

Pt-Rh Alloy Catalysts for Hydrogen Generation developed by Direct Current/Pulse Method

praveen bm (✉ bm.praveen@yahoo.co.in)

Srinivas University <https://orcid.org/0000-0003-2895-5952>

Bharath K Devendra

Srinivas University

Tripathi V S

Radiation & Photochemistry Division, Bhabha Atomic Research Centre

Nagaraju DH

Reva University

Nayana K O

Bangalore University

Research Article

Keywords: Electrodeposition, Platinum-Rhodium alloy, HER, CV, Chrono-potentiometry

Posted Date: May 18th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-519373/v1>

License:   This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Abstract

Highly active Pt-Rh alloy catalyst coatings were developed by direct current (DC) and pulse current (PC) electrodeposition method for efficient hydrogen evolution reaction (HER) catalysts. The coatings were characterized by scanning electron microscopy (SEM) and atomic force microscopy (AFM) linear sweep voltammetry (LSV) studies. Pt-Rh alloy catalyst coatings showed almost similar behavior as pure platinum metal. The Pt-Rh coating were obtained by PC method showed low over potential for HER. Very low slope of 41.2 mV/dec is obtained represents the Volmer-Tafel mechanistic path way for HER process. Chronopotentiometry was conducted and amount of hydrogen collected during these experiments was 24 ml for PC method 75% duty cycle sample.

Introduction

Techniques for exploiting promising clean, renewable energy sources need to be established due to the depletion of traditional fossil fuels and the gradual degradation of the environment. Due to its excellent theoretical mass energy density (120 mJ kg^{-1}) and zero greenhouse emissions, hydrogen is a highly efficient and environmental friendly energy medium [1–3]. Hydrogen can be generated by water electrolysis efficiently electrochemically using a catalysts with long-term stability. It is necessary to enable large-scale practical applications that are affordable. Platinum is the best catalyst for HER because of high activity with zero over potential [4]. But, platinum is costly (\$988 per ounce) and low abundant makes it difficult to use in large scale HER process [5–7]

Recently, large amount of research work has been carried out to develop the alternatives to platinum catalyst. In this direction, catalyst based on molybdenum, nickel, cobalt, Molybdenum oxides, sulfides, selenides compounds have been explored [8–12]. These catalysts show quite good HER activity in acidic medium. However, these catalysts do not compete with Pt in terms of over potential and current densities. In addition, the preparation of these compounds is highly complex and environmentally unfriendly.

In spite of numerous efforts, only 4% of H_2 was produced by water electrolysis due to high cost of the process [13]. These all are due to the high energy losses in electrolysis, lack of state-of-the-art electrodes, the key barriers to the wider use of water electrolysis.

Platinum is the best catalyst for hydrogen generation because it is having zero over potential. The only hindrance of using noble metals and its alloys is low abundance and costly. Using of bulk noble metal is not favorable to use in hydrogen generation. Catalytic activities mainly depend on the surface properties and by using this principle, thin layer of noble metal and its alloy coating on base metal usage as catalyst is good alternative and cost-effective method in hydrogen generation. Pt-Rh alloy coating is more durable and superior than pure platinum coatings [14]. Pt-Rh coating is best option on boiler water reactors because of neutron activation considerations. Alloying of Pt with Rh is another method to achieve lower over potential with higher efficiency in hydrogen generation. In this work Pt-Rh coating was developed on SS 304 with very small amount of $0.5 \mu\text{g}/\text{cm}^2$ noble metal. The Pt-Rh coatings were performed by both

DC and PC methods at different conditions. These developed coatings are characterized and studied by electrochemical methods to know the efficiency in hydrogen generation. The Pt-Rh catalysts displays Pt like behavior for HER process in acidic medium. The PC coated Pt-Rh coating outperforms compared to the DC coated samples.

Experimental

Electrodeposition Process: Platinum 5Q plating solution $[\text{Pt}(\text{NH}_3)_2]\text{HPO}_4$ and Rhodium Sulphate solution $\text{Rh}_2(\text{SO}_4)_3$ purchased from Arora Matthey Limited, Kolkata was used as the main content in the electrolyte for Electrodeposition process. 1.5 ml Platinum solution and 0.075 ml of Rhodium solution from the 5Q plating solution was taken to prepare the electrolyte solution. This solution is marked to 50 ml by adding 5 ml $\text{ConcH}_2\text{SO}_4$ and distilled water. A Pt-Rh alloy coating was developed on SS 304 with an exposed surface area of 1.7 cm^2 from a bath solution containing 50 ml. The anode and cathode were held parallel to each other during Electrodeposition. To achieve a smooth finish, stainless steel panels are manually polished, cleaned ultrasonically then electrochemically cleaned before electroplating.

The SS 304 circular form cathode with a diameter of 15 mm and a thickness of 1 mm was used during electrodeposition for coating with a total surface area of 1.7 cm^2 , while the remaining portion of the back side was masked during the deposition process. Platinized titanium was used as an anode. Electrodeposition was carried out by using a current source N6705B Key sight of direct current (DC) and pulse current (PC) for 18 minutes. After each deposition, the coatings obtained were rinsed carefully with distilled water and then air dried. Amount of coating was estimated by weighing the cathode before and after coating.

Coatings characterization

The morphology analysis of coated samples was conducted by scanning electron microscopy (FESEM) (ZEISS sigma) after electroplating. SEM assessment explored the surface morphology and porosity of DC and PC coating on SS304. Platinum-coated samples were mounted on a sample holder and SEM photographs were taken using a 5.00 kV and 15 kV (model: FESEM Carl ZEISS) scanning electron microscope, 3.7 mm average wide distance at varying magnification. Atomic force microscopic tests (Nanosurf® EasyScan 2 AFM & STM) have shown the surface morphologies of coated samples have been reported to support the findings of other experimental methods. AFM micrographs have shown surface morphological characteristics for both coated samples and bare as a reference.

Electrochemical studies

The electrochemical cell was designed for quantitative measurement of hydrogen, where the electrodeposited Pt-Rh electrode was subjected to cathodic polarization, respectively. Electrodeposited alloy coatings obtained under different deposition conditions were used as the test electrode and platinum electrode with high surface area was used as the counter electrode. Saturated calomel electrode

(SCE) was used as the reference electrode. All potentials reported in the present study are with reference to SCE and converted to standard hydrogen electrode (SHE)

Electrochemical behavior of the coatings, in terms of HER, was evaluated by subjecting it to cyclic voltammetry, linear sweep voltammetry and chronopotentiometry studies in 0.5M H₂SO₄ medium, using computer controlled using electrochemical workstation (compactostath 10800 from Ivium Technologies, Netherlands). The cell was fitted with a graduated gas collector where the liberated hydrogen replaces corresponding amount of solution. This facility allows relating the amount of gas liberated at given time for electrode materials deposited at a given current density. The schematic diagram of the setup is given in Figure 1.

Results And Discussion

In order to get a good desirable coating, bath parameters like pH, temperature, Current density, and composition plays a very important role in the coating. Optimized bath conditions are given in table 1.

TABLE 1 Optimized constituent's bath solution

Components	Composition
Platinum solution [Pt (NH ₃) ₂] HPO ₄	1.5 ml
Rhodium sulphate solution Rh ₂ (SO ₄) ₃	0.075 ml
H ₂ SO ₄	5 ml
Distilled water	43.425
Electrodeposition Parameter	
Temperature	40°C
pH	1.0
Current density	4.0 A/dm ²
Deposition time	18 min
PC Duty cycle	25%, 50% and 75%
DC	Direct current flow

Coating Characterization

Scanning electron microscope

SEM images of the coatings obtained from PC and DC method are shown in Figure 2. The 75% duty cycle coating exhibited the smaller and uniform grains result in the smoother coating surface compared to

remaining coatings. In 75% PC coating we have observed more number of pores with uniform size. In other coatings, pores size was uneven. The degree of uniformity decreased as duty cycle percentage decreases the value from 75% to 25% while pores with larger and uneven size has been observed in DC coating samples. As observed in figures, duty cycle has a significant effect on the surface morphology. All these coatings were highly adhesion and bright. The 75% duty cycle sample showed more uniformity than other coatings.

Atomic Force Microscopy

TABLE 2 Presents the surface topography of DC and PC electrodeposition of platinum-rhodium alloy coating.

Specimen	Mean (S_m) (fm)	Valley depth (S_v) (nm)	Peak height (S_p) (nm)	Peak valley height (S_y) (nm)	Average roughness (S_a) (nm)	Root mean square roughness (S_q) (nm)
DC	-2872.2am	-109.83	75.786	185.62	14.637	19.572
25	-2872.1am	-222.63	138.97	361.6	23.748	31.734
50	-4.2823fm	-70.167	48.551	118.72	10.831	13.669
75	-4.9253fm	-61.429	141.88	203.31	7.6879	11.184

AFM is an important instrument for studying the surface morphology at nano-to-microscale and has become a modern approach for studying the effect of the different electrodeposition methods like DC and PC at various duty cycle. AFM research includes details on average roughness (S_a) on the surface of coated SS304 sample, which helps to assess the effectiveness of the coated sample by electrodeposition method as shown in the Table 2. The 3D images of Pt-Rh alloy coating for DC, 25%, 50% and 75% duty cycle are shown in Figures (3a) to (3d). Sample obtained by 75% duty cycle by PC method showed lesser roughness than other coatings which indicates Pt-Rh is deposited quite uniformly. The decrease in roughness value (Table 2. and Figure 3 (a)) is due to the reduction of the grain size on metal (SS 304) surface. It can be concluded that higher the crystal grain size, the greater the roughness of the coatings. The instability of the duty cycle has a significant effect on the surface morphology of their crystalline measurements. In our studies, good coating was achieved in 75% duty cycle and it gives smaller grain size with lower roughness. In DC coating, sufficient time was not available to achieve the small grain size with uniform coating.

Energy Dispersive X-Ray Spectroscopy

The EDX (using 20 keV beam energy Model: Oxford Instrument 250) analysis was performed to measure the amount of metal ions on the substrate in the coating and offers valuable information on the

percentage of specific metal ions in the coating. Details are given in Table3 and Figure 4. In the course of our studies EDX were observed for both DC and PC techniques. It also contains trace amount of iron, chromium, nickel and manganese. It shows more amount of iron along with Platinum and Rhodium it may due to porosity in the coating as shown in Figure 2.

Amount of Platinum – Rhodium Alloy in the coating

Pt-Rh coating was done by PC and DC method. Weight of the cathode coupons were taken before and after the experiments. Amount of alloy in the coating was given in the below Table 4.

TABLE 3 Amount of Pt-Rh alloy in the coating

SI NO	Method of coating	Amount of Pt-Rh deposited after coating ($\mu\text{g}/\text{cm}^2$)
01	DC	10
02	PC 25%	07
03	PC 50%	06
04	PC 75%	05

Linear Sweep voltammetry

The electrocatalytic activity of Pt-Rh was first evaluated for H_2 evolution in an acidic medium as shown in Figure 5. All the samples show good hydrogen evolution reaction. Pt –Rh coated by PC method at 75% duty cycle shows very low over potential for hydrogen evolution. Pt-Rh catalyst deposited by 75% duty cycle sample shows over potential similar to that of pure Pt for HER. These results confirm the better performance of the sample (75% duty cycle). 25% and 50% sample shows more over potential and also less current observed during hydrogen evolution reaction. It was anticipated that Pt–Rh is very active for HER. Indeed, the Pt–Rh catalyst exhibited a catalytic onset at nearly zero over potential and catalytic current rapidly rose for the sample obtained at 75% duty cycle. Vibrant H_2 bubble growth and release from the surface were observed upon further cathodic sweeping.

TABLE 4 The Tafel slopes obtained for the different Pt-Rh electrodes

Si No	Pt-Rh electrode sample	Slope Value mV/dec
01	Pure platinum	36.0
02	DC	69.6
03	PC- 75%	41.2
04	PC- 50%	63.6
05	PC- 25%	83.1

The catalytic activity of Pt-Rh electrocatalysts were evaluated by Tafel plots as shown in the Figure 6. The Tafel slopes provides insight mechanism of HER process. The kinetics parameter of electrocatalytic HER is expressed in terms of either Volmer-Heyrovsky or Volmer-Tafel mechanistic pathways. The Tafel slopes of 41.2, 63.6 and 83.1 mV/dec for Pt-Rh catalysts coated by PC method using 75%, 50% and 25% duty cycles, respectively from Table 4. Very low Tafel slope of 41.2 mV/dec of 75% duty cycle deposited Pt-Rh catalysts implies that better electrocatalytic performance which is also higher than the DC coated sample (69.9 mV/dec). The low Tafel slope of 41.2 mV/dec implies that the Volmer-Tafel reaction mechanism and the rate determining step is the desorption of hydrogen atoms [20].

Chronopotentiometry

The simplest way to estimate the electrocatalytic activity of the electrodes to monitor the electrode potential at constant current density applied over a sufficient period of time [19]. The chronopotentiometry study for the evolution of hydrogen on Pt-Rh coatings obtained by different methods, were made at a constant current of -0.3 mA cm^{-2} for a duration of 21,600 seconds. The nature of chrono-potentiograms for the alloy coatings obtained by different methods is given in Figure 7. The electrocatalytic performance of these coatings were evaluated by measuring the amount of H_2 liberated in first 150 seconds as shown in Figure 8. The electrodeposited catalysts show constant and stabilized potential for HER. This phenomenon is ascribed to the formation of hydrogen bubble on the surface of the electrode.

Coating with uniform grain size and porosity gives more hydrogen evolution reaction. In electrolysis, formed hydrogen gas detached from the cathode only after it became a bigger in size. During this time contact between cathode and electrolyte was seized and reduces the hydrogen evolution. If the sample has more uniform pores, these gas bubbles avoid the ohmic resistance and enhance the catalytic activity of the coating [21]. It may be seen that the coating obtained by 75% duty cycle gives more volume of hydrogen evolution compare to other samples. This sample has more porosity with uniform coating this enhance the hydrogen generation activity of the catalyst.

Conclusions

Pt- Rh Alloy Coating was successfully done by the PC and DC method. Bath parameters were optimized to get the desired coating. SEM infers the smaller grain size of the coating obtained by PC method at 75% duty cycle. AFM analysis showcases the surface roughness and this is confirmed the SEM results. Linear sweep voltammetry gives the evidence of zero over potential of developed alloy coating and also it gave more current than pure platinum coating. Small Tafel slopes confirms the efficient catalysts and follows the Volmer-Tafel reaction mechanism for the HER. Chronopotentiometry values again confirm overall results by giving more volume of hydrogen collection during electrolysis. This work has the potential to commercialize for industrial applications.

Declarations

Funding and acknowledgement

The experiment was funded with the approval of Project No. 37(2)/14/18/2018 by the Department of Atomic Energy (DAE), Board of Research in Nuclear Sciences (BRNS), Mumbai, Government of India, 11/07/2018. The writers express their appreciation to Srinivas University, College of Engineering & Technology, Srinivas Nagar, Mangaluru, Karnataka, for providing laboratory assistance.

References

1. Chen A, Ostrom C. Palladium-Based Nanomaterials: Synthesis and Electrochemical Applications. *Chem Rev.* 2016; 115:11999-12044.
2. Stamenkovic VR, Mun BS, Arenz M, Mayrhofer KJJ, Lucas CA, Wang G, Ross PN, Markovic NM. Trends in electrocatalysis on extended and nanoscale Pt-bimetallic alloy surfaces, *Nat. Mater.* 2007;6:241-247.
3. Mccrory CCL, Jung S, Ferrer IM, Chatman SM, Petersand JC, Jaramillo TF. Electrocatalysis for Energy and Environmental Chemistry. *J Am Chem Soc.* 2015; 137:4347-4356.
4. Thomas G. Overview of Storage Development DOE Hydrogen Program. Sandia National Laboratories, Livermore CA. 2000.
5. Turner JA. Sustainable hydrogen production. *Science.* 2004; 305:972-973.
6. Dresselhaus IL, Thomas. Alternative energy technologies. *Nature.* 200; 414:332-336.
7. Su JW, Yang Y, Xia GL, Chen JT, Jiang, Chen QW. Pt-like electrocatalytic behavior of Ru-MoO₂ nanocomposites for the hydrogen evolution reaction. *Nat. Comm.* 2017; 8:16029-16038.
8. Zeng M, Li Y. Recent advances in heterogeneous electrocatalysts for the hydrogen evolution reaction. *J. Mater. Chem A.* 2015;3:14942-14961.
9. Deng J, Ren P, Deng D, Yu L, Yang F, Bao X. Highly active and durable non-precious-metal catalysts encapsulated in carbon nanotubes for hydrogen evolution reaction. *Energy Environ. Sci.* 2014; 7:1919-1923.
10. Liu T, Ma X, Liu D, Hao S, Du G, Ma Y, Asiri AM, Sun X, Chen L. Mn Doping of CoP Nanosheets Array: An Efficient Electrocatalyst for Hydrogen Evolution Reaction with Enhanced Activity at All pH Values. *ACS Catal.* 2017; 7:98-102.
11. Yang Y, Zhang K, Lin H, Li X, Chan HC, Yang L, Gao Q. Tailorable surface sulfur chemistry of mesoporous Ni₃S₂ particles for efficient oxygen evolution. *ACS Catal.* 2017;7:2357-2366.
12. Li H, Tsai C, Koh AL, Cai LL, Contryman AW, Fragapane AH, Zhao JH, Han HS, Manoharan HC, Abild-Pedersen F, Norskov JK, Zheng XL. Activating and optimizing MoS₂ basal planes for hydrogen evolution through the formation of strained sulphur vacancies. *Nat. Mater.* 2016; 15:48-53.
13. Tymoczko J, Calle-Vallej F, Schuhmann W, Aliaksandr Bandarenka S. Making the hydrogen evolution reaction in polymer electrolyte membrane electrolyzers even faster. *Nature communications.* 2016;7:10990.

14. Hettiarachchi S, Robert Cowan L, Thomas Diaz P, Robert Law J, Susan Garcia E. Noble metal chemical addition form development of commercial application. 7th International conference on nuclear engineering. 1999; 19-23.
15. Baumgartner ME, Ch. Raub J. The Electrodeposition of Platinum and Platinum Alloys. *Platinum. Metals Rev.* 1988; 32:188-198.
16. Baraka A, Shaarawy HH, Hamed HA. Electrodeposition of Platinum Metal and Platinum-Rhodium Alloy on Titanium Substrates. *Journal of Material Engineering and Performance.* 2013; 13:5-17.
17. Mohan Reddy R, Praveen BM, Praveen Kumar CM, Venkatesha TV. Pulse Electrodeposition, Characterization, and Corrosion Behavior of Ni-Si₃N₄ Composites. *Journal of Material Engineering and Performance.* 2015; 24:1987-2004.
18. Choquette Y, Brossard L, Lasia A, Menard H. Study of the Kinetics of Hydrogen Evolution Reaction on Raney Nickel Composite-Coated Electrode by AC Impedance Technique. *J. Electrochem. Soc.* 1990; 137:1723-1729.
19. Tasić GS, Lačnjevac U, Tasić MM, Kaninski MM, Nikolić VM, Žugić DL, Jović DV. Influence of electrodeposition parameters of Ni-W on Ni cathode for alkaline water electrolyser. *Int. J. Hydrogen Energy.* 2013; 38:4291-4297.
20. Shwetharani R, Nagaraju D.H, Geetha Balakrishna R, Suvina V, Hydrogenase Enzyme like Nanocatalysts FeS₂ and FeSe₂ for Molecular Hydrogen Evolution Reaction. *Materials letters.* 2019; 248:39-42.
21. Zeng K, Zhang D. Recent progress in alkaline water electrolysis for hydrogen production and applications. *Progress in Energy and Combustion Science: an international review journal.* 2010; 36:307-327.

Figures

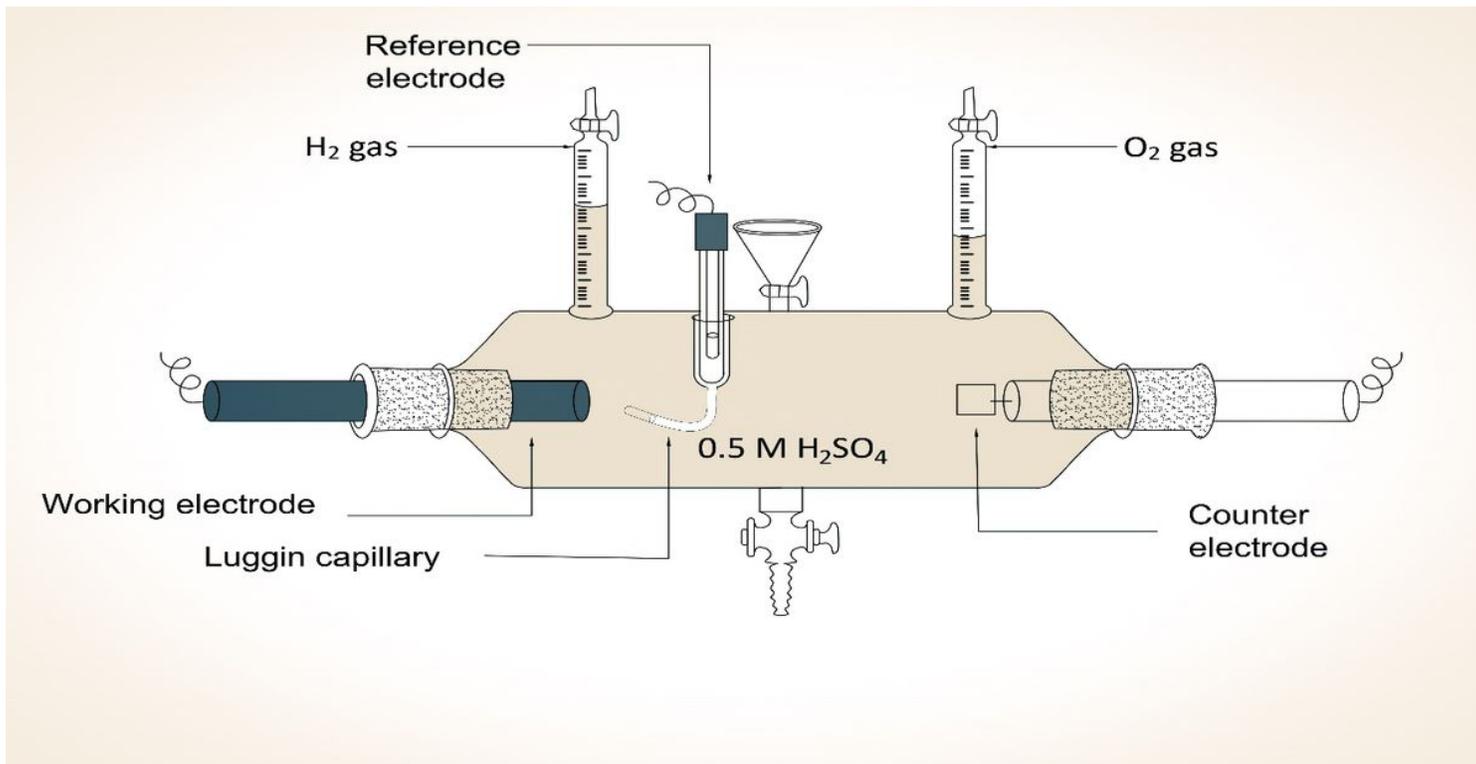


Figure 1

Tubular three-electrode glass cell used to measure the electro catalytic activity of the platinum-rhodium metal alloy electrodeposit in terms of H₂ released on the surface of electrode.

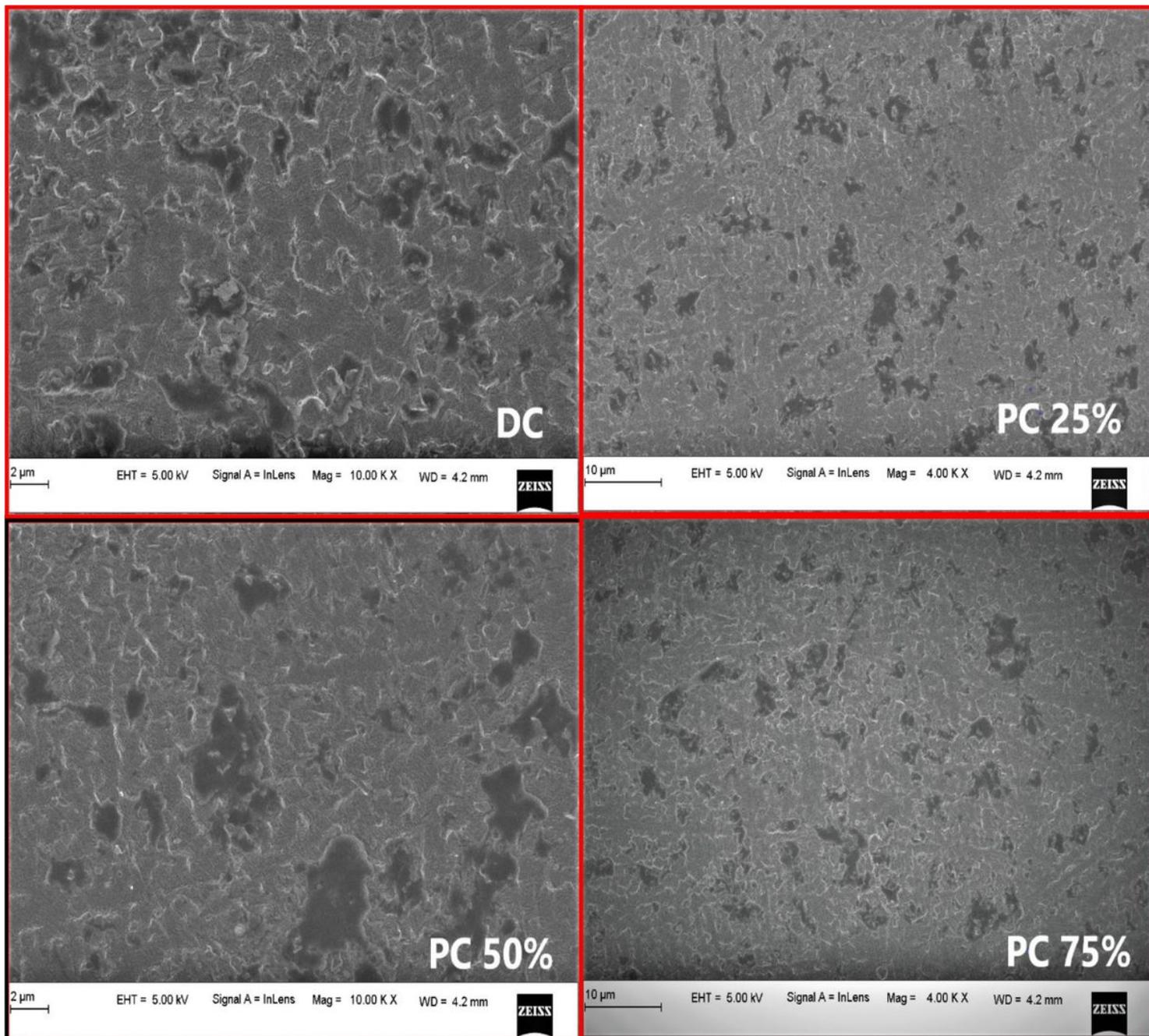


Figure 2

Surface morphology of Pt-Rh coating produced at different conditions. (a) DC (b) PC 25% (c) PC 50%, (d) PC 75%

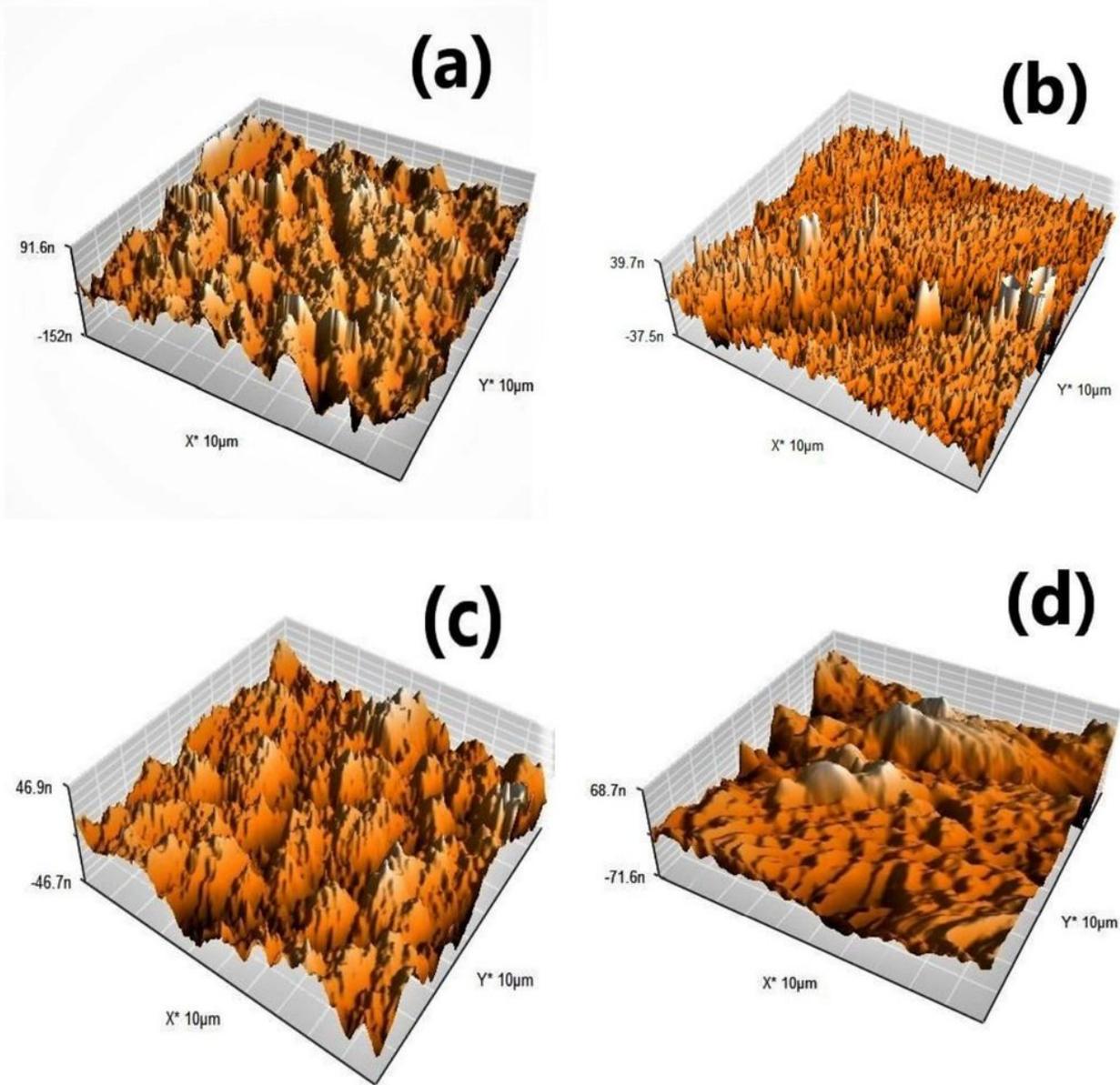


Figure 3

(a) (b) (c) and (d) is the 3D figures representing the platinum-rhodium coating roughness of DC, PC at 25%, 50% and 75% duty cycle respectively.

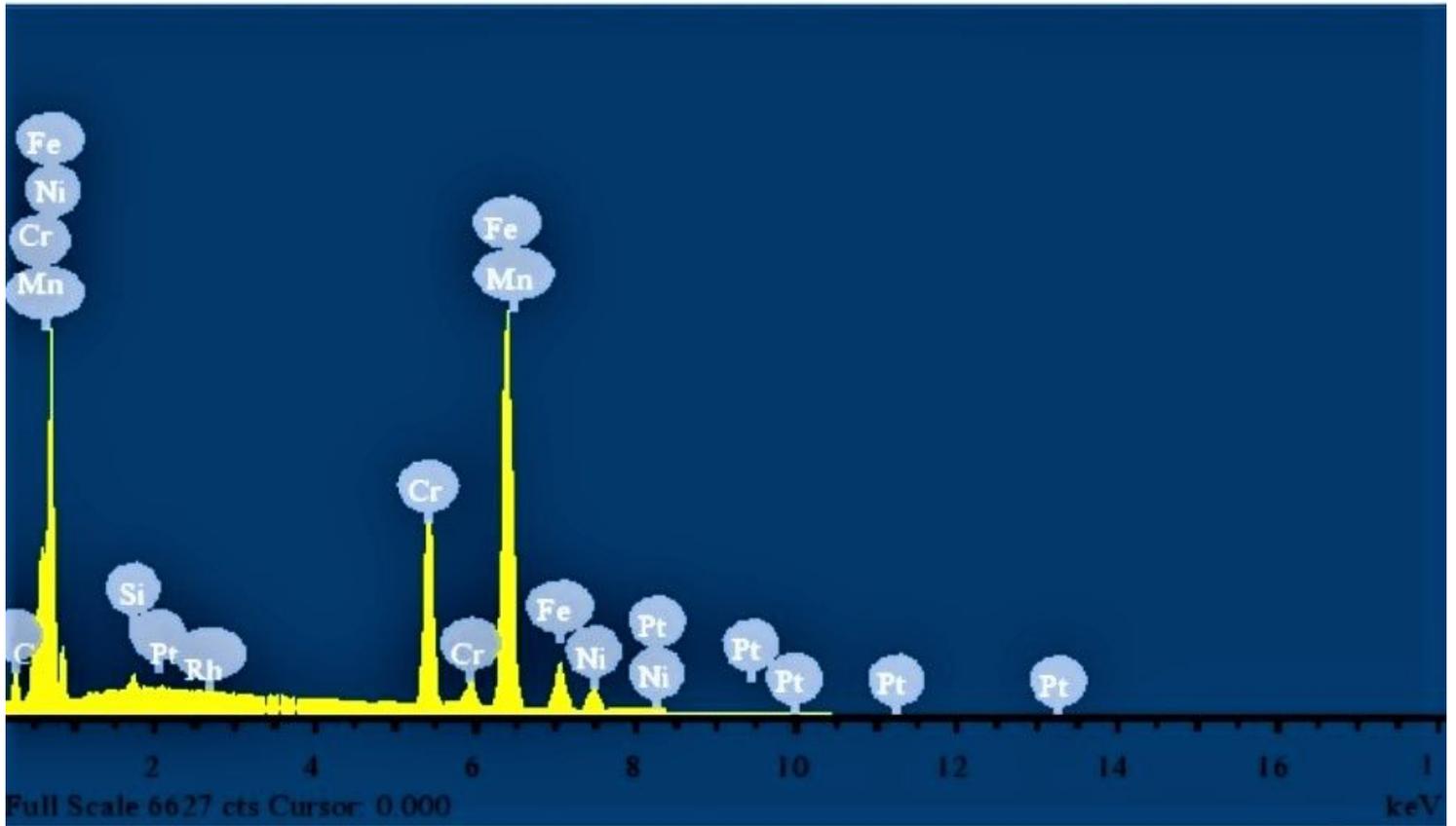


Figure 4

Designates the presence of Pt and Rh in its alloy coating by EDX technique.

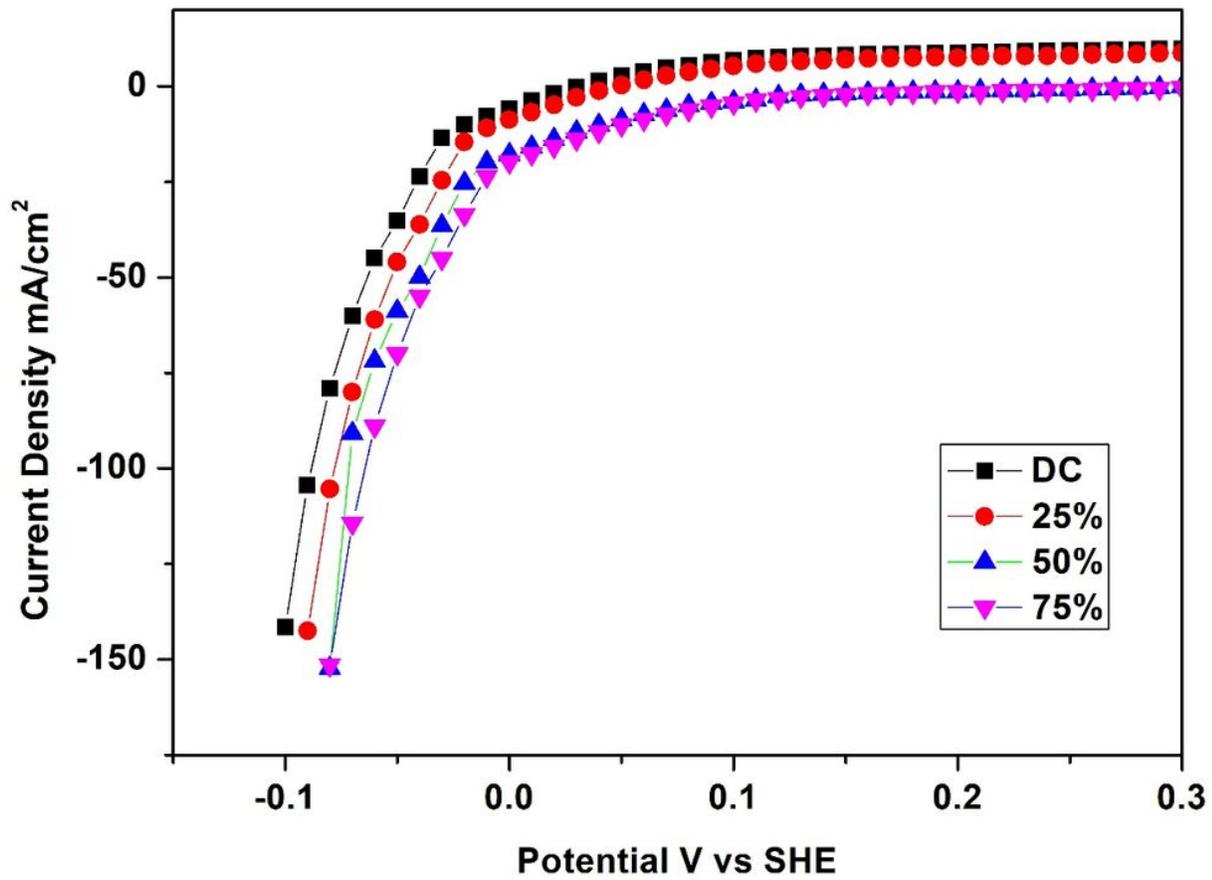


Figure 5

LSV curves for HER on the surface of the Platinum-Rhodium coatings

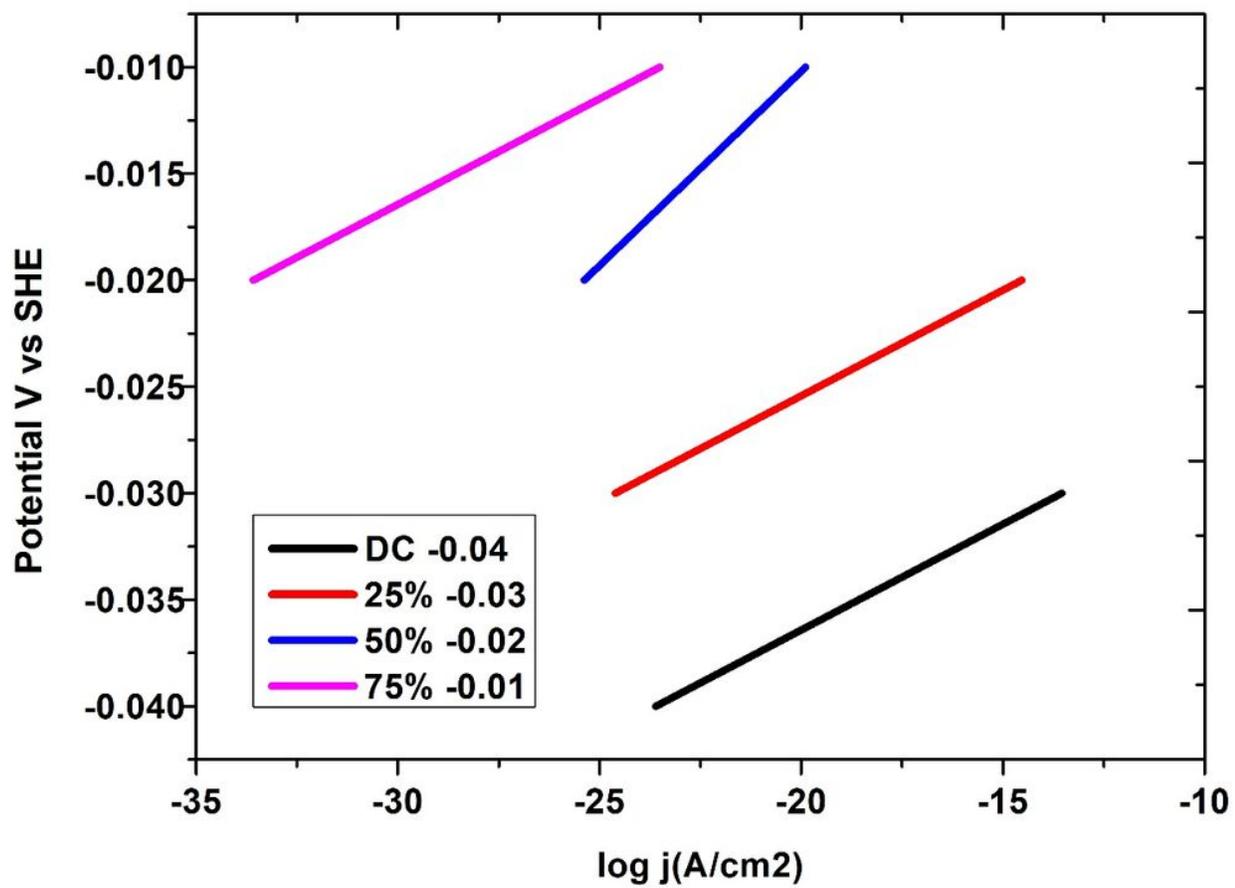


Figure 6

Tafel plots for various electrodes in 0.5 M H₂SO₄

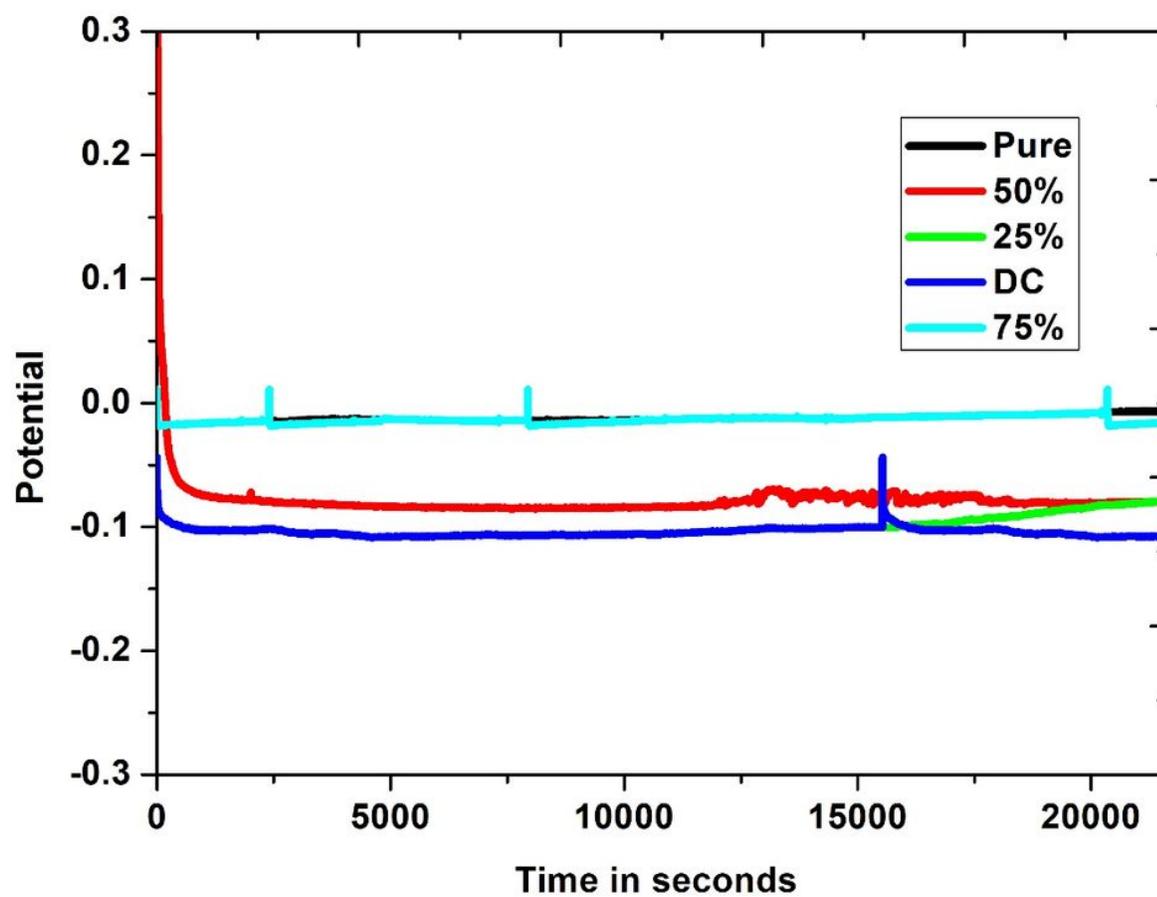


Figure 7

Chronopotentiometry curves measured in 0.5M H₂SO₄ at a current density of 4.0 A/cm²

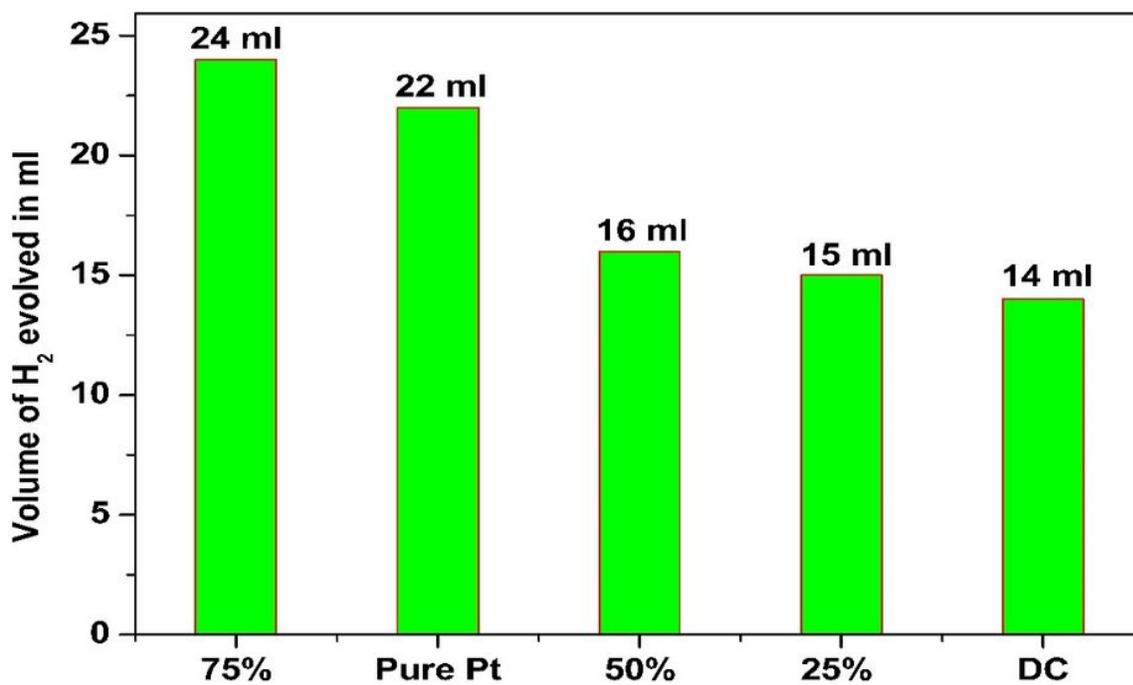


Figure 8

Volume of H₂ evolved in 150 seconds on each test electrodes are shown here.