Contents

Volume 104
Issue 5
May 2009

www.sensorsportal.com  ISSN 1726-5479

Research Articles

Biosensors Development Based on Potential Target of Conducting Polymers
Ravindra P. Singh and Jeong-Woo Choi ............................................................... 1

Designing Binocular Stereo Omni-Directional Vision Sensors
Yi-ping Tang, Chen-jun Pang, Yi-hua Zhu ............................................................... 19

A Stainless Steel Electrode Phantom to Study the Forward Problem of Electrical Impedance Tomography (EIT)
Tushar Kanti Bera and J. Nagaraju ................................................................. 33

Single-mode D-type Optical Fiber Sensor in Spectra Method at a Specific Incident Angle of 89°
Ming-Hung Chiu, Po-Chin Chiu, Yi-Hsien Liu, Wei-Ding Zheng ........................................ 41

Effect of Low Frequency Pulsed DC on Human Skin in Vivo: Resistance Studies in Reverse Iontophoresis
Pavan Kumar Kathuroju and Nagaraju Jampana .................................................. 47

Low Frequency Noises of Hydrogen Sensors
Zara Mkhitaryan, Ferdinand Gasparyan, Armine Surmalyan ....................................... 58

Fe₂O₃ - ZnO Based Gas Sensors
L. A. Patil ........................................................................................................ 68

Effect of Yttria on Gas Sensitivity of Tungsten Trioxide
M. H. Shahrokh Abadi, M. N. Hamidon, Rahman Wagiran, Abdul Halim Shaari, Norhisam Misron, Norhafizah Abdullah ................................................................. 76

Liquefied Petroleum Gas (LPG) Sensing Properties of Nanosized Sprayed CdIn₂O₄ Thin Films
R. J. Deokate, R. R. Salunkhe, K. Y. Rajpure ............................................................. 87

Optimization of a Novel Humidity Sensing Mechanism Strip Length
Souhil Kouda, Zohir Dibi, Abdelghani Dendouga, Samir Barra ....................................... 96

Humidity Sensing Studies of WO₃-ZnO Nanocomposite
N. K. Pandey, Anupam Tripathi, Karunesh Tiwari .................................................. 109

Electrochemical Reduction of Potassium Ferricyanide Mediated by Magnesium Diboride Modified Carbon Electrode
WeeTee Tan, Farhan Yusri and Zulkarnain Zainal .................................................... 119

Authors are encouraged to submit article in MS Word (doc) and Acrobat (pdf) formats by e-mail: editor@sensorsportal.com
Please visit journal’s webpage with preparation instructions: http://www.sensorsportal.com/HTML/DIGEST/Submition.htm

International Frequency Sensor Association (IFSA).
Electrochemical Reduction of Potassium Ferricyanide Mediated by Magnesium Diboride Modified Carbon Electrode

*WeeTee TAN, FARHAN Yusri and ZULKARNAIN Zainal
Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, 43400 UPM, Serdang, Selangor D.E., Malaysia
E-mail: wttan@science.upm.edu.my

Received: 10 February 2009   /Accepted: 19 May 2009   /Published: 25 May 2009

Abstract: Use of a glassy carbon (GC) modified by adhered microparticles of MgB$_2$ mediates the reduction process of Fe(III)(CN)$_6^{3^-}$ during cyclic voltammetry. Peak potential was observed to shift slightly to less negative value by about 50 mV and current is significantly enhanced by about two folds. The sensitivity under conditions of cyclic voltammetry is significantly dependent on pH, electrolyte and scan rate. The result of scanning electron micrograph of MgB$_2$ obtained before and after electrolysis show the size increased slightly to the size ranging from 2 - 5.5 µm attributing to the hydration effect and/or incorporation of some ionic species into the crystal lattices of MgB$_2$. Interestingly, redox reaction of Fe(III) solution using modified GC electrode remain constant even after 15 cycling. It is therefore evident that the MgB$_2$ modified GC electrode possesses some degree of stability. Potential use of MgB$_2$ as a useful electrode material is therefore clearly evident. Copyright © 2009 IFSA.

Keywords: Solid state voltametry of microparticles, MgB$_2$ modified GC electrode, Fe(III)/(II) redox couple, Electro catalysis

1. Introduction

Magnesium diboride (MgB$_2$) is an odourless and brittle compound, exists in the form of powder, crystals and ceramics where the colour varies from one form to the other; black in powder, yellow in crystals and pink in ceramics. It has simple crystal structure with Mg layer alternating with honeycomb B layer [1]. It is also a simple binary compound which contains only 3 atoms per hexagonal cell. In year 2001, Jun Akamitsu et al. discovered that T$_c$ for MgB$_2$ is 39 k. The T$_c$ is double from previous
record of intermetallic $T_c$ [1]. The isotopes studies in previous report showed that $T_c$ was shifted by 1 K if MgB$_2$ with B10 isotope was used instead of MgB$_2$ with B11 isotope [2,3] while there was no effect when change from isotope Mg 24 to isotope Mg 25 [3]. There is a growing consensus that the electro-phonon interaction is responsible for the superconductivity [4]. It was not discovered 40 years ago due to difficulty in preparation [1]. However, recently method of growing MgB$_2$ such as single crystal [5], powder [6], and wires [7] have been developed. In application it can be used as a magnet due to light weight for magnetic-resonans-imaging application [1]. The study of electrochemistry for MgB$_2$ is still rather lacking. Electrochemical characterization and mediation studies using MgB$_2$ modified solid electrode has not been reported. In this work, an attempt is made to report the work done using MgB$_2$ as sensing electrode materials which is mechanically attached to the surface of glassy carbon (GC) working electrode via solid phase voltammetry of microparticles (SPVM).

2. Experimental

2.1. Instrument and Electro Analytical Analysis Methods

Electrochemical workstations of Bioanalytical System Inc. USA: Model BAS 50W with potentiostat driven by electroanalytical measuring software were connected to PC computer to perform cyclic voltammetry (CV), chronoamperometry (CC), and chronoamperometry (CA). An Ag/AgCl (3M NaCl) and platinum wire were used as a reference and counter electrodes respectively. The working electrode used in this study was 3 mm diameter glassy carbon (GC). Unless otherwise stated, the voltammetric experiments were carried out at 25 ± 2°C using 1.0M KCl as supporting electrolyte. Solution was degassed with nitrogen for ten minutes prior to recording the voltammogram.

2.2. Reagents

All reagents were analytical reagent or electrochemical grade purity. All solutions were prepared using distilled water. Unless otherwise specified, the supporting electrolyte was 1.0 M KCl in aqueous media at room temperature.

2.3. Procedures

The solid compound magnesium diboride (MgB$_2$) was transferred to the surface of the glassy carbon (GC) electrode as followed: Sample amount of 1-3 mg of MgB$_2$ were placed on a coarse grade filter paper. Glassy carbon was pressed onto the substance and rubbed over the material, causing some compound to adhere to the electrode surface. For electrochemical measurements, the electrode was transferred into the solution. The clean glassy carbon surface could be renewed after the measurement by polishing with 0.5 µm alumina slurry, followed by ultrasonic cleaning for about 2-3 minutes, rinsing with distilled water.

3. Result and Discussion

3.1. Characterization of Magnesium Diboride Using Different Solid State Electrodes

Fig. 1 shows the cyclic voltammograms of using the bare GC working electrode and MgB$_2$ modified GC electrode in 0.1 M KCl supporting electrolyte. The working potential window (where electroactivity due to electrode materials and electrolyte is negligible) was found to be in the range of -1.0 to at least 1.0 V and 0.0 V to -1.30 V for bare GC electrode and MgB$_2$ modified GC electrode.
during the initial potential cycle. A considerable extension of the working window at the cathodic region is observed when MgB$_2$ modified GC is used. Although the working window at anodic region is deteriorating due to the “electrocatalysed” oxidation of the aqueous electrolyte or the reactivity of MgB$_2$ microparticles giving rise to a limiting current appearing at about 0.2 V. This limiting current, however diminishes in subsequent cycle (2$^{nd}$ cycle) allowing potential working window to be widened at the anodic region to near 0.8 V. It shows that MgB$_2$ modified GC electrode is useful for redox reaction studies appearing at a more negative potential of up to at least -1.3 volt and is only useful at anodic region if 2$^{nd}$ cycle is used.

![Cyclic voltammogram (Background) obtained for the bare GC working electrode (a) and magnesium diboride modified GC electrode (b) in 0.1M potassium chloride.](image1)

**Fig. 1.** Cyclic voltammogram (Background) obtained for the bare GC working electrode (a) and magnesium diboride modified GC electrode (b) in 0.1M potassium chloride.

Fig. 2 shows the CV of 0.1 M KCl taken at varying working electrodes modified with magnesium diboride in 0.1M KCl. The MgB2 modified solid electrodes exhibit potential working range of -1.3 to 0.6 V, -0.8 to 0.6 V and -0.4 to 0.6 V for GC, Pt and Au electrodes respectively. Hence in terms of the degree of accessibility of potential working window for various solid electrodes, GC > Pt > Au. It is interesting to note that both GC and Au modified electrodes have quite a similar background / capacitance current despite the fact that GC electrode (3 mm diameter) used has a larger surface area than that of Au (1 mm diameter).

![Cyclic voltammetry obtained for the (a) GC (b) pt (c) gold electrode modified with magnesium diboride in 0.1M potassium chloride, scan rate 100 mV/s.](image2)

**Fig. 2.** Cyclic voltammetry obtained for the (a) GC (b) pt (c) gold electrode modified with magnesium diboride in 0.1M potassium chloride, scan rate 100 mV/s.
3.2. Electrochemical Characterization in Electrolyte of Varying pH

For these studies, the pH of 0.1M KCl solution was varied by addition of either dil. HNO₃ or KOH solution. The cyclic voltammograms obtained (Fig. 3) in 0.1M KCL at neutral (pH7) and basic (pH12) solution were found to be similar with working potential region detected between -1.3 V and 0.6 V while in a more basic solution of greater than pH 12, the working potential range is widened to a more positive potential by 200 mV (ie to - 0.8 V. However, in acidic solution (pH4), the working range was shortened to between -0.8 V and 0.4 V due to the reduction of hydrogen gas in acidic solution and oxidation of the aq. electrolyte. There is a small peak appearing at near 0 V probably due to the oxidation of oxygen trapped inside the magnesium diboride. As MgB₂ modified solid electrode based on glassy carbon, GC possesses characteristics of a more superior working electrode, it is therefore used in subsequent studies.

![Cyclic voltammetry obtained for the GC electrode modified with magnesium diboride in 0.1 M potassium chloride at (a) pH7 (b) pH4 (c) pH10, scan rate 100 mV/s.](image)

**Fig. 3.** Cyclic voltammetry obtained for the GC electrode modified with magnesium diboride in 0.1 M potassium chloride at (a) pH7 (b) pH4 (c) pH10, scan rate 100 mV/s.

3.3. Effect of Magnesium Diboride Modified GC Electrode on the Redox Reaction of Potassium Ferricyanide During CV

Potassium Ferricyanide is commonly used as a reference standard for the purpose of calibrating a voltammetric system in aqueous solutions. During the calibration process of an electroanalytical workstation (BAS Model 50W) using GC and MgB₂ modified GC electrode. Oxidative current of Fe³⁺/Fe²⁺ redox couple appears to be significantly enhanced (Fig. 4).

![Cyclic voltammetry of 1mM potassium ferricyanide in 0.1M potassium chloride, at scan rate 100 mV/s for the GC unmodified working electrode and GC electrode modified with magnesium diboride.](image)

**Fig. 4.** Cyclic voltammetry of 1mM potassium ferricyanide in 0.1M potassium chloride, at scan rate 100 mV/s for the GC unmodified working electrode and GC electrode modified with magnesium diboride.
It was also observed that the redox potential with $E_a = 227 \text{ mV}$ and $E_c = 320 \text{ mV}$ with peak separation of 93 mV (for $n=1$) in 0.1M KCl electrolyte indicating the reversible reaction of the Fe(III)/Fe(II) couples in KCl solution and agree well with the accepted values. In subsequent studies, various chemical and physical effects were assessed in order to determine the optimum conditions under which maximum current response at the MgB$_2$ modified GC electrode can be obtained.

3.4. Effect of Varying Supporting Electrolyte

The different type of supporting electrolyte exerts slight influence on the reduction peak potential of Fe$^{3+}$ as expected esp. in noncomplexing solutions (Table 1). In general, redox peaks of Fe$^{3+}$ appearing at have a similar pattern of peak formation in varying supporting electrolyte. However, redox current esp. the oxidation peak of Fe$^{3+}$/Fe$^{2+}$ couple show that the greatest enhancement effect is obtained when potassium chloride is used as electrolyte. In general, degree of current enhancement in varying electrolyte varies in the following order:

$$\text{KCl} > \text{KH}_2\text{PO}_4 > \text{KNO}_3 > \text{KClO}_4 > \text{K}_2\text{SO}_4$$  (Table 1).

Table 1. Cyclic voltammetry of 1mM potassium ferricyanide in different electrolyte, at scan rate 100 mV/s for the GC unmodified working electrode and GC electrode modified with magnesium diboride.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Reduction Current/$\mu$A</th>
<th>Enhancement</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Without MgB$_2$</td>
<td>With MgB$_2$</td>
</tr>
<tr>
<td>0.1M Potassium oxalate</td>
<td>15.34</td>
<td>16.10</td>
</tr>
<tr>
<td>0.1M Potassium dihydrogen orthophosphate</td>
<td>12.55</td>
<td>15.98</td>
</tr>
<tr>
<td>0.1M Potassium nitrate</td>
<td>15.14</td>
<td>16.19</td>
</tr>
<tr>
<td>0.1M Potassium chloride</td>
<td>12.49</td>
<td>23.60</td>
</tr>
</tbody>
</table>

3.5. Effect of Varying pH

The solution was varied from 2.0 to 12.0 in order to determine its effect on the catalytic reduction of potassium ferricyanide at the magnesium diboride modified electrode. Table 1 and Fig. 5 show that the highest current was observed under a neutral condition. A much higher current is generally observed in acidic media as compared with those in a more basic solution. It is as expected as Fe(III) hydrolysis sets in under strongly alkaline conditions. The hydrolysed Fe(III) product is usually electroinactive.

3.6. Effect of Potential Cycling

The potential cycling of the reduction of Fe(III) solution, 1.0 mM $K_3\text{Fe(CN)}_6$ was carried out at the electrode surface of a glassy carbon electrode (3 mm diameter) modified with MgB$_2$ microparticles during cyclic voltammetry. Continuous potential cycling did not seem to affect the redox current of potassium ferricyanide at magnesium diboride modified GC electrode since the faradaic activity appears reproducible even after 15 cycles reflecting the stability of the MgB$_2$ coat/film at the surface of GC electrode (see also SEM results given below).
Fig. 5. Cyclic voltammetry of 1mM potassium ferricyanide diboride in different pH, at scan rate 100 mV/s for the GC modified electrode with magnesium diboride.

3.7. Effect of Varying Fe(III) Concentration

Linear current dependent on K₃Fe(CN)₆ concentration was observed up to 10 mM described by the equation of y = 40.02x + 12.90 with R² = 0.9854. The slope of 40.0 mA mol⁻¹ K₃Fe(CN)₆ showed high sensitivity response is readily obtained using MgB₂ modified GC electrode.

3.8. Effect of Varying Scan Rate

The effect of varying scan rates on the cyclic voltammograms of 1 mM Ferricyanide using magnesium diboride as working electrode 1.0 M KCl supporting electrolyte was studied over 5 – 1000 mV/s. Oxidation and reduction currents of Fe(III)/Fe(II) couple was observed to increase with scan rate due to heterogeneous kinetics.

Based on a plot of log (peak current) versus log (scan rate, v) for reduction current of the first cycle, a straight line was obtained fulfilling the equation y = 0.565x + 0.249 with R² = 0.9886. A slope of 0.57 which is quite comparable with theoretical slope of 0.5 for diffusion controlled process.

3.9. Chronoamperometry

In Chronoamperometry (CA) the potential is stepped from an individual value E_i to E_t and the accompanying current is recorded as a function of time for an electrode in unstirred solution [14]. The current decays as the electrolysis proceeds to deplete the solution near the electrode of electroinactive species. The current response is described by the Cottrell equation:

\[ I = nFAC(D/\pi t)^{1/2} \]  

where \( I \) = Current
\( n \) = Number of electron per molecule
\( F \) = Faraday constant
\( A \) = Electrode area
\( D \) = Diffusion coefficient of electroactive species
\( C \) = Concentration of electroactive species
\( T \) = Time

124
Fig. 6 shows the monotonous rising and decaying current transient in accordance to the diffusion process based on the diffusion process to a planar electrode.

![Graph showing current transient](image)

**Fig. 6.** Chronoamperograms of 1mM potassium ferricyanide in 0.1M potassium chloride for the GC modified electrode with magnesium diboride.

### 3.10. Chronocoulometry

Chronocoulometry (CC) is the integral analogs of the corresponding chronoamperometry approaches. The integral of the Cottrell equation gives the cumulative charge passed in reducing or oxidizing the diffused component [14]:

\[
Q = 2nFAD^{1/2}C_0 \pi^{1/2}t^{1/2}
\]  

(2)

where \(Q = \) Charge and the other parameters have its usual meanings.

The analysis of chronocoulometry (CC) data is based on the Anson equation above (Eq. 2), which defines the charge-time dependence for linear diffusion control. The Anson plot shows linear dependency of \(Q\) upon \(t^{1/2}\) (Fig. 7) indicating that the process involved is diffusion controlled.

Based on Anson’s plot of the above, surface charge can be calculated by taking the difference between two intercepts of forward and reverse steps at \(t=0\). It was found that the MgB\(_2\)/GC has a total charge transferred of 3.13 µC when 1mM potassium ferricyanide was reduced.

![Graph showing chronocoulometry](image)

**Fig. 7.** Chronocoulograms of 1mM potassium ferricyanide in 0.1M potassium chloride for the GC modified electrode with magnesium diboride.
3.11. Scanning Electron Microscopy

As is shown in Fig. 8, prior to the application of a reducing potential, magnesium diboride had a size range of the order of 0.5 to 1.3 µm. After controlled-potential electrolysis was carried out in the presence of $K_2Fe(CN)_6$, the size increased slightly to the size ranging from 2 - 5.5 µm attributing to the hydration effect and/or incorporation of some ionic species into the crystal lattices of MgB2.

![Fig. 8. Scanning electron micrographs of magnesium diboride microparticles mechanically attached to a basal plane pyrolitic graphite electrode (a) before and (b) after electroanalysis.](image)

4. Conclusion

Among the various solid electrodes used, GC electrode by far a better choice of solid state electrode to be modified with MgB2 microparticles; les as it has an extended negative potential working region under weakly acidic to strongly alkaline region. Although the oxidative region is limited, the use of potential cycling helps to widen the oxidative working potential range significantly.

Use of a glassy carbon (GC) modified by adhered microparticles of MgB2 mediates the reduction process of $Fe(III)(CN)_6^{3-}$ during cyclic voltammetry. Peak potential shifts slightly to less negative value by about 50 mV and current is significantly enhanced by about two folds. The sensitivity under conditions of cyclic voltammetry is significantly dependent on pH, electrolyte and scan rate. The stability of MgB2 film coated at the GC electrode surface is also evident from SEM and potential cycling experiments. Potential use of MgB2 as a useful electrode material is therefore clearly evident.

Acknowledgement

The authors wish to thank Ministry of Science, Technology and Innovation, Malaysia (MOSTI) for a research grant and Universiti Putra Malaysia for the use of research facilities. One of us (F.Y.) expresses appreciation of obtaining a research assistantship via the MOSTI’s grant.

References


---

2009 Copyright ©, International Frequency Sensor Association (IFSA). All rights reserved.
(http://www.sensorsportal.com)
Guide for Contributors

Aims and Scope

*Sensors & Transducers Journal (ISSN 1726-5479)* provides an advanced forum for the science and technology of physical, chemical sensors and biosensors. It publishes state-of-the-art reviews, regular research and application specific papers, short notes, letters to Editor and sensors related books reviews as well as academic, practical and commercial information of interest to its readership. Because it is an open access, peer review international journal, papers rapidly published in *Sensors & Transducers Journal* will receive a very high publicity. The journal is published monthly as twelve issues per annual by International Frequency Association (IFSA). In additional, some special sponsored and conference issues published annually. *Sensors & Transducers Journal* is indexed and abstracted very quickly by Chemical Abstracts, IndexCopernicus Journals Master List, Open J-Gate, Google Scholar, etc.

Topics Covered

Contributions are invited on all aspects of research, development and application of the science and technology of sensors, transducers and sensor instrumentations. Topics include, but are not restricted to:

- Physical, chemical and biosensors;
- Digital, frequency, period, duty-cycle, time interval, PWM, pulse number output sensors and transducers;
- Theory, principles, effects, design, standardization and modeling;
- Smart sensors and systems;
- Sensor instrumentation;
- Virtual instruments;
- Sensors interfaces, buses and networks;
- Signal processing;
- Frequency (period, duty-cycle)-to-digital converters, ADC;
- Technologies and materials;
- Nanosensors;
- Microsystems;
- Applications.

Submission of papers

Articles should be written in English. Authors are invited to submit by e-mail editor@sensorsportal.com 8-14 pages article (including abstract, illustrations (color or grayscale), photos and references) in both: MS Word (doc) and Acrobat (pdf) formats. Detailed preparation instructions, paper example and template of manuscript are available from the journal’s webpage: http://www.sensorsportal.com/HTML/DIGEST/Submition.htm Authors must follow the instructions strictly when submitting their manuscripts.

Advertising Information

Advertising orders and enquires may be sent to sales@sensorsportal.com Please download also our media kit: http://www.sensorsportal.com/DOWNLOADS/Media_Kit_2009.pdf
‘Written by an internationally-recognized team of experts, this book reviews recent developments in the field of smart sensors systems, providing complete coverage of all important systems aspects. It takes a multidisciplinary approach to the understanding, design and use of smart sensor systems, their building blocks and methods of signal processing.’

Order online: http://www.sensorsportal.com/HTML/BOOKSTORE/Smart_Sensor_Systems.htm

www.sensorsportal.com