

## ELECTROCATALYTIC PROPERTIES OF NANOSTRUCTURED MULTIMETALLIC Pt-Sn-Cs/C AND Pt-M/C (M=Ag, Ca, Cd, Cs, Cu, Fe, Ir, Mg, Pd, Sn, Zr) DIRECT ETHANOL FUEL CELL CATALYSTS

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**ABSTRACT:** Carbon supported Pt and Pt-M (M=Ag, Ca, Cd, Cs, Cu, Fe, Ir, Mg, Pd, Sn, Zr) bimetallic nanocatalysts (10% Pt loading) and Pt-Sn-Cs trimetallic nanocatalysts were prepared by ethylene glycol (EG) reduction method. The ethanol electrooxidation (EOR) performance of these catalysts were studied by cyclic voltammetry (CV), chronoamperometry (CA), electrochemical impedance spectroscopy (EIS) techniques. Considering Pt-M bimetallic nanocatalysts, carbon supported Pt-Sn bimetallic nanocatalyst showed the best EOR activity as a result of these CV, CA, EIS measurements. Furthermore, Cs promoted Pt bimetallic nanocatalyst also improved the activity of reverse current, attributed to the basic character of Cs. Pt-Sn nanocatalyst was promoted by Cs to neutralize the surface acid sites of the Pt-Sn nanocatalyst. Pt-Sn-Cs/C nanocatalyst showed the superior activity compared to Pt-Sn nanocatalysts. Hence, we further performed EIS measurements on Pt-Sn-Cs, Pt-Sn, Pt-Cs nanocatalysts to compare their electrocatalytic activities.

**Keywords:** Ethanol Electrooxidation, Pt, Sn, Cs, Anode Catalyst

### Nanoyapılı Multimetalik Pt-Sn-Cs/C ve Pt-M/C (M=Ag, Ca, Cd, Cs, Cu, Fe, Ir, Mg, Pd, Sn, Zr) Doğrudan Beslemeli Etanol Yakıt Pili Katalizörlerinin Elektrokatalitik Özellikleri

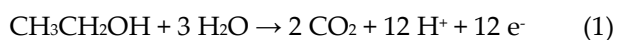
**ÖZET:** Karbon destekli Pt ve Pt-M (M=Ag, Ca, Cd, Cs, Cu, Fe, Ir, Mg, Pd, Sn, Zr) bimetalik nanokatalizörler (10% Pt yüklemesi) ve Pt-Sn-Cs trimetalik nanokatalizörler etilen glikol (EG) indirgenme yöntemi ile hazırlanır. Etanol elektro oksitlenme (EOR) performansları döngüsel voltametre (CV), kronoamperometre (CA) ve elektrokimyasal impedans spektroskopisi (EIS) yöntemleri ile çalışılmıştır. Yapılan CV, CA ve EIS ölçümleri sonucunda bimetalik nanokatalizörlerinden karbon destekli Pt-Sn kalay katalizörü en iyi EOR aktivitesini göstermiştir. Ayrıca, Cs katkılanmış Pt bimetalik katalizöründe geri akım pikinin aktivitesinin arttığı gözlenmiştir. Bu artışın sebebi Cs metalinin bazik karakterde olmasına bağlanmıştır. Pt-Sn bimetalik nanokatalizörü de Pt-Sn katalizörünün yüzeyindeki asit sitelerini nötralize etmek amacı ile Cs ile katkılanmıştır. Pt-Sn-Cs/C trimetalik katalizörü Pt-Sn da dahil olmak üzere diğer bimetalik katalizörler ile karşılaştırıldığında en iyi aktiviteyi göstermiştir. Bu yüzden Pt-Sn-Cs, Pt-Sn, Pt-Cs nanokatalizörleri üzerinde EIS ölçümleri yapılarak bu katalizörlerin elektrokimyasal özellikleri ayrıntılı olarak incelenmiştir.

**Anahtar Kelimeler:** Etanol Elektrokoksitlenmesi, Pt, Sn, Cs, Anot Katalizörü.

## 1. INTRODUCTION

Ethanol is preferred fuel over methanol from an energy storage point of view because ethanol substantially exceeds methanol with respect to volumetric energy density. Thus, Direct Ethanol Fuel Cells (DEFC) are promising power sources for portable electronic devices. The complete ethanol

electrooxidation reaction EOR (eq. 1) requires the breaking of C-H bonds and C-C bonds as well as the formation of C=O bonds.



Pt is the best known electrooxidation catalyst. However, CO is formed as an intermediate during the electrooxidation reaction. Hence, Pt based nanocatalysts for EOR are prone to poisoning by CO. Pt based multimetallic catalysts were found to be more active than monometallic Pt for alcohol electrooxidation reaction due to their resistance to CO poisoning (Lamy et al., 2003; Li et al., 1997; Spinace et al., 2004; Zhou et al., 2003). Numerous studies have been reported on Pt based multimetallic nanocatalysts for EOR. Carbon supported Pt-Ru and Pt-Sn nanocatalysts are the most extensively investigated anode materials for DEFCs. On the other hand, Pt-Pd (Tsiakaras, 2007), Pt-W (Tsiakaras, 2007), Pt-Re (Vigier et al., 2004), Pt-Rh (Bergamaski et al., 2008; de Souza et al., 2002; Kowal et al., 2009a; Kowal et al., 2009b; Lima and Gonzalez, 2008a, b), Pt-Pb (Li and Pickup, 2006; Suffredini et al., 2007), Pt<sub>3</sub>TeX (Huang et al., 2008), Pt-Sb (Lee et al., 2008), Pt-CeO<sub>2</sub> (Bai et al., 2007; Diaz et al., 2007; Wang et al., 2007a; Xu et al., 2007), Pt-ZrO<sub>2</sub> (Bai et al., 2007; Bai et al., 2005), Pt-MgO (Xu et al., 2005), Pt-TiO<sub>2</sub> (Jiang et al., 2008; Lei et al., 2008; Song et al., 2008a; Song et al., 2008b; Song et al., 2007), Pt-SiO<sub>2</sub> (Liu et al., 2007) were investigated for EOR. It has been reported that these catalysts presents lower activity than that of Pt and lower than that of Pt-Ru and Pt-Sn. Furthermore, Pt-Sn was reported as one of the highly efficient DEFC bimetallic anode catalysts (Li et al., 2007). Not only a second metal addition but also third metal addition to platinum enhances the cell performance of DEFC. Pt-Sn/C and Pt-Ru/C nanocatalysts were modified by adding third metal to present higher specific activity of dehydrogenation and overcome C-H and C-C bond cleavage problem during the EOR (Antolini et al., 2007). Pt-Sn-Ru (Antolini, 2007; Antolini et al., 2007; Neto et al., 2007; Ribadeneira and Hoyos, 2008; Rousseau et al., 2006; Sine et al., 2007), Pt-Ru-Ni (Ribadeneira and Hoyos, 2008), Pt-Ru-Mo (Wang et al., 2007b), Pt-Sn-Ni (Bonesi et al., 2007; Ribadeneira and Hoyos, 2008; Spinace et al., 2005), Pt-Sn-Ir (Calearo et al., 2006; Hefny and AbdelWanees, 1996; Liang et al., 2006; Riberio et al., 2007), Pt-Sn-P (Xue et al., 2007), Pt-Sn-Rh (Bonesi et al., 2007; Colmati et al., 2008), Pt-Sn-CeO<sub>2</sub> (Neto et al., 2008) are the mostly examined multimetallic nanocatalysts.

C-H and C-O bond cleavage is crucial for the complete EOR. On the other hand, C-H and C-C bond cleavage on Pt and Pt-based multimetallic nanocatalysts have a negative effect on the performance of EOR because strongly adsorbed intermediates formed during EOR, causing the loss of nanocatalyst activity. Similar problem (coke formation) is also encountered during alkane reforming. Thus, alkaline (K, Cs, etc.) promoted Pt-based multimetallic catalysts were used to increase coke formation resistance (Lobera et al., 2011; Sntamaaria et al., 2002; Srihiranpullo et al., 2000). For instance, it has been reported that the addition of Sn and K resists coke formation both on the metal and support sites and reduces the density of carbon radicals (Srihiranpullo et al., 2000). Pt-Sn and Pt-Sn-K catalysts have noticeably higher values of dispersion factor obtained than that of Pt, indicating that coke on the Pt-Sn and Pt-Sn-K catalysts has a softer coke. Likewise, it has been demonstrated that Cs promoted Pt catalysts have better catalytic activity and selectivity compared to Pt for n-heptane reforming reactions (Sntamaaria et al., 2002). Although numerous studies have been devoted to explore the EOR activities of Pt based multimetallic catalysts, Cs promotion effect on Pt and Pt-Sn nanocatalysts for EOR has not been studied yet. At present, the effect of Cs promotion on Pt and Pt-Sn for EOR has also been examined to evolve out of these alkaline promoted catalysts having high alkane reforming activity, selectivity, and high coke formation resistance.

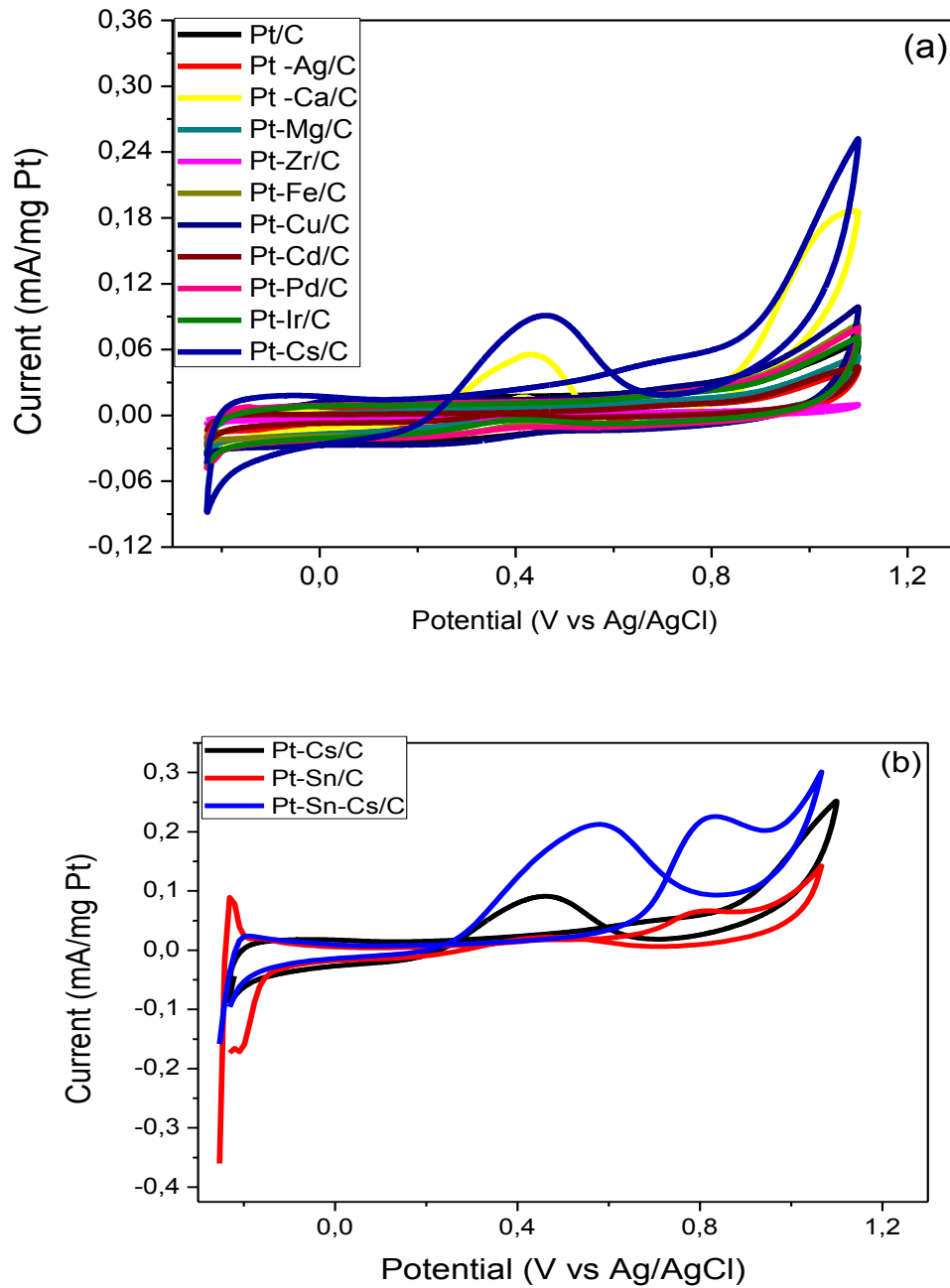
Herein, Pt and Pt-M (M=Ag, Ca, Cd, Cs, Cu, Fe, Ir, Mg, Pd, Sn, Zr) bimetallic and Pt-Sn-Cs trimetallic nanocatalysts were prepared by polyol method for EOR. The electrochemical activities of these catalysts towards EOR were examined by CV, CA, and EIS techniques.

## 2. MATERIAL AND METHOD

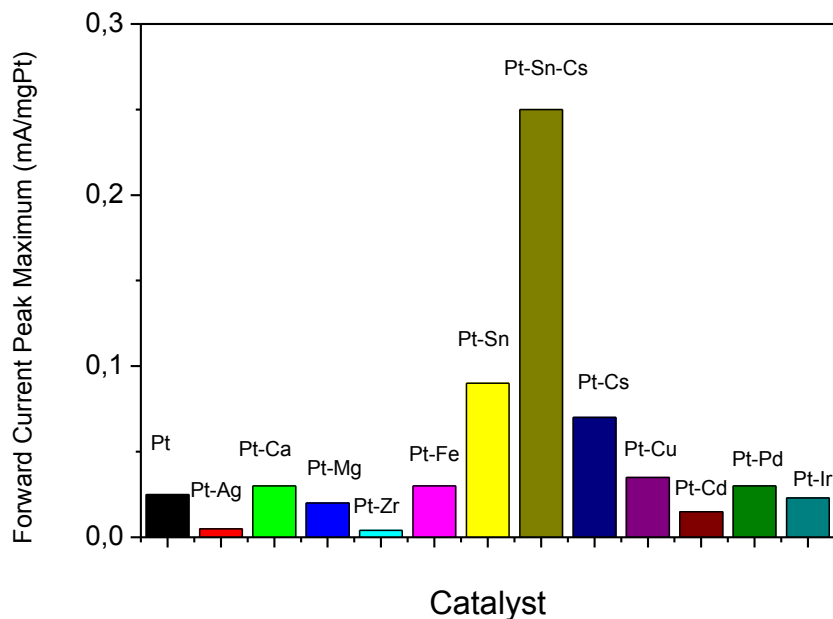
Carbon supported Pt and Pt-M (M=Ag, Ca, Cd, Cs, Cu, Fe, Ir, Mg, Pd, Sn, Zr) bimetallic and Pt-Sn-Cs trimetallic nanocatalysts (10% Pt loading) were prepared by ethylene glycol (EG) reduction method (Chen et al., 2004; Das et al., 2008; Guo et al., 2007; Kivrak et al., 2011; Lee et al., 2010). Metal precursors were dissolved in 200 mL ethylene glycol solution per gram carbon support. The pH of the solution was fixed at 10 by the addition of KOH solution and carbon support (Vulcan XC-72 R) was dispersed in this solution. Consequently, the temperature was increased to 130 °C and kept constant at this temperature by refluxing in an oil bath during 2 h. After refluxing at 130 °C for 2 h, the slurry suspension was rapidly cooled down in cold water, filtered, and dried. In order to prepare the electrodes, these catalysts were dispersed in 1 mL Aldrich 5% Nafion® solution to obtain the catalyst ink. Furthermore, the appropriate amount of this ink was spread on the surface of the glassy carbon electrode and dried at room temperature. Electrochemical measurements were performed with a CHI 660C potentiostat in a conventional three-electrode cell with Pt wire as a counter electrode, Ag/AgCl as a reference electrode, and a glassy carbon working electrode with a diameter of 3.0 mm held in a Teflon cylinder. Cyclic voltammograms, chronoamperograms, and electrochemical impedance measurements were recorded in 0.5 M H<sub>2</sub>SO<sub>4</sub> + 1M C<sub>2</sub>H<sub>5</sub>OH solution on Pt and Pt-M (M=Ag, Ca, Cd, Cs, Cu, Fe, Ir, Mg, Pd, Sn, Zr) bimetallic and Pt-Sn-Cs trimetallic nanocatalysts under the same amount of Pt loading. Prior to each experiment, the electrode surface was activated in 0.5 M H<sub>2</sub>SO<sub>4</sub>. CV was recorded between -0.1 V and 1.2 V with a scan rate of 50 mV s<sup>-1</sup> in 0.5 M H<sub>2</sub>SO<sub>4</sub> + 1M C<sub>2</sub>H<sub>5</sub>OH at 25 °C. Furthermore, CA was performed in 0.5 M H<sub>2</sub>SO<sub>4</sub> + 1M C<sub>2</sub>H<sub>5</sub>OH solution on these Pt-based bimetallic and trimetallic nanocatalysts at 0.65 V for 500 s. EIS as a dynamic method was used to examine the electrochemical behavior of Pt-Sn-Cs trimetallic catalysts were examined at frequencies between 100 kHz and 0.01 Hz in 0.5 M H<sub>2</sub>SO<sub>4</sub> at 10 mV amplitude at the 650 mV.

## 3. RESULTS AND DISCUSSION

The electrochemical characterization of Pt and Pt-M (M=Ag, Ca, Cd, Cs, Cu, Fe, Ir, Mg, Pd, Ru, Sn, Zr) bimetallic and Pt-Ru-Sn trimetallic nanocatalysts was carried out by CV in the 0.5 M H<sub>2</sub>SO<sub>4</sub> + 1 M C<sub>2</sub>H<sub>5</sub>OH solution at 25 °C. The cyclic voltammograms were recorded at 50 mV s<sup>-1</sup> for these nanocatalysts. The cyclic voltammetric behaviors of Pt-M (M=Ag, Ca, Cd, Cs, Cu, Fe, Ir, Mg, Pd, Sn, Zr) bimetallic and Pt-Sn-Cs trimetallic nanocatalysts were evaluated and compared with monometallic Pt nanocatalyst. Results on these measurements were presented in Fig. 1a and Fig. 1 b. Higher current value of EOR for every bimetallic and trimetallic catalyst was given in the bar diagram. According to the Fig. 1 and Fig. 2, it has been found that highest current value was obtained for Pt-Sn-Cs/C catalyst. Then, the order of the peak current was obtained as Pt-Sn > Pt-Cs > Pt-Cu > Pt-Fe=Pt-Ca=Pt-Pd > Pt > Pt-Ir > Pt-Mg > Pt-Ag > Pt-Zr (Fig. 2).

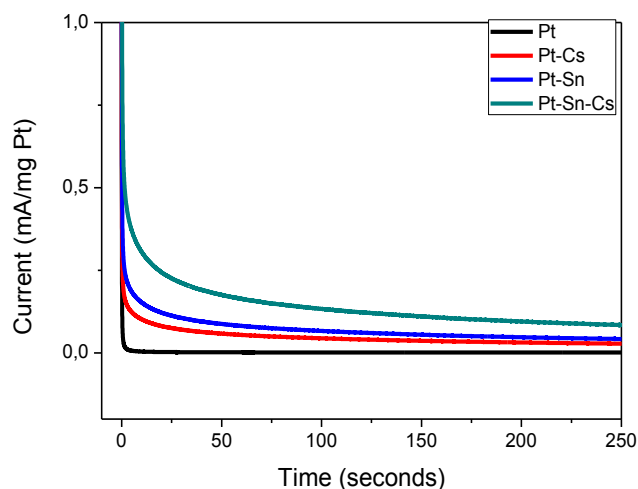


**Fig.1.** (a) Cyclic voltammogram of carbon supported (10% Pt loading) Pt, and Pt-M (M=Ag, Ca, Cd, Cs, Cu, Fe, Ir, Mg, Pd, Zr ) and (b) Pt-Cs, Pt-Sn, and Pt-Sn-Cs in 0.5 M H<sub>2</sub>SO<sub>4</sub>+ 1 M C<sub>2</sub>H<sub>5</sub>OH at 50 mV s<sup>-1</sup> .



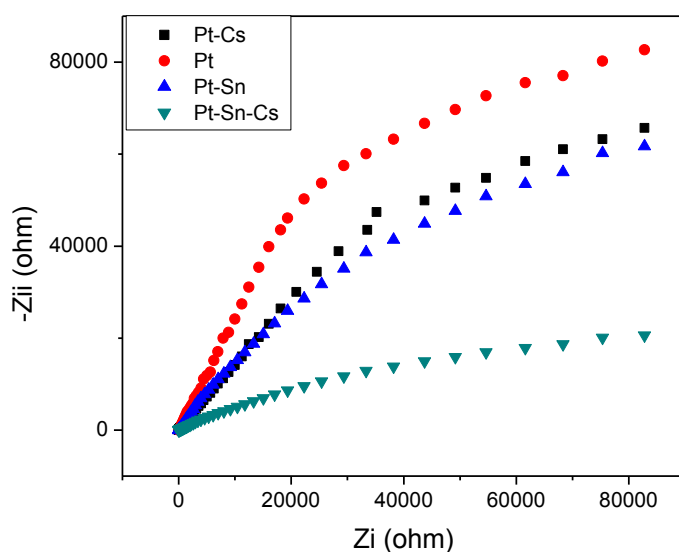
**Fig.2.** Maximum current value of EOR of carbon supported (10% Pt loading) Pt-Cs, Pt-Sn, and Pt-Sn-Cs catalysts obtained from Fig.1

Fig. 3 shows the chronoamperograms in 0.5 M  $\text{H}_2\text{SO}_4$  + 1.0 M 1 M  $\text{C}_2\text{H}_5\text{OH}$  solution of Pt monometallic, Pt-Cs, Pt-Sn bimetallic, and Pt-Sn-Cs trimetallic nanocatalysts. EOR chronoamperometric decays were normalized with respect to the amount of treated platinum. The selected potential was 0.65 V vs. Ag/AgCl. As it has been demonstrated in Fig.3, there is gradual decay of current by the time. At initial period, there is a fast decrease because intermediate species accumulate at the surface of catalysts. Pt-Sn-Cs catalyst demonstrates a higher initial current and a higher current value during all time. This also confirms that electrocatalytic activity of Pt-Sn-Cs nanocatalyst is higher than that of Pt monometallic, Pt-Cs, Pt-Sn bimetallic nanocatalysts, which could be ascribed to increasing basic character and CO resistance by Cs promotion of Pt catalysts.



**Fig.3.** Chronoamperomogram of carbon supported (10% Pt loading) Pt, Pt-Cs, Pt-Sn, and Pt-Sn-Cs in 0.5 M  $\text{H}_2\text{SO}_4$  + 1 M  $\text{C}_2\text{H}_5\text{OH}$ .

EIS technique is a powerful tool for characterizing the electrochemical processes occurring at the solution/electrode interface. A typical electrochemical impedance spectrum presented in the form of a Nyquist plot (Sahin and Kivrak, 2012). This plot includes a semicircle region lying at higher frequencies, related to the electron transfer limited process. The semicircle diameter is equal to the electron-transfer resistance ( $R_{ct}$ ). Nyquist plots of Pt, Pt-Sn, Pt-Cs, and Pt-Sn-Cs nanocatalysts in 0.5 M  $H_2SO_4$  + 1.0 M  $C_2H_5OH$ . At 650 mV, it has been observed at large arc, which is attributed the slow reaction rate of ethanol dehydrogenation oxidation. This slow kinetics is caused by  $CO_{ads}$  blocks further adsorption and dehydrogenation of ethanol. There are only capacitive behaviors from double layer charge in the impedance plots at this potential. As shown in Fig. 4, the electrontransfer resistance ( $R_{ct}$ ) decreases with the introduction cesium to tin.



**Fig.4.** Nyquist plot of carbon supported (10% Pt loading) Pt, Pt-Sn, Pt-Cs, and Pt-Sn-Cs 0.5 M  $H_2SO_4$  + 1 M  $C_2H_5OH$  at 650 mV.

This implies that Sn and Cs doping enhances the conductance of Pt, which is beneficial to the electrooxidation of ethanol. Furthermore, it has been observed that the addition of Cs to Pt-Sn decreases the electron transfer resistance. Pt-Sn-Cs catalyst has the lowest electron transfer resistance compared the Pt, Pt-Sn, and Pt-Cs. Cs promotion increases the CO resistance of catalyst by reducing the density of carbon radicals on both metal and support sites, which is in agreement with the literature studies (Lobera et al., 2011; Sntamaaria et al., 2002; Srihiranpullop et al., 2000). Coke formation encountered during alkane reforming was decreased by using alkaline (K, Cs, etc.) promoted Pt-based multimetallic catalysts (Lobera et al., 2011; Sntamaaria et al., 2002; Srihiranpullop et al., 2000).

#### 4. CONCLUSIONS

At present, Pt and Pt-M (M=Ag, Ca, Cd, Cs, Cu, Fe, Ir, Mg, Pd, Sn, Zr) bimetallic and Pt-Sn-Cs trimetallic nanocatalysts were prepared by polyol method for EOR. The electrochemical activities of these catalysts towards EOR were examined by CV, CA, and EIS techniques. It has been observed that the highest ethanol electrooxidation current value is obtained for Pt-Sn-Cs/C catalyst. The electrochemical performances of the bimetallic nanocatalysts are in the order of Pt-Sn > Pt-Cs > Pt-Cu > Pt-Fe=Pt-Ca=Pt-Pd > Pt > Pt-Ir > Pt-Mg > Pt-Ag > Pt-Zr. EIS measurements on Pt-Sn-Cs, Pt-Cs, Pt-Sn, and Pt reveals that by the addition of Cs to Pt-Sn electron transfer resistance decreases, which could be attributed to the fact that Cs neutralize the acidic sites of Pt-Sn and increases the ethanol electrooxidation activity.

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