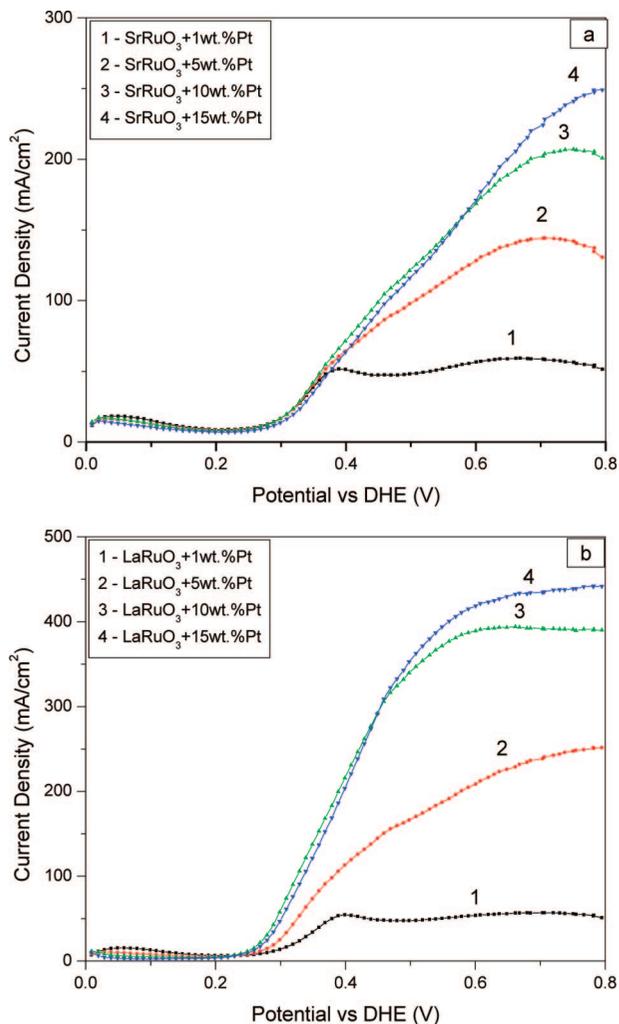
Figure 3. Polarization curves of methanol oxidation by different perovskite-based catalysts: (a) SrRuO$_3$−Pt; (b) LaRuO$_3$−Pt. The curves are obtained in conditions such as flow rate of 8 mL/min, potential scan rate of 20 mV/s, and 90 °C.

Figure 4. Polarization curves of ethanol oxidation by different perovskite-based catalysts: (a) SrRuO$_3$−Pt; (b) LaRuO$_3$−Pt. The curves are obtained in conditions such as a flow rate of 8 mL/min, potential scan rate of 20 mV/s, and 90 °C.

interest from 0.4 to 0.6 V almost no difference in current densities can be observed for catalysts with 10 and 15 wt % of loaded Pt.

Again it is essential that oxide−Pt catalysts having three to five times lower Pt loading (see Table 1) show comparable current densities with Pt-based standards. Also note that specific surface areas of the composite catalysts ($\sim$7 m^2/g) are much lower as compared to Pt−Ru standard ($\sim$62 m^2/g). Such behavior can be related to the following: (i) the high activity of platinum sides distributed along the perovskite surface during solution combustion synthesis loading and/or (ii) the active role of perovskite constituent.

The effectiveness of the preparation of the composite oxide−Pt catalyst by different (i.e., one wave[9] or two waves[18]) "internal" combustion approaches was recently demonstrated. It is known that when the perovskite surface is exposed to water, the vapor hydroxyl [OH] groups can readily be formed.[19] A high concentration of hydroxyl groups on the surface certainly favors the complete oxidation. Comparison between perovskite + Pt catalysts and Pt-black quite clearly reveals that the presence of perovskite in the material is responsible for initiation of methanol oxidation at lower potential. At higher potential the slack of fuel chemisorption of perovskite is complemented by the addition of Pt.

It is interesting that Pt does not contribute much to electroconductivity of membrane electrode assembly. The current−voltage (I−V) curves with hydrogen as an anode fuel can be used as a qualitative measure of MEA's electroconductivity. Such I−V curves obtained for electrodes with different catalysts are presented in Figure 5. First, a distinct difference between two systems of perovskites (LaSrO$_3$ and SrRuO$_3$) in their electroconductivities can be observed. Second, it can be seen that, in each system, an increase of the Pt content leads only to an insignificant increase of anode conductivity. This indicates that conductivity of the composite catalysts is primarily determined by the conductivity of the perovskite phase.

However, it was shown that the use of other conductive perovskites, e.g., SrFeO$_3$, with high specific surface area does not lead to measurable catalytic activities on alcohol electrooxidation.[10] Since catalytic behavior is primarily determined by transition metal at the B-site of perovskite ABO$_3$ structure, the futility of SrFeO$_3$ toward oxidation of considered alcohols simply indicates that the Fe element does not form an electrocatalytic active site on the surface. Up to now all ABO$_3$-based catalysts that showed significant catalytic activity for methanol/ethanol electrooxidation contain Ru on its B-site. But not all AReO$_3$ structures possess high activity; e.g., CaRuO$_3$-based catalyst showed very low efficiency.[10] It can be explained by the fact that metal at the A-site not only defines perovskite
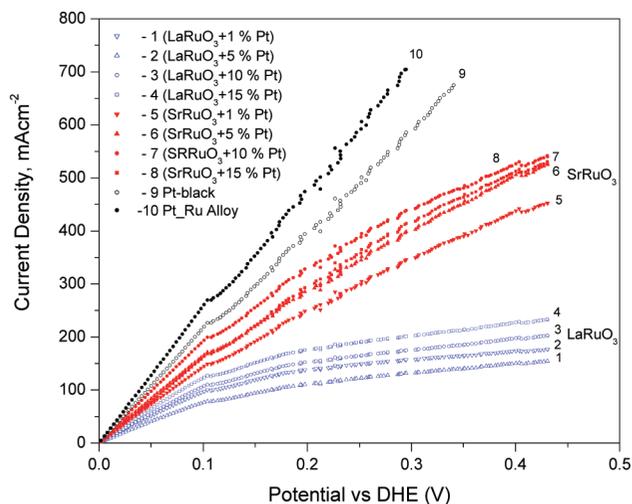
Figure 5. Linear scan voltammetry (LSV) results for various catalyst electrodes with hydrogen flows through anode with a flow rate of 180 cm^3(STP) min^{-1} (all data are obtained under 60 °C with a potential sweeping rate of 6 mV/s).

electroconductivity (see Figure 5) but also is responsible for the absorption property of the oxide.[19]

The potential sweep approach described above has some limitations related to the relatively high scanning rates; thus, we used also so-called potentiostatic measurements at different *constant* potentials. Such measurements were conducted at different constant potentials in the range of 0.1−0.7 V for time periods of 1−5 h in NuVant systems. Figure 6 shows examples of such current−time transients recorded for perovskite-based and standards.

To understand these results, one has to account for that in the response to a potential step; the total measured current, i_T, involves at least three components, faradaic current i_F, the charging current i_C, both decaying with time t, and a noise current, $i_T = i_F + i_C + \text{noise}$. As i_C decays exponentially, after a short period (several seconds) the current becomes predominantly of faradaic nature, approaching a steady-state value. For both fuels the measured steady current density value for perovskite/Pt composites (curves 3, 4) are comparable with Pt−Ru alloy catalyst (curve 1) and much higher than that for Pt-black (curve 2).

The longest conducted measurements (similar to those presented in Figure 6) did not exceed 48 h, which was connected with the limitation of the experimental procedure. It is interesting that after the first 5 min of the test the observed changes of the current densities for oxide-based catalysts were comparable with the accuracy of the measurements. The experiments with much longer duration are currently under the investigation to verify stability of the new catalysts.

Concluding Remarks

Utilizing a screening strategy featuring (a) energy efficient, rapid solution combustion synthesis technique and (b) the high-throughput NuVant system, a series of ruthenium-based perovskite was synthesized and tested. Considerable electrocatalytic activity in oxidation of methanol and ethanol was found for several perovskite-based compositions. Further, it was demonstrated that the catalytic activity of Pt can be significantly enhanced by being mixed with perovskites, leading to superior performance even at lower noble metal loadings.

The above findings undoubtedly show that suggested approach for design of multifunctional catalyst is effective. The
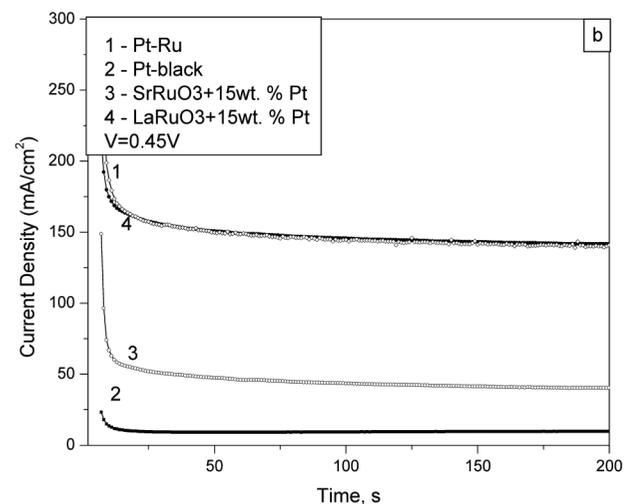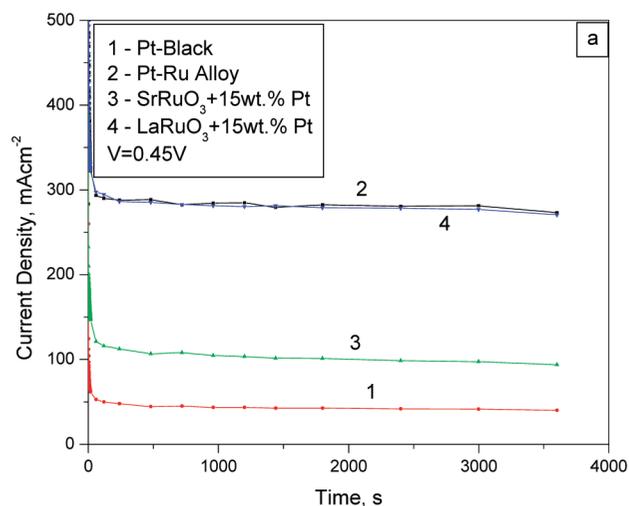
Figure 6. Time potential step of methanol (a) and ethanol (b) oxidation results for several catalysts (cell temperature of 90 °C; flow rate of 8 mL/min).

bifunctional, i.e., conductive perovskite/Pt catalyst, directly synthesized by combustion method, shows high catalytic activities for electrooxidation of both fuels in conditions close to those in direct alcohol fuel cells. While currently LaRuO$_3$/Pt composition possesses the highest activity, optimization of perovskite structure (by doping from A and B sites) may lead even to more advanced catalysts. These encouraging results are suggesting the optimistic component and structure design of an electrode constituted by Pt and perovskite oxide may hold the key for solution of low anodic electroactivity of DAFC.

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