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Electrochemical performance of Mo₂C@PtRu synthesized by electrochemical deposition method on methanol oxidation

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Abstract

The electrodeposition of Platinum and Ruthenium nanoparticles into Molybdenum carbide/ glassy carbon electrodes and their catalytic activity for the oxidation of methanol are described. These Mo₂C@PtRu electrodes exhibit good activity with respect to the catalytic oxidation of methanol. The electrodes exhibited excellent long term stability in the acidic methanol solutions.

Keywords: Molybdenum carbide, Methanol oxidation reaction, Direct methanol fuel cells, Electrodeposition.

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Introduction

We report herein an electrochemical study to demonstrate the feasibility of using $\text{Mo}_2\text{C}@\text{PtRu}$ catalyst synthesized through electrochemical deposition method to replace platinum (Pt) as anode electrocatalysts for the electrooxidation of methanol. An effective anode electrocatalyst in direct methanol fuel cell (DMFC) should be active for the decomposition of methanol while remaining stable under the relatively harsh anode environment. It should also have high activity for the oxidation of carbon monoxide (CO), which is a reaction intermediate that poisons the surface by occupying the active sites. Although the Pt/Ru bimetallic alloy is currently the most effective anode electrocatalyst, both Pt and Ru are expensive due to limited supplies and both are susceptible to CO poisoning due to the strong bonding of CO on the active surface[1-3]. Consequently, the use of a support may influence the methanol oxidation, by decreasing the amount of Pt/Ru catalysts used and their contamination by CO. The discovery of less expensive and more CO tolerant alternative electrocatalysts is of both fundamental and practical importance for the understanding and development of DMFC[4].

Hence, efforts are being channeled toward obtaining a support material that simultaneously optimizes the catalyst dispersion, loading, and electrocatalytic efficiency. An ideal support-catalyst assembly should ensure facile molecular transport of reactants and products, have good electronic conductivity, and possess high surface reactivity; these would enhance the molecular conversion. Molybdenum carbides, with their resemblance in electronic structure to noble metals, have similar catalytic properties to noble metal catalysts in various organic chemical reactions. It makes molybdenum carbides to be a promising support of Pt catalysts[5, 6].

In this work, the $\text{Mo}_2\text{C}@\text{PtRu}$ electrocatalysts prepared by spontaneous electrochemical deposition of Ru and Pt on Glass Carbon supported Molybdenum carbide particles were tested for methanol oxidation using Cyclic voltammetry and Amperometric techniques.

Experimental

2.1 Chemicals

Reagent-grade Molybdenum carbide and spectro-grade methanol (Fisher Scientific), Ruthenium Chloride and potassium hexachloroplatinate (Aldrich) were used as received. Water was distilled and subsequently passed through a Millipore Q water purification system prior to use. Aqueous solutions were prepared daily with the Millipore Q water.

2.2 Electrodes, Electrochemical Cells, and Instrumentation.

A silver/silver chloride (saturated KCl) electrode was used as the reference electrode and potentials are reported with respect to this reference. The glass carbon electrodes were hand-polished successively with 600 grit, 1.0, 0.3, and 0.05- μm alumina slurries with copious rinsing with Millipore Q water and ultrasonicated between subsequent polishing stages. The counter electrode was a Pt wire, which was isolated by a frit.

All electrochemical measurements were performed with either a PAR Model 760 potentiostat. Data were acquired with a HP 7035 B X-Y recorder (cyclic voltammetry) or a Houston Omniscrite recorder (chronoamperometry).

2.3 Preparation of the $\text{Mo}_2\text{C}/\text{GC}$ electrode.

The $\text{Mo}_2\text{C}/\text{GC}$ electrode were prepared as follows: 5mg of Mo_2C were dispersed in 2ml of water under ultrasonication agitation for 30 min to form the electrocatalyst ink. 20 μl of ink was deposited on GC electrode and dried at room temperature. After six hours, 5 μl of ethanol and 15 μl of 5wt% of Nafion were added to the electrodes and dried at room temperature.



2.4 Electrochemical deposition of Pt and Ru on Mo₂C/GC electrode.

Platinum and Ruthenium were electrodeposited into Mo₂C/GC electrode by cyclic voltammetric technique. The Mo₂C/GC electrodes were allowed to remain in contact with a 5 mM RuCl₃/0.1 M HClO₄ and K₂PtCl₆/0.1 M HClO₄ solutions simultaneously for at least 100 min prior to deposition by cyclic 50 cycles at 20mV/s.

Exhaustive electrodepositions were accomplished by applying a potential which is in -0.20 to 0.25 V range under bubbling Nitrogen.

2.5 Evaluation of the Mo₂C@PtRu electrodes

The catalytic activities of the Mo₂C@PtRu were evaluated with regard to the generation of hydrogen from 0.1 M perchloric acid solutions by slow scan cyclic voltammetry (10 mV/s) under continuous purging by nitrogen gas. Oxidation of methanol was examined in 1 M methanol/0.1 M HClO₄ solution by cyclic voltammetry from 0 to 1 V under a nitrogen purge and chronoamperometry technique was used to test the stability of the synthesized electrodes.

Generally, the working electrodes (i.e., PtRu with 1:3 ratio deposited through electrochemical deposition method Mo₂C support) were obtained by depositing Mo₂C on free GC and then the resulted electrode was used as a supporter of Ru and Pt. The electrooxidation of methanol on the Mo₂C@PtRu electrodes were performed at different temperatures (from 25 to 70 °C) using 0.1 M HClO₄ and 1M CH₃OH as the electrolytes. The methanol oxidation of the catalyst electrodes were carried out in the potential range of 0 to 1.0 V vs. Ag/AgCl with a sweep rate of 10 mV/s. All CV measurements in this work were performed under N₂ atmosphere

Results and discussion

The results of cyclic voltammetry on absence of Methanol are illustrated in **Fig1 (1) and(2)**. **Fig 1(1)** shows the cyclic voltammetry of Mo₂C electrocatalyst measured after 100 cycles. Three peaks appeared at 0.1, 0.375 and 0.5 V (vs Ag/AgCl) in the forward direction and three others in the backward directions were recorded. These three peaks may correspond with the oxidation and reduction of Mo at different oxidation states (+3, +4 and +6) [6, 7].

Fig 1(2) shows the CV results of 0.1M HClO₄ after deposition of 5mmol Pt and Ru on Mo₂C/GC electrode and the scan rate was 50mV/s solution saturated with N₂ atmosphere. The potential scan rate was 50 mV/s and the sweep range from -0.2 V to 0.8 V. We studied four regions with peaks. During the forward sweep, an anodic peak is present at -0.06 V, which is caused by desorption of hydrogen (the first region). During the backward sweep, another peak is present at -0.13 V which is caused by adsorption of hydrogen (the second region). The presence of these peaks indicates that Mo₂C@PtRu electrode strongly bonds to hydrogen atoms on the surface-active sites [8]. In the second region, it is known that Pt oxide formation on the electrode surface. The Pt oxide formation is more complex than hydrogen adsorption. During the reverse sweep, we observed a single peak in the third region one normally assigned to Pt oxide reduction. As shown in this figure, the Pt oxide reduction peak potential was 0.52 V on the Mo₂C@PtRu electrode. After 100 repetitive cycles, the remaining current of Pt oxide reduction on the Mo₂C@PtRu electrode was 96.4% of the initial current. This indicated that the Mo₂C@PtRu electrode is highly stable in acidic medium.

The Mo₂C@PtRu electrocatalysts have a very defined hydrogen oxidation in the potential range of (-0.2 to 0V), which is common for all platinum based catalysts, and the double layer region (0 to 0.4V) are large which characterize the Mo₂C@PtRu electrocatalysts. The electrocatalyst Mo₂C/GC has low current compare with the Mo₂C@PtRu electrocatalyst, this could be attributed to the synergistic effect between Mo₂C and PtRu.

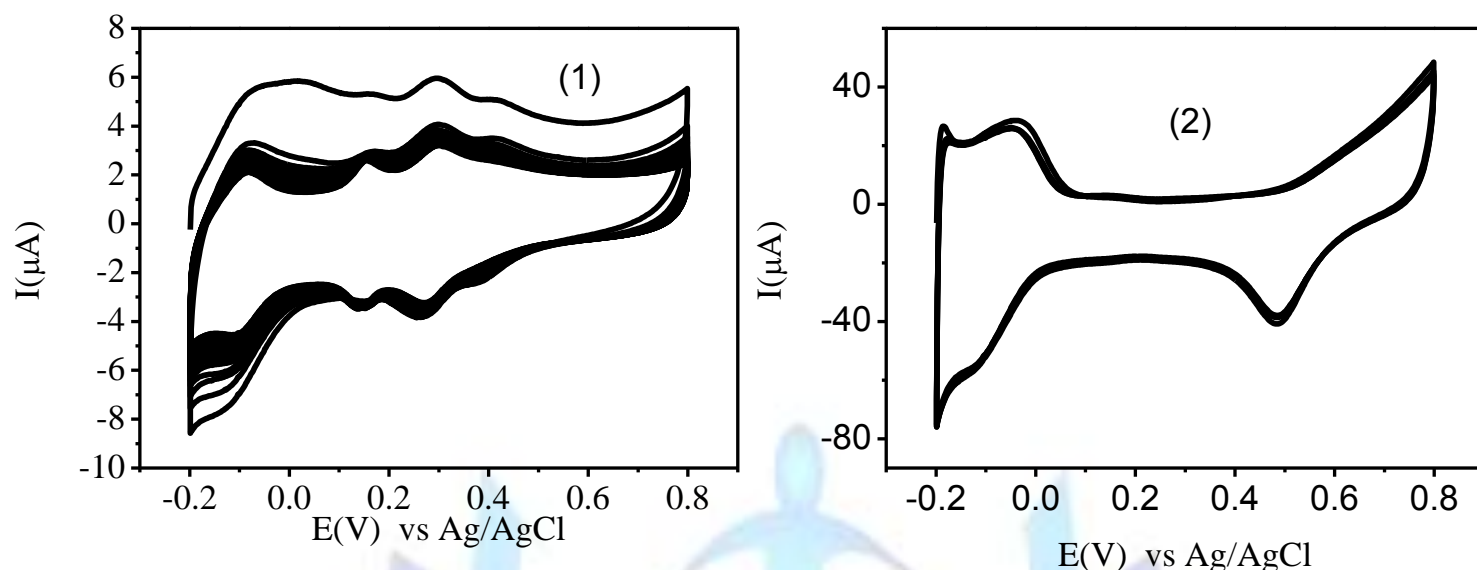


Fig1: (1) CV of 0.1M HClO₄ using Mo₂C/GC electrode, the scan rate was 100 mV/s and 100cycles were recorded. (2)CV of 0.1M HClO₄ after deposition of 5mmol Pt and Ru on Mo₂C/GC electrode and the scan rate was 50mV/s.

At elevated temperatures, the methanol oxidation reaction at platinum and platinum ruthenium electrodes have been studied extensively[6]. Generally, on pure Pt electrodes the current density of MeOH change with temperature and the peak of MeOH oxidation shifts towards more negative potentials with increasing temperature thus indicating that the methanol oxidation mechanism is affected by the temperature referring to **Fig.2.A**. However, to obtain real performance of the electrocatalysts a subtraction of the background currents is necessary. **Fig.2.B** illustrates the linear sweep voltammetry of methanol oxidation when the temperature was set as 70 °C and the scan rate was changed from 10 to 200mV/s. The results indicate that the current increases as the scan rate rises and there is a shift of onset potential to the more negative value for low scan rate. Thus, the shift of onset potential to the negative position could be attributed to the enhancement of oxidation of adsorbed intermediates promoted by the low scan rate which refers to 10mV/s.

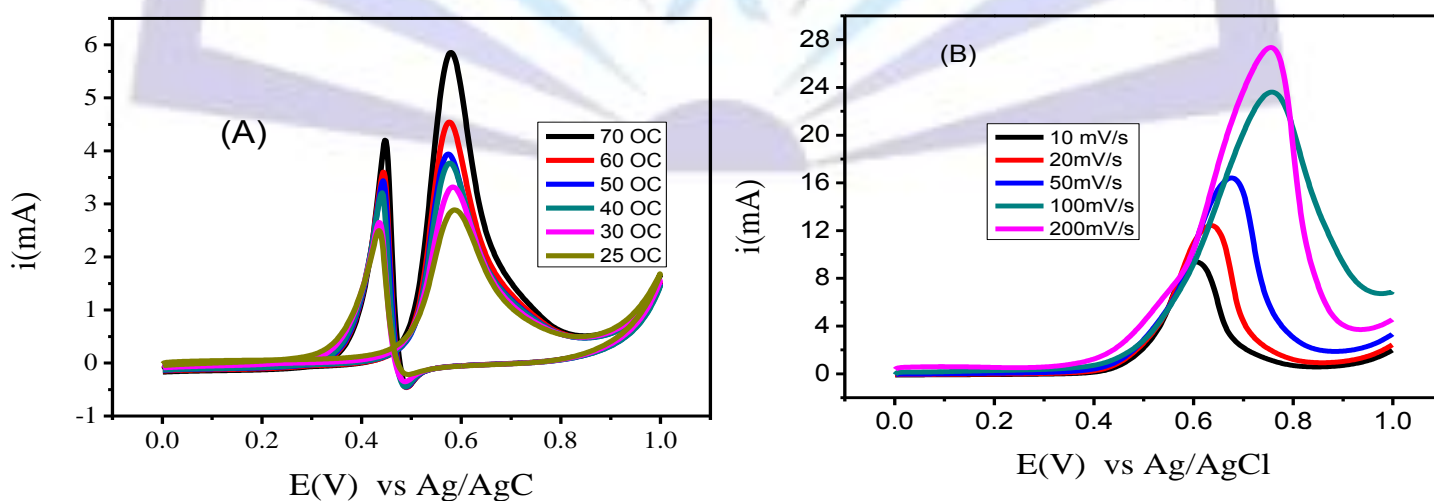


Fig. 2.(A)CV of 1M MeOH oxidation using the Mo₂C@PtRu electrode;0.1M HClO₄ was used as a supporting electrolyte and the scan rate was 10mV/s and the temperature changed from 25 to 70 °C.(B)

Linear sweep voltammetry of Methanol oxidation using $\text{Mo}_2\text{C}@\text{PtRu}$ electrode at 70°C ; the scan rate changed from 10 to 100mV/s .

The electrooxidation of carbon monoxide on platinum in aqueous acidic electrolytes is one of the most extensively studied electrochemical reactions over the past decades. The main interest is centred on two practical problems pertaining to the application of platinum based catalysts; (i) the search for catalysts for DMFC's and (ii) the development of CO-tolerant anodes for DMFCs. For both types of fuel cells, it is essential to oxidize and remove CO from the platinum surface at lower over potentials. Fig.3 displays the CV of Carbon monoxide oxidation on $\text{Mo}_2\text{C}@\text{PtRu}$, when the scan rate changed from 10 to 100mV/s . It is observed that the carbon monoxide mixed with HClO_4 influences the variation of current as the scan rate changed and the synthesized catalyst may be contaminated with CO at high potential 0.7V.

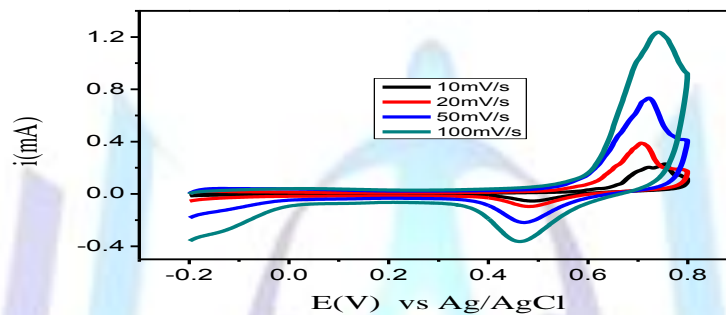


Fig.3: Investigating the variation of current when CO was purged into the system. $\text{Mo}_2\text{C}@\text{PtRu}$ electrode was used as the working electrode and the scan rate changed from 10 to 100mV/s . Ru:Pt ratio was 1:3.

A direct investigation of stability of the electrocatalyst could not be accurate using CV technique, due to the contributions of capacitive currents to the anodic peaks obtained with this method. Chronoamperometric technique is a powerful method used to check the stability of electrodes. Fig.4 indicates the comparison of $\text{Mo}_2\text{C}@\text{PtRu}$ synthesized catalyst and PtRu commercial catalyst. An initial decay of the capacitive current was observed until a clear steady state current was reached, which is related to the methanol oxidation. At the oxidation potential of 0.5V the current suddenly drops to a low steady state current value. The origin of this low current is mostly rooted from the presence of strong adsorbed intermediates such as CO. The activity shown by Mo_2C appears to coincide with the $\text{Mo}_2\text{C}@\text{PtRu}$ surface and marks a higher current than PtRu commercial catalyst. This enhancement in activity is attributed to an improved CO tolerance of the Mo_2C surface, which is consistent with the observation of lower CO desorption[9].

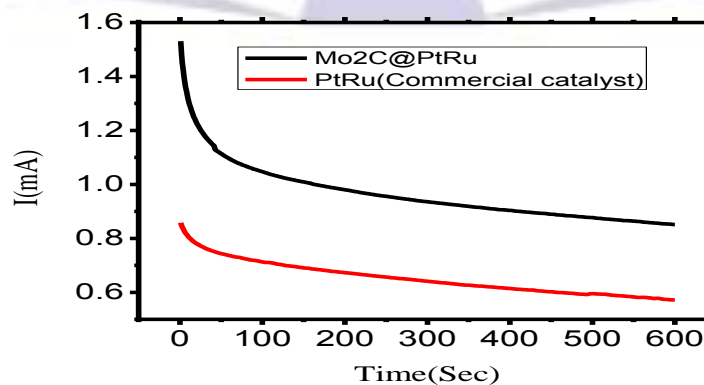


Fig. 4. Chronoamperometric response recorded at 500mV (vs Ag/AgCl) of $\text{Mo}_2\text{C}@\text{PtRu}$ and PtRu catalysts for methanol electro-oxidation in nitrogen saturated 0.1M HClO_4 and 1M methanol at 25°C .



Conclusion

Our results show that Mo₂C@PtRu synthesized through electrochemical deposition is active to methanol oxidation and is a promising alternative electrocatalyst of Pt catalyst at voltages up to 0.8 V. At the same time, our findings also indicate that Mo₂C@PtRu is more stable for applications with significantly increasing the activity. In our view the potential applications of Mo₂C@PtRu rooted from the strong interaction of Mo₂C support with the PtRu. By Comparing with the PtRu commercial catalyst, where only the surface Pt and Ru atoms of the Pt and Ru particles are used for electrocatalysis, all Pt and Ru atoms in Mo₂C@PtRu remain in the surface, which should lead to a significant reduction in the noble metals loading.

Conflicts and Interest

The authors declare that there is no conflict of interest.

Acknowledgements

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Author' biography with Photo



NESTOR UWITONZE, A NATIVE OF RWANDA COUNTRY, KIGALI CITY, HAS BEEN SELECTED INTO CAS TWAS PRESIDENTIAL SCHOLARSHIP TO PURSUIT HIS PhD AT UNIVERSITY OF SCIENCE AND TECHNOLOGY OF CHINA FROM 2014. NESTOR IS ENGAGED IN THE RESEARCH OF CATALYSIS AND FUEL CELLS. NESTOR HAS PUBLISHED A PAPER WITH HIGH IMPACT FACTOR (6.37) IN CHEMICAL COMMUNICATION JOURNAL.

