

2nd International Symposium on Electrochemistry

Electrochemistry for Energy

19-20 July 2012



University of the Western Cape, Bellville, SOUTH AFRICA

Hosted by

ELECTROCHEMSA

(Electrochemistry Division, of the South African Chemical Institute)

Scientific committee:

Prof. Priscilla GL Baker, SensorLab, Chemistry department, UWC

Prof. Emmanuel Iwuoha, SensorLab, Chemistry department UWC

Prof. Bruno Pollet, HySA systems Competence Center, UWC

Dr Abd Baleb, SensorLab UWC

Dr Nicolette Hendricks, SensorLab, UWC

Dr Chinwe Ikpo, SensorLab, UWC

Dr Yasmina Martinovic, SensorLab, UWC

Dr Njagi Njomo, SensorLab, UWC

Dr Rasaq Olowu, SensorLab, UWC

Dr Tesfaye Wayro, SensorLab, UWC



UNIVERSITY of the
WESTERN CAPE



2nd International symposium on Electrochemistry

Electrochemistry division

of

South African Chemical Institute (SACI)

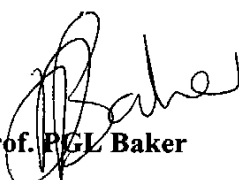
Dear Delegate

We welcome you to the 2nd International symposium on Electrochemistry at the University of the Western Cape, Bellville, SOUTH AFRICA from 19-20 July 2012. The symposium will focus on “Electrochemistry for Energy” and the main themes identified for this symposium include Electrochemical applications of nano-materials in energy related fields such as supercapacitors, batteries, fuel cells, Sensors and sensor technology as well as Industrial Electrochemistry.

The conference is open to participation by scientists, research students, industrialists, and policymakers involved in electrochemistry research and practice in order to identify and exploit the advantages of electrochemistry as a practical problem solving tool, for all concerned.

We wish you fruitful deliberations at this exciting international Electrochemistry symposium and a warm South African welcome in the “mother city - Cape Town.

Sincerely,



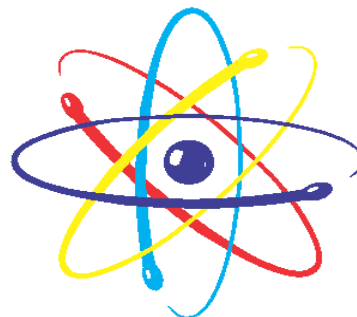
Prof. PGL Baker

Chairperson: ElectrochemSA (2006-)



UNIVERSITY *of the*
WESTERN CAPE

KIMIX
Chemical and Laboratory Suppliers



SensorLab

 **Metrohm**

WIPACAM
SCIENTIFIC & PRECISION EQUIPMENT (PTY) LTD.

The 2nd International Symposium on Electrochemistry
themed
 “Electrochemistry for Energy”



African Routes Conference
Centre
 University of the Western Cape
 Bellville, SOUTH AFRICA
 19-20 July 2012



Final Scientific Programme

Thursday, 19 July 2012

Friday, 20 July 2012

Time	Presentation	Time	Presentation
08h00-09h00	Registration	08h00-09h00	Registration
09h00-09h30	Plenary: Prof. B. Pollet	09h00-09h30	Keynote: Dr N Hendricks
09h30-09h50	Mr K. Makgopa	09h30-09h50	Ms K. Nohako
09h50-10h10	Ms E. Nxusani	09h50-10h10	Mr M Billibana
10h10-10h30	Ms P. Tshikalaha	10h10-10h30	Ms O Tovide
10h30-11h00	Keynote: Dr N Njomo	10h30-11h00	TEA/COFFEE
11h00-11h20	TEA/COFFEE	11h00-11h30	Keynote: Dr R. Olowu
11h20-11h50	Keynote: Dr C. Ikpo	11h30-11h50	Ms A. Jijana
11h50-12h10	Mr J. Lekitima	11h50-12h10	Ms H Makelane
12h10-12h30	Ms N. Mphahlele	12h10-12h30	Mr A Tsegaye
12h30-12h50	Group photo	12h30-12h50	Mr C. Sunday
12h50-14h00	LUNCH	12h50-13h00	Closing remarks
14h00-14h30	Keynote: Dr S. Gouws	13h00-14h00	LUNCH
14h30-14h50	Mr S. Mailu		
14h50-15h10	Mr M. Masikini		
15h10-15h30	Mr L. Ngqongqwa		
15h30-16h00	TEA/COFFEE		
16h00-18h00	POSTERS		
18h00-20h00	Networking dinner		

Scientific Programme

Thursday, 19th July 2012

08h00-08h50: **Registration**

08h50-09h00 Opening ceremony

Session Chair: Dr Tesfaye Waryo

09h00-09h30: **Plenary :** Electrochemistry for Energy – The Impending Reality: Opportunities for South Africa. *Sivakumar Pasupathi and Bruno G Pollet*

09h30-09h50 Supercapacitive properties of nickel oxide (NiO) integrated with nickel (II) tetra-aminophthalocyanine (NiTAPc). *Katlego Makgopa and Kenneth I. Ozoemena*

09h50-10h10 3-Mercaptopropionic acid capped Ga₂Se₃ nanocrystal-CYP3A4 biosensor for the determination of 17-alpha-ethinyl estradiol in water. *Ezo Nxusani, Emmanuel Iwuoha.*

10h10-10h30 Electrochemical study of dendrimer-gold nanocomposites platform using glass carbon electrode for immobilisation of anti-cholera toxin. *P. Tshikalaha, O.A. Arotiba and B.B. Mamba.*

10h30-11h00 **Keynote:** Graphitic carbon anchored sulphonated and transition metal oxide doped polyaniline nanocomposite materials for supercapacitor electrodes. *Njagi Njomo, Kenneth Ozoemena and Emmanuel Iwuoha.*

11h00-11h20 **TEA/COFFEE**

Session Chair: Dr Jasmina Martinovic

11h20-11h50 **Keynote:** Topotactic Intercalation and Electrochemical Performance of Nanostructured LiFePO₄ Composite Cathode Material for Lithium Ion Batteries. *Chinwe Ikpo, Kenneth Ozoemena, Priscilla Baker and Emmanuel Iwuoha*

11h50-12h10 Supercapacitive behavior of MWCNTs and Iron(II) tetrapyrizinoporphyrazine composites. *J.N. Lekitima and K.I. Ozoemena*

12h10-12h30 Photoelectrochemistry of Metallo-octacarboxyphthalocyanines for the Development of Dye Solar Cells. *Nonhlanhla Mphahlele, Kenneth I. Ozoemena, Lukas J. le Roux, Mkhulu K. Mathe and Leskey M. Cele*

12h30-12h50 A Novel Ultrasensitive Electrochemiluminescent Immunosensor Design Based On Enhanced Electrogenenerated Chemiluminescence From Ru(Bpy)₃²⁺ Ion Exchanged In Pani-GAu_xCu_y Ternary Hybrid Nanomaterial Film For The Determination Of Deoxynivalenol In Grains And Peanut Products. *Christopher Edozie, Priscilla Baker and Emmanuel Iwuoha*

12h50-14h00

LUNCH

Session Chair: Dr Rasaan Olowu

14h00-14h30 **Keynote:** Electrochemical flocculation studies of micro-algae. *Shawn Gouws, Koos Bosma, and Ben Zeelie*

14h30-14h50 Synthesis, Characterization and Application of Novel (100) Preferentially Oriented Platinum Nanoalloys for Direct Ammonia Fuel Cells. *Stephen N. Mailu, Priscilla G. Baker and Emmanuel I. Iwuoha.*

14h50-15h10 Impedimetric response of tert-octylphenol on multi-wall carbon nanotubes - poly (2,5-dimethoxyaniline) composite modified glassy carbon electrode. *Milua Masikini, Priscilla G. Baker and Emmanuel I. Iwuoha.*

15h10-15h30 Chrono-amperometric investigation of Platinum group metal alloys/graphene nano-sheet composite for application in electrochemical supercapacitors. *Lundi V. Ngqongwa, Tesfaye Waryo, Priscilla Baker and Emmanuel Iwuoha*

15h30-16h00

TEA/COFFEE

16h00-18h00

POSTERS and NETWORKING DINNER

Friday, 20th July 2012

Session Chair: Chinwe Ikpo

- 09h00-09h30 **Keynote:** Reagentless mediator-based cytochrome P450-3A4 biosensor – Toward decentralized drug detection devices. *Nicolette Hendricks, Fanelwa Ngece, Priscilla Baker, Nazeem Jahed and Emmanuel Iwuoha.*
- 09h30-09h50 Immunosensors developed on clathrate compound platforms. *Kanyisa L. Nohako and Priscilla Baker*
- 09h50-10h10 Development of DNA aptamer nanobiosensor on sulphonated polyaniline platform doped with silver nanoparticles. *Mawethu P. Bilibana and Emmanuel Iwuoha*
- 10h10-10h30 Graphenated–polyaniline nanocomposite for real time determination of polyaromatic Hydrocarbons. *Tovide Omotunde Oluwakemi, Nazeem Jahed and Emmanuel Iwuoha.*

10h30-11h00

TEA/COFFEE

Session Chair: Dr Njagi Njomo

- 11h00-11h30 **Keynote:** Poly(propylenethiophenoimine)-co-poly(3,4ethylenedioxythiopene)dendritic star copolymer aptameric nanobiosensor for estrogenous 17 β -estradiol. *Rasaq A. Olowu, Peter M. Ndangili, Ikpo Chinwe, Njagi Njomo, Stephen N. Mailu, Priscilla Baker and Emmanuel Iwuoha.*
- 11h30-11h50 Electrochemical nanosensor based on dendrimers for the determination and monitoring of Polyaromatic hydrocarbons in oil-polluted waste water. *Hlamulo Makelane, Rasaq Olowu, Tesfaye Waryo, Priscilla Baker and Emmanuel Iwuoha*
- 11h50-12h10 Voltammetric and Electrochemical Impedance Studies of 4,7-Dithien-2,1,3-Benzothiadiazole in Nonaqueous Electrolytes. *Abebaw Tsegaye, Tesfaye Waryo, Emmanuel Iwuoha*

12h10-12h30

Closing remarks

12h30-14h00

LUNCH

ORAL PRESENTATIONS

Electrochemistry for Energy – The Impending Reality: Opportunities for South Africa.

Sivakumar Pasupathi, Bruno G Pollet

HySA Systems Competence Centre, SAIAMC, University of the Western Cape, South Africa

Everything in the world runs on Energy. The way we produce energy over the generations mirrors the technological advancements of our modern civilization. The transition in energy generation from high carbon containing fuels to low carbon containing fuels will be outlined. The reasons for why the “Hydrogen economy” could be the future will be discussed and the role of electrochemistry for the future energy generation will be highlighted.

There are immense benefits and opportunities to South Africa from this impending hydrogen economy, credit to the rich mineral resources of the country. The South African National program on hydrogen and fuel cell technologies, HySA, aimed at maximizing the benefits of local resources, will be presented with special emphasis on the RDI activities within HySA Systems.

Supercapacitive properties of nickel oxide (NiO) integrated with nickel (II) tetra-aminophthalocyanine (NiTAPc).

Katlego Makgopa¹ and Kenneth I. Ozoemena^{1,2}

¹*Department of Chemistry, University of Pretoria, Pretoria 0002, South Africa.*

^{1,2}*Energy and Processes, Materials Science and Manufacturing, Council for Scientific & Industrial Research (CSIR), Pretoria 0001, South Africa. E-mail: kozoemena@csir.co.za*

Supercapacitor also known as electrochemical capacitor or ultracapacitor is an electrochemical energy storage and conversion system, that have high cycling stability, energy and power density. Supercapacitors are well recognised for their application in a variety of everyday applications such as laptop computers, cell phone, hybrid electric vehicles, etc. These devices store energy using either ion adsorption (electrochemical double layer capacitors) or fast surface redox reactions (pseudocapacitors) [1]. Various materials such as transition metal oxides, metal hydroxides and polymeric materials have been explored for pseudocapacitor application [2]. Among them, NiO is an attractive pseudocapacitive material because of its high specific capacitance, well-defined electrochemical redox activity and good capability retention [1,2]. However, little knowledge exist on metallophthalocyanine complex incorporated on metal oxide for electrochemical energy storage [3,4]. In this study, we report the synthesis of NiO integrated with nickel tetraaminophthalocyanine, NiTAPc-NiO using successive ionic layer adsorption reaction (SILAR) and electrodeposition techniques. The binary nanocomposites have been characterised with FESEM and EDX. This presentation will describe the supercapacitive behaviour of NiTAPc-NiO film on nickel foam substrate.

References

- [1] Y.F. Yuan, X.H. Xia, J.B. Wu, J.L. Yang, Y.B. Chen, S.Y. Guo, *Electrochimica Acta* 56 (2011) 2627.
- [2] A. S. Adekunle, K. I. Ozoemena, *Electroanalysis*, 23 (2011) 971
- [3] A.T. Chidembo, K.I. Ozoemena, B. O. Agboola, V. Gupta, G.G. Wildgoose and R.G. Compton, *Energy Environ. Sci.* 3 (2010) 228.
- [4] B.O. Agboola, K.I. Ozoemena, *J. Power sources* 195 (2010) 3841.

3-Mercaptopropionic acid capped Ga₂Se₃ nanocrystal-CYP3A4 biosensor for the determination of 17-alpha-ethinyl estradiol in water

Ezo Nxusani and Emmanuel Iwuoha

SensorLab, Department of Chemistry, University of the Western Cape, Bellville, 7535, South Africa.

Water soluble and biocompatible 3-mercaptopropionic acid capped gallium selenide nanocrystals, were synthesized from hydrated gallium (III) perchlorate and selenide ions. The 3-Mercaptopropionic acid capped gallium selenide nanocrystals, was non-fluorescent but showed a sharp UV-vis absorption maximum at 250 nm. The synthesized nanoparticle was used to develop an electrochemical biosensor for the detection of 17-alpha-ethinyl estradiol, an estrogenic endocrine disrupting compound (e-EDC). The biosensor was fabricated by potentiostatic deposition of novel gallium selenide nanocrystals on a L-cystine modified gold electrode, followed by covalent coupling of genetically engineered cytochrome P450-3A4 (CYP3A4), a Heme containing enzyme. The biosensor gave an electrochemical response at about -220 mV. The results revealed that 3- Mercaptopropionic acid capped Gallium Selenide nanocrystals can be used in conjunction with CYP3A4 as an electrode modifier for the detection of 17-alpha ethinyl estradiol. The 3- Mecarptopropionic acid capped Gallium Selenide nanoparticles exhibited a semiconductor like behaviour.

Electrochemical study of dendrimer-gold nanocomposites platform using glass carbon electrode for immobilisation of anti-cholera toxin

P. Tshikalaha, O.A. Arotiba*, B.B. Mamba

Department of Applied Chemistry, University of Johannesburg, Doornfontein 2028, Johannesburg, South Africa, 0115596200, 0866129734

emails: tshikalaha.portia@gmail.com and oarotiba@uj.ac.za

Cholera, a disease caused by cholera toxin, continues to be a major public health concern in developing countries and accounts for considerably high cases of illnesses. Most recently, cholera outbreaks have been reported in many countries including Haiti, Zimbabwe, Mozambique, Liberia, Iraq, the Democratic Republic of the Congo, India and South Africa. These sudden outbreaks could have been mitigated if there were faster, cheaper, and on-site cholera detection devices that do not need much expertise to operate. Such a device will be useful for prompt cholera alert in rural areas where challenges in water sanitation and laboratory facilities are common. In the quest for such devices, we present the development of an electrochemical immunosensor based on a generation 2 poly (propylene imine) dendrimer-gold nanocomposite platform. The nanocomposite was prepared on a glassy carbon electrode by electro-co-deposition using cyclic voltammetry in a potential range of -300 mV to +1000 mV. The modified electrodes were electrochemically characterised in phosphate buffer saline and ferrocyanide electrolytes. Anti-cholera toxin antibody was then immobilised on this nano-platform by drop coating for 2 hr at a temperature of 38 °C to form the immunosensor. For the detection of cholera toxin, the immunosensor was incubated for one hour at different concentrations of cholera toxin. The antibody-toxin bio-recognition event was monitored by square wave voltammetry and electrochemical impedance spectroscopy (EIS). The square wave currents were inversely proportional to the concentrations of the toxin while the charge transfer resistance (EIS) increased linearly with toxin concentrations to a detection limit in the nanomolar region. The developed immunosensor was able to detect cholera in spiked and real water samples.

Graphitic carbon anchored sulphonated and transition metal oxide doped polyaniline nanocomposite materials for supercapacitor electrodes.

Njagi Njomo¹, Rasuq Adewale¹, Peter Ndangili¹, Priscilla Baker¹, Kenneth Ozoemena², Emmanuel Iwuoha¹.

1. SensorLab, Department of Chemistry, University of the Western Cape, Private Bag X17, Bellville, 7535, South Africa.

2. Energy and Processes Division, Materials Science and Manufacturing, Council for Scientific and Industrial Research (CSIR), Pretoria 0001, South Africa.

e-mail: njaginjomo@yahoo.co.uk

To meet a fast-growing market demand for renewable energy storage systems, electro-mechanical, robotic, automobile green energy demands and next generation portable electronic devices with higher performance and increased device functionalities, efficient electrical energy devices with substantially higher energy, power densities and faster recharge times are needed. Supercapacitors occupies a pivotal role in this context. In this work, nanostructured sulphonated polyaniline and transition metal single, binary and ternary mixed oxides (Tantalum(IV)oxide, tantalum(IV)oxide-nickel(II)oxide, tantalum(II)oxide-manganese(III)oxide, tantalum(II)oxide-nickel(II)oxide-manganese(II,III)oxide) doped nanocomposites with electro-conductive properties were synthesised using modified sol-gel methods. These were then dispersed, individually, in acidic media and incorporated *in-situ* into the polymeric matrix during the oxidative chemical polymerization of poly(4-styrene sulphonic acid) doped aniline. On being integrated with activated graphite, they were used in the design of supercapacitors.

Topotactic Intercalation and Electrochemical Performance of Nanostructured LiFePO₄ Composite Cathode Material for Lithium Ion Batteries

Chinwe Ikpo*, Kenneth Ozoemena, Priscilla Baker and Emmanuel Iwuoha*

*SensorLab, Department of Chemistry, University of Western Cape, Bellville, Cape Town, South Africa.
e-mail: cikpo@uwc.ac.za & eiwuoha@uwc.ac.za

The global quest for clean energy and a green planet has made the development of sustainable and efficient energy storage devices inevitable. The lithium-ion batteries are top among current technologies designed to store electricity from renewable sources, power electric vehicles, hybrid electric vehicles and plug-in hybrid electric vehicles, as well as myriads of portable electronic devices including mobile phones, digital cameras and high performance computing systems. However, the development, performance and cost of lithium-ion batteries are mainly limited by the properties of the cathode materials. The electrochemical performance of the cathode is measured in terms of charge-discharge capacity, cyclability, rate capability, and coulombic efficiency. These parameters are closely related to the reversibility and efficiency of lithium ion intercalation/de-intercalation in the active material. In this study, composite lithium ion cathode systems based on lithium iron phosphate (LiFePO₄), iron-cobalt-derivatised carbon nanotubes (FeCo-CNT) and polyaniline (PA) nanomaterials were developed. The FeCo-functionalised CNTs were obtained through *in-situ* reductive precipitation of iron (II) sulfate heptahydrate (FeSO₄·7H₂O) and cobalt (II) chloride hexahydrate (CoCl₂·6H₂O) within a CNT suspension via sodium borohydride (NaBH₄) reduction protocol. Impedimetric, voltammetric and charge/discharge properties of the composite (LiFePO₄/FeCoCNT-PA) and pristine (LiFePO₄) cathodes were investigated using crimp-sealed lithium ion rechargeable (LIR) 2032 coin cells. The galvanostatic charge-discharge results showed that 99.72% of the capacity of the composite cathode was retained after 20 cycles and with a coulombic efficiency of 90% while the pristine cathode gave capacity retention of 89.61% and coulombic efficiency of 80.36%.

Supercapacitive behavior of MWCNTs and Iron(II) tetrapyrzainoporphyrazine composites

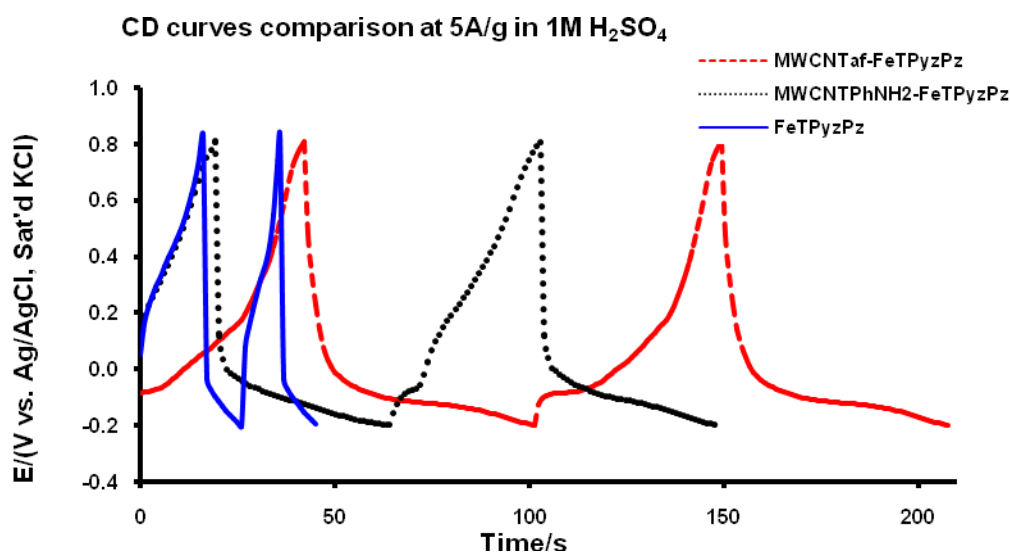
J.N. Lekitima¹, K.I. Ozoemena²

¹University of Pretoria, Department of Chemistry, Pretoria, South Africa, 012 420 3542, 012 420 4687

²Energy and Processes, Materials Science and Manufacturing, Council for Scientific and Industrial Research, Pretoria, South Africa, 012 841 3664

Joel.lekitima@up.ac.za

Due to the global energy challenges, supercapacitive materials have recently received a lot attention in research. An excellent energy storage material is been sought for our modern technological advancements to provide high power and high energy. In our study we interrogated functionalized multi-walled carbon nanotubes (MWCNTs) and Iron (II) tetrapyrzaino porphyrzine (FeTPyzPz) as suitable capacitive materials. Supercapacitive properties of acid functionalized and phenylamine functionalized MWCNTs and their FeTPyzPz composites have been studied in acid and neutral electrolyte using cyclic voltammetry, galvanostatic charge-discharge and electrochemical impedance spectroscopy. MWCNT_{af}/FeTPyzPz gave a superior specific capacitance of 410 F.g⁻¹ at current density of 3A.g⁻¹ as compared other electrodes. The composite has been found to have perform much better to MWCNT_{af} (50 F.g⁻¹) and FeTPyzPz (132 F.g⁻¹) at the same current density. Other techniques like FTIR, SEM and TEM have been used for analysis.



Photoelectrochemistry of Metallo-octacarboxyphthalocyanines for the Development of Dye Solar Cells.

Nonhlanhla Mphahlele¹, Kenneth I. Ozoemena^{1,*}, Lukas J. le Roux¹, Mkhulu K. Mathe¹, Leskey M. Cele²

¹ *Energy Materials, CSIR Materials Science and Manufacturing, Pretoria, South Africa*

² *Department of Chemistry, Tshwane University of Technology, Pretoria, South Africa*

E-mail: kozoemena@csir.co.za

Significant attention is being paid to dye solar cells (DSCs) as the next generation in solar cell technology for their low cost alternative to the currently implemented solid state solar cells. Metallophthalocyanine (MPc) complexes, especially those with diamagnetic metal centres (M = Zn, Si) are efficient photosensitisers. However, the use of MPc complexes in dye solar cells (DSCs) is rare, despite their ability to absorb light at long wavelengths, and physico-chemical stability [1]. Significant efforts have been made to enhance the photosensitization properties by modifying MPcs with carbon nanotubes (CNTS) [2]. Motivated by these stated factors, we study the MPc-CNT hybrids for possible application in DSCs. This presentation will describe the electron transport properties of MPc-CNT hybrids in the dark and under illumination using voltammetry and electrochemical impedance spectroscopy.

References

- [1] K. Ozoemena, N. Kuznetsova, T. Nyokong, *J. Photochem. Photobiol. A: Chem.* 139 (2001) 217–224
- [2] J. Pillay, K.I. Ozoemena, *Electrochim. Acta* 52 (2007) 3630–3640

ELECTROCHEMICAL FLOCCULATION STUDIES OF MICRO-ALGAE

Shawn Gouws; Coos Bosma and Ben Zeelie

InnoVenton, Gomery Avenue, Summerstrand, Nelson Mandela Metropolitan University, 6031,

Corresponding: shawn.gouws@nmmu.ac.za

Cost effective harvesting of micro-algae is a major bottleneck in the commercial exploitation micro-algae technologies.¹ Due to their small size (10 – 50 μm) and their tendency to rapidly screen filter media, centrifugation remains the harvesting technique of choice. The addition of chemical flocculants to algae slurries can lead to contamination of the flocs with the flocculating agent, which can complicate downstream processing such as combustion, pyrolysis and liquefaction. Electrochemical flocculation is an alternative flocculation option that, according to literature reports, does not involve the addition of any additional chemicals. Furthermore, electrochemical flocculation is claimed to be a low energy process, a key requirement for an economical micro-algae harvesting process. In this presentation, we present and discuss the results of work we have done on the electrochemical flocculation of micro-algae at InnoVenton: NMMU Institute of Chemical Technology. This includes the results of cyclic voltammetry studies on the micro-algae biomass, the effect of electrolysis on pH of the growth medium and how electrolysis may be used to aid auto-flocculation of micro-algae, and the stability of electrode materials. We will also present an estimate of the energy requirements for electrochemical flocculation in comparison to centrifugation when flocculation is carried out with a stable electrode system.

Reference

E Poelman, N. De Pauw, and B Jeurissen, Resources, Conservation and Recycling, (1997), 19, p1-10

Synthesis, Characterization and Application of Novel (100) Preferentially Oriented Platinum Nanoalloys for Direct Ammonia Fuel Cells

Stephen N. Mailu, Priscilla G. Baker and Emmanuel I. Iwuoha*

SensorLab, Department of Chemistry, University of the Western Cape, Bellville, 7535, South Africa.

Corresponding author email: eiwuoha@uwc.ac.za.

Ammonia has attracted attention as a possible fuel for direct fuel cells since it is easy to handle under low pressure, costs only slightly higher than methanol and can easily be cracked into hydrogen and nitrogen. However, on noble metal electrodes ammonia oxidation is a sluggish reaction at low temperature and efficient catalysts are required to convert ammonia to nitrogen and hydrogen at reasonable reaction rates. Platinum based catalysts have been found to be the most suitable ones since they are less poisoned by the ammonia oxidation by-products. Ammonia oxidation on platinum surfaces is a very structure sensitive reaction and takes place almost exclusively on Pt(100). In this work, the synthesis of novel polyacrylate acid capped Pt(100), Pt(100)Pd, Pt(100)Au and Pt(100)Pd-Au nanoparticles is reported. The shapes and the structures of the nanoparticles were studied using high resolution transmission electron microscopy (HRTEM) and cyclic voltammetry (CV). HRTEM analysis showed 5-10 nm spherical and cubic nanoparticles, whereas CV of the nanoparticles in the hydrogen adsorption/desorption region was used to obtain qualitative information about the surface structure of the nanoparticles with the Pt(100) nanoparticles showing a voltammetric profile very similar to that of Pt(100) single crystal electrode. The results reported in this work demonstrate the importance of controlling the intrinsic structural properties of Pt nanoparticles; in terms of nature of the active sites and the effect of adding adatoms in order to understand their catalytic properties. The electrochemical activity of these nanoparticles for ammonia oxidation in basic medium showed that the anodic current density is very sensitive to the existence of (100) domains. Pt(100) nanoparticles showed the highest catalytic properties as shown in the trend: Pt(100) > Pt(100)Pd > Pt(100)Au and > Pt(100)Pd-Au nanoalloys.

Chrono-amperometric investigation of Platinum group metal alloys/graphene nano-sheet composite for application in electrochemical supercapacitors

Lundi V. Ngqongwa, Tesfaye Waryo, Priscilla Baker, Emmanuel Iwuoha

SensorLab, Department of Chemistry, University of the Western Cape

*Modderdam Road, Bellville 7535, Cape Town, South Africa Tel: +27-219593079; email:
2413716@uwc.ac.za*

Electrochemical capacitors (ECs) provide a mode of electrical charge and energy storage, complementary to that by batteries. Electrochemical capacitors are a special kind of capacitors based on charging and discharging the interfaces of high specific-area material such as porous carbon material or porous oxides of some metals. They can store electric charge and corresponding energy at high densities in a highly reversible way, as does a regular capacitor, and hence can be operated at specific power densities (watts/kg) substantially higher than can most batteries. They (ECs) have promising applications as backup or auxiliary power sources in electric vehicles and other electronic devices for the purpose of power enhancement. In this study, we combine the exceptional properties of graphene nanosheets with that of some of the Platinum Group Metals (Pt, Pd and Rh) to provide uncompromised electrochemical properties of the composite for application in electrochemical supercapacitors. Platinum group metals (PGM) are of our main interest due to their attractive electronic and physical properties alongside carbon based materials such as graphene nanosheets (GN). GN sheets have been considered as one of the most promising flexible electrode materials because of their low cost, high specific surface area, ultra-low resistivity for electron transport and extraordinary pliable properties. The composite of graphene/PGM was constructed by electrodeposition of the nano-alloys of PGM onto a graphene modified glassy carbon electrode in order to examine the electrochemical properties of the composite. Galvanostatic charge-discharge cycles of the composite demonstrated an improved capacitance of the modification. An increasing trend of specific capacitance of the constructed composite was established with significant improvement from graphene/nanoparticles < graphene/binary nano-alloys < graphene/ternary nano-alloys of the platinum groups elements.

Impedimetric response of tert-octylphenol on multi-wall carbon nanotubes - poly (2,5-dimethoxyaniline) composite modified glassy carbon electrode

Milua Masikini, Priscilla G. Baker and Emmanuel I. Iwuoha*

SensorLab, Department of Chemistry, University of the Western Cape, Bellville, 7535, South Africa.

Corresponding author: Tel.: + 27- 21-959- 3054; Email: eiwuoha@uwc.ac.za

The electrochemical oxidation of 4-tert-octylphenol was carried out using MWCNT-PDMA modified glassy carbon electrode in neutral medium. The composite was characterized by electrochemical impedance (EIS), cyclic voltammetry (CV), ultra-violet visible (UV-Vis), fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and high resolution transmission electron microscopy (HRTEM). The impedimetric response of the composite on the oxidation peak of 4-tert-octylphenol an endocrine disruptor, gave good linearity range, sensitivity and less fouling compare to cyclic voltammetry.

Reagentless mediator-based cytochrome P450-3A4 biosensor – Toward decentralized drug detection devices

Nicolette Hendricks*, Fanelwa Ngece, Priscilla Baker, Nazeem Jahed, Emmanuel Iwuoha

*SensorLab, Department of Chemistry, University of the Western Cape
Private Bag X17 Bellville, Cape Town 7535, South Africa
e-mail: nrhendricks@uwc.wc.za and eiwuoha@uwc.ac.za*

In an era in which reducing mortality, particularly with regard to chronic disease is highly envisaged, a myriad of newly structured drug-based treatment modalities finds itself on the market. Appropriately, the human body is equipped with a highly structured group of drug metabolizing enzymes, which enable the pivotal first-pass metabolism of such drugs to their pharmacokinetically active form. However, successful treatment is highly dependant on therapeutic drug monitoring (TDM), defined as a strategy by which patient dosing regiment is guided by repeated measurements of plasma drug concentrations. If the concentration is not within the predefined target range, it necessitates dosage adjustment to bring this level within the required target range. Described here is a reagentless, mediator-based amperometric biosensor with potential application for decentralized therapeutic drug monitoring of selected antiretroviral drugs. In this regard, major human hepatic drug metabolizing enzyme, cytochrome P450-3A4 was interfaced with the transducer without the inclusion of physiological reducing equivalents, with subsequent electrochemical driving of the catalytic cycle of the immobilized enzyme. With regard to the experimentally-based preparative protocol: Firstly, CYP450-3A4, synthesized as a catalytically active histidine-tagged, N-terminally modified enzyme construct (nCYP3A4), was prepared through genetic engineering. Secondly, the carrier matrix, was assembled through a facile electrochemical method by applying a constant potential of +450 mV for 1200 seconds in an aqueous solution with cobalt (III) sepulchrates trichloride (1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosaine cobalt trichloride) as starting material and a nafion-modified glassy carbon (GCE) as working electrode, yielding an electroactive nafion/Cobalt(III) sepulchrates film (GCE||Naf|E|Co(Sep)³⁺). Lastly, enzyme immobilization was achieved through entrapment within a biocompatible ionic hydrogel-composite membrane consisting of agarose (AG), polyvinyl alcohol (PV) and polyethylene amine (PE). Optimization with respect to all aspects of biosensor design including type of inner-ionomer film; Co(Sep)³⁺ loading time; enzyme loading; outer-film component types/ loading amount were all thoroughly investigated. The electrochemistry of the prepared biosensor, denoted GCE||Naf|E|Co(Sep)³⁺|nCYP3A4| AG-PE-PV, as well as its response dynamics with respect to selected probe drugs were studied. Control electrocatalysis experiments with enzyme-free electrodes were also conducted to confirm enzyme activity.

Development of immunosensors on clathrate compound platforms

Kanyisa L. Nohako and Priscilla Baker

SensorLab, Chemistry Department, University of the Western Cape, Bellville, South Africa

The development and application of biochemical sensors and immunosensors is of great interest. The key step is to develop an immunosensor that is simple, fast and lead to robust materials with stable and highly active immobilized reagent which do not leach from the substrate. Organic macrocyclic compounds will be used for this purpose. Flourene derivatives show unique chemical and physical properties because they contain a rigid planar biphenyl unit, and the facile substitution at C₉ position of the flourene can improve the solubility and processability of materials containing flourene without significantly increasing of steric interactions in the compounds backbone. Porphyrins are heterocyclic macrocycles composed of four modified pyrrole subunits interconnected at their α carbon atom via methine bridges. These compounds will be used for the inclusion of antibodies through incubation, drop coating and electrochemical attachment. The biological activity of the encapsulated antibodies will be evaluated. Spectroscopic, microscopic and electrochemical techniques (such as CV, FTIR, UV-Vis, EIS) will be used to characterize these compounds.

Development of DNA aptamer nanobiosensor on sulphonated polyaniline platform doped with silver nanoparticles

Mawethu P. Bilibana and Emmanuel Iwuoha

*SensorLab, Department of Chemistry, University of the Western Cape
Private Bag X17 Bellville, Cape Town 7535, South Africa*

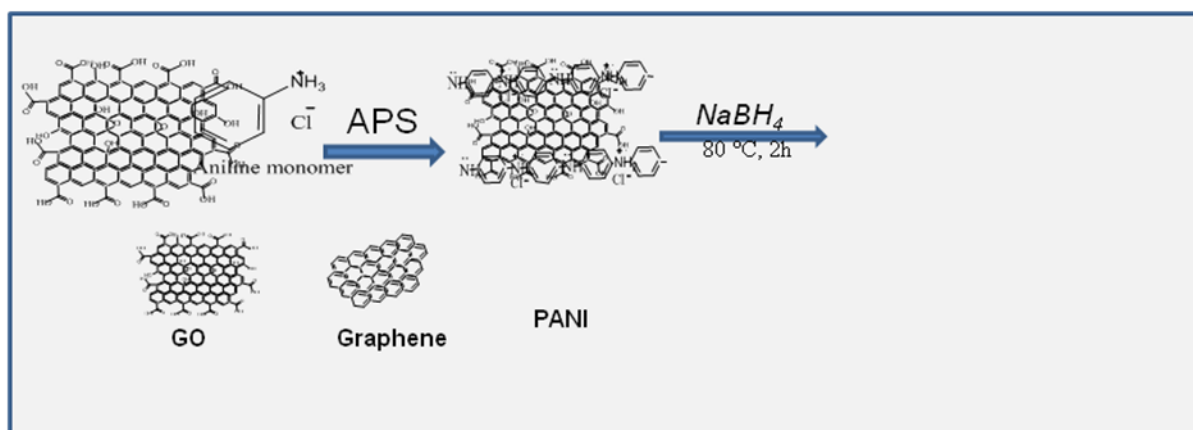
We developed a Cyanobacteria toxins-specific aptamer nanobiosensor on metallised polymeric electrode transducers. Cyanobacteria toxins are classified according to their mode of action into hepatotoxins (e.g. microcystins), neurotoxins (e.g. anatoxins) and skin irritation. Based on the fact that there is a lack of fast reporting diagnostic tools for algal toxins produced by fresh water blue-green algae which kills fish, shellfish, humans, livestock and wildlife. The nanoscale electrochemical biosensors that we prepared use aptamers as molecular recognition elements based on the advantages of aptamers over antibodies. Antibodies are more thermally sensitive, and denaturation of antibodies is usually irreversible. The use of aptamers offers a wide range of assay conditions. The binding of aptamers with their targets usually relies on specific conformations, such as G-quaduplex and hairpin. Conformational variations before and after the formation of aptamer-ligand complexes offer a great possibility and feasibility for the construction of aptamer-based biosensors. Owing to their oligonucleotide nature, they could interact with range of molecules include microcystin, thus fabricate versatile oligonucleotides machines for either biosensing or other clinical applications. In study will detail the properties and the selection methods of aptamers, progress in engineering biosensors, and the prospect of water toxin dictation. Hence, we develop an aptameric nanobiosensor system on the self-reporting thiol terminated 6-carbon spacers 18-bases guanine aptamer. The sensor conductive platform is based on sulphonated Poly (2, 5-dimethoxyaniline) (PDMA) with metal silver nanoparticles.

Graphenated–polyaniline nanocomposite for real time determination of polyaromatic Hydrocarbons.

Tovide Omotunde Oluwakemi, Nazeem Jahed and Emmanuel Iwuoha.

SensorLab, Department of Chemistry, University of the Western Cape, Private Bag X17 Bellville, Cape Town 7535, South Africa

A graphenated – polyaniline nanocomposite electrode was prepared and used to construct a sensor for the determination of Anthracene. The direct electro oxidation behaviour of anthracene on the graphene – polyaniline modified glassy carbon electrode was carefully investigated by cyclic voltammetry. The results indicated that, Anthracene showed an increase of the oxidation peak current with shift of the oxidation peak potential in contrast to that on the bare glassy carbon electrode. The nanocomposite formed has exhibited a remarkable electroactive activity towards oxidation of anthracene. A detection limit of 4.39×10^{-7} M was established. The sensor exhibited some advantages , such as sensitivity, good reproducibility and long-term stability.



Poly(propylenethiophenimine)-co-poly(3,4ethylenedioxythiophene)dendritic star copolymer aptameric nanobiosensor for estrogenous 17 β -estradiol

Rasaq A. Olowu*, Peter M. Ndangili, Ikpo Chinwe, Njomo Njagi, Stephen N. Mailu, Priscilla Baker, Emmanuel Iwuoha*.

SensorLab, Department of Chemistry, University of the Western Cape, Bellville, 7535,

South Africa; Emails:rolowu@uwc.ac.za

A novel electrochemical biosensor based on 17- β -estradiol (E2)-binding- SELEX-synthesized 76-mer biotinylated aptamer as a molecular recognition element developed on a Poly(propylene thiophenimine)-co-poly(3,4ethylenedioxythiophene) {Au|G2PPT-co-PEDOT|} dendritic star copolymer modified gold electrode platform via biotin-avidin interaction was constructed for the determination of endocrine disrupting 17- β -estradiol. The nanoelectrode Au|G2PPT-co-PEDOT and the aptasensor (Au|G2PPT-co-PEDOT|ssDNA) were investigated with Fourier transform infra red spectroscopy (FTIR), and fluorescence spectroscopy. The morphology and electrochemical characterization were carried out with scanning electron microscopy (SEM), electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and square wave voltammetry (SWV) respectively. In the measurement of 17- β -estradiol, the interfacial electron transfer of the aptasensor using [Fe(CN) $_6$] $^{3-/4}$ redox probe was monitored with cyclic voltammetry(CV) and square wave voltammetry (SWV). The CV and SWV values were measured to evaluate the chemical binding to the aptamer. The biosensor response to 17 β -estradiol was based on the decrease in the SWV current as the target binds to the ssDNA aptamer on the biosensor due to the formation of aptamer-complex layer which hindered the free flow of electron from the redox probe to the surface of the electrode as a result of its insulating behavior. The kinetic parameters of the nanoelectrode such as exchange current, heterogeneous rate constant and time constant gave values of 3.01×10^{-4} A, 3.10×10^{-2} cm s $^{-1}$ and 2.97×10^{-5} s rad $^{-1}$ compared to the value of 5.18×10^{-5} A, 5.35×10^{-3} cm s $^{-1}$ and 3.21×10^{-4} s rad $^{-1}$ obtained for bare gold electrode respectively. The result showed that electron transfer on the nanoelectrode platform was faster than the bare electrode illustrating the catalytic behavior of Au|G2PPT-co-PEDOT. Bode plot showed improved conductivity of the Au|G2PPT-co-PEDOT modified electrode over bare gold electrode with marked reduction in the impedance and phase angle shift from 49 $^\circ$ to 11.6 $^\circ$. A dynamic linear range of 0.01 nM to 0.09 nM was observed for the aptasensor ($r^2=0.999$), with a sensitivity of 328 μ A/nM and detection limit of 4.10 pM. This work demonstrated that the aptasensor exhibited favorable selectivity, stability, reproducibility for 17- β -estradiol and that Au|G2PPT-co-PEDOT provides a promising platform for immobilization of DNAaptamer.

Electrochemical nanosensor based on dendrimers for the determination and monitoring of Polyaromatic hydrocarbons in oil-polluted waste water.

Hlamulo Makelane; Rasaan Olowu, Tesfaye Waryo; Priscilla Baker; Emmanuel Iwuoha.

Sensorlab, Department of Chemistry, University of the Western Cape, Modderdam Road, Bellville 7535, Cape Town South Africa, Tel: +27 21 959 3079;

Corresponding author email: Hlamuu@webmail.co.za

Novel dendrimeric polypropyleneimine (PPI) and polythiophene (PTH) smart nanocatalysts were used as platforms to construct highly sensitive electrochemical nanosensors for detecting and monitoring of the distribution of polyaromatic hydrocarbons (PAHs) (which are priority persistent organic pollutants) released as liquid and gaseous effluents during the processing of fossil fuel (coal, oil and tar), among other sources. In this research project, nanosensor of novel copolymer based on poly(propylene imine) generation 3 dendrimer and 2-thiophene carboxaldehyde were prepared chemically to achieve G3PPT according to methods modified from literature. Electrochemically, generation 3 poly(propylene imine)-polythiophene (G3PPT-co-P3HT) star copolymer with Au electrode was obtained. The star copolymers electro-polymerization mechanism, structure, and properties are intensively investigated in view of their multiple potential technological uses due to their conductivity. The constructed nanosensors platform were studied and characterized by cyclic voltammetry (CV), scanning electron microscopy (SEM), ¹HNMR, Fourier Transform infra-red spectroscopy (FTIR), Square wave voltammetry (SWV) and alternating current voltammetry (ACV).

Keywords: Novel dendrimer, Polyaromatic hydrocarbons, polypropylene imine, polythiophene.

star copolymer, Ac voltammetry

References

1. Olowu, R.A.; Ndagili, M.P.; Baleg, A.A.; Ikpo, C.O.; Njomo. N.; Baker, P.; Iwuoha, E. *Int. J. Electrochem.Sci.*, **2011**, *6*, 1686-1708.
2. Krasteva, N.; Guse, B.; Besnard, I.; Yasuda, A.; Vossmeier, T. *Sensors and Actuators b*, 2003, *92*, 137-143.

Voltammetric and Electrochemical Impedance Studies of 4,7-Dithien-2,1,3- Benzothiadiazole in Nonaqueous Electrolytes.

Abebaw Tsegaye; Tesfaye Waryo; Emmanuel Iwuoha

SensorLab, University of the Western Cape, Modderdam Road, Belleville 7535, Cape Town, South Africa email: 3080361@uwc.ac.za

Donor – acceptor polymer, poly(4,7-dithien-2,1,3-benzothiadiazol) which have been electrochemically polymerized from the monomer 4,7-dithien-2,1,3-benzothiadiazol is a promising material for electrochromic, solar cell, charge storage and biosensors applications. The present study serves for the diagnostic test of poly(4,7-dithien-2,1,3-benzothiadiazol) properties such as band gap, film thickness and charge transport in the polymer film. The electrochemistry of 4,7-dithien-2-yl-2,1,3-benzothiadiazole ($(C_4H_3S)_2C_6H_2N_2S$) was investigated using cyclic Voltammetry (CV) and electrochemical impedance spectroscopy (EIS) in 0.1 M tetrabutylammonium perchlorate in acetonitrile (ACN), dichloromethane (DCM) and their mixtures DCM-ACN (2:3 (v/v)) at platinum (Pt) and gold (Au) electrode. Anodic (E_{pa}) and cathodic (E_{pc}) peak potentials as well as the corresponding anodic (i_{pa}) and cathodic (i_{pc}) peak currents acquired at different scan rates between 0.03 to 0.5 V/s. Anodic and cathodic peak potentials as well their differences (ΔE_p) were independent of scan rate, shows the reversibility of $(C_4H_4S)_2C_6H_2N_2S/(C_4H_4S)_2(C_6H_2N_2S)^-$ system. One electron was involved in this redox reaction. The formal potential obtained in the different solvents were in ACN (-1.56 V) vs ferrocene/ferrocinium (Fc/Fc^+), DCM-ACN (-1.52 V) and DCM (-1.62 V) at Pt electrode and ACN (-1.50 V), DCM-ACN (-1.52 V) and DCM (-1.57 V) at Au electrode. The diffusion coefficient (D) has been calculated using Randles – Sevcik equation were in ACN ($1.11 \times 10^{-5} \text{ cm}^2/\text{s}$), DCM-ACN ($5.06 \times 10^{-6} \text{ cm}^2/\text{s}$) and DCM ($7.45 \times 10^{-6} \text{ cm}^2/\text{s}$) at Pt electrode and ACN ($1.22 \times 10^{-5} \text{ cm}^2/\text{s}$), DCM-ACN ($6.04 \times 10^{-6} \text{ cm}^2/\text{s}$) and $6.10 \times 10^{-6} \text{ cm}^2/\text{s}$) at Au electrode. The diffusion coefficient of $(C_4H_4S)_2C_6H_2N_2S$ was larger by the order of nearly 10 times in the less viscous medium ACN than DCM. EIS measurement was performed in the frequency range 100 mHz to 100 kHz at amplitude voltage of 5 mV. Standard heterogamous rate constant (k^0) calculated from impedance data were in ACN (0.069 cm/s), DCM-ACN (0.083 cm/s), (0.061 cm/s) at Pt electrode and ACN (0.434 cm/s), DCM-ACN (0.240 cm/s) and DCM (0.072 cm/s) at Au electrode. The kinetics of charge transfer was faster at gold electrode in ACN.

A Novel Ultrasensitive Electrochemiluminescent Immunosensor Design Based On Enhanced Electrogenerated Chemiluminescence From Ru(Bpy)₃²⁺ Ion Exchanged In Pani-GAu_xCu_y Ternary Hybrid Nanomaterial Film For The Determination Of Deoxynivalenol In Grains And Peanut Products.

Christopher Edozie, Priscilla Baker and Emmanuel Iwuoha

*SensorLab, Chemistry Department, University of the Western Cape, Bellville, South Africa,
3105918@uwc.ac.za*

Deoxynivalenol (DON) is a type of mycotoxin, a naturally occurring chemical by-product of ubiquitous fungi species (particularly *Fusarium graminearum* and *Fusarium culmorum*) which originate in the soil of crop fields. Its acute effect in animal and human includes reduced feed uptake, nausea, vomiting, diarrhoea, abdominal pain, headache, dizziness, fever, skin irritation and immune-suppression. DON has been isolated from grains and even peanut products meaning that it is not destroyed by milling processes. This research is aimed at producing a fast, easy-to-use electrochemiluminescence immunosensor with simplified set up, re-usability, ultra-sensitivity and will not require expertise, for monitoring these products before and after harvest (i.e. during storage) so as to control contamination outbreaks. A thin film platform of novel ternary hybrid nanomaterial comprising of gold-copper bimetallic nanoparticles, graphene and polyaniline (Pani-GAu_xCu_y) has been produced chemically for the design of this sensor. First, well dispersed gold-copper bimetallic nanoparticles was synthesised on graphene sheets by an improved one pot chemical reduction method of copper chloride (CuCl₂), chloroauric acid (HAuCl₄) and graphene oxide. The photochemical and physical characterizations of this material are very promising but it is not stable when immobilized on glassy carbon electrode for electrochemical studies. Polyaniline therefore was chemically intercalated into the graphene-Au_xCu_y layers to construct this novel inorganic-polymer nano-assembly with unusual structure and interesting perspectives. This is evident from the HRTEM, SEM, EDX and FTIR characterizations. Voltammetric interrogations of this material showed that the platform (GCE/ Pani-GAu_xCu_y) exhibited irreversible electrochemistry in pH 7.2 phosphate buffer saline solution (PBS). Photochemical studies by Uv-vis spectroscopy and Fluorescence spectroscopy showed increased absorbance. Its conductivity in PBS and the increased absorbance confirmed that GCE/Pani-GAu_xCu_y can serve as a suitable electron transfer mediator platform for electrochemiluminescent and as well voltammetric biosensors. Subsequently, by immune-reaction involving DON antibody and antigen, a novel ultra-electrochemiluminescent solid-state immunosensor for the determination of DON in grains and peanut products will be designed with greatly enhanced electro-generated luminescence by applying tripropylamine (TPA) as a co-reactant in PBS of pH 7.2 and coupling the light emission from Ruthenium (II) tris (bipyridine) with: (a) surface plasmon resonance of gold-copper bimetallic nanoparticles, and (b) the excellent conductivity/electro-activity of Polyaniline and graphene. This is expected due to increased radiative decay rate of luminophores in the vicinity of nanostructures and the increased electrophoretic migration of charged molecules within the polycationic matrix of the oxidated polymer.

POSTER PRESENTATIONS

List of poster presentations:

- P1. Electrochemical Kinetics and Sensing of Conjugated Dienes in Acetonitrile; Noluthando Myedi, Tesfaye Waryo and Emmanuel Iwuoha.
- P2. Transition Metal Alloy-Modulated Lithium Manganese Oxide Nanosystem for Energy Storage in Lithium-Ion Battery Cathodes; Natasha West, Kenneth Ozoemena, Emmanuel Iwuoha
- P3. Preliminary investigation of anti cancer potential of ethanolic extracts of *nauclea latifolia* and *pleiocarpa pycnantha* leaves. O.A Omoyeni, I.R.Green and E. I.Iwuoha.
- P4. Structure and Electrochromism in thin films of Urchin-like WO₃ microspheres prepared by Aqueous Chemical Growth; B.T. Sone , T. Malwela, R. Bucher , E. Iwuoha and M. Maaza.
- P5. Synthesis and characterization of pt-sn/c cathode catalysts for use in direct methanol fuel cells. Lynwill G. Martin, Ivan R. Green and Bruno G Pollet
- P6. Screen-printed carbon electrodes modified with a bismuth film for stripping voltammetric analysis of environmental samples; B. Silwana, C. van der Horst, E. Iwuoha and V. Somerset
- P7. Electrophoretic deposition of Pt/C nanocatalysts onto gas diffusion layers for MEAs in HT-PEMFC applications; C. Felix, S. Pasupathi, B. Pollet, V. Linkov.
- P8. Stripping voltammetric determination of palladium, platinum and rhodium in freshwater and sediment samples from South African water resources; C. van der Horst, B. Silwana, E. Iwuoha and V. Somerset
- P9. Design and Synthesis of Highly Active Platinum Group Metal Electrocatalysts Using Organometallic Chemical Vapour Deposition Method; Q. Naidoo, S. Naidoo, L.Petrik, A. Nechaev and P. Ndungu
- P10. Determination of the antioxidant potentials via electrochemical and spectro-photochemical methods of a selection of South African medicinal plants; O. J. Babajide and O.O. Babajide.

- P11. Polyaniline composite: potential application in electrochemical sensing of polychlorinated biphenyls; F.O. Okumu and M.C. Matoetoe.
- P12. Development of L-phenylalanine biosensor and its application in the real samples; Z. A. Mangombo, E. I. Iwuoha and P. G. L. Baker.
- P13. Electrochemiluminescence of Poly(8-anilino-1-naphthalenesulfonic acid) Derivatised with Novel Ruthenium(II)phenanthroline Complex; Kerileng M. Molapo, Anitha Venkatanarayanan, Ciaran Dolan, Tia E. Keyes, Robert J. Forster, Emmanuel I. Iwuoha
- P14. Synthesis and Electrochemistry of Novel Conducting Dendrimeric Star Copolymers on Poly(propylene imine) Dendrimer; A. Baleg, N. Jahed, E. Iwuoha, P. Baker
- P15. Cytochrome c biosensor for determination of trace levels of cyanide and arsenic compounds. Xolile G Fuku, Priscilla GL Baker and Emmanuel I Iwuoha
- P16. Hydrogel Systems based on Polysulfone and Polyvinyl alcohol. Gcineka Mbambisa, Priscilla Baker, Emmanuel Iwuoha
- P17. Gas diffusion electrodes for high temperature PEMFCs. *O. Barron**, *S. Pasupathi*, *B. Pollet*, *V. Linkov*
- P18. Electrochemical characterization of Platinum based catalysts for fuel cell applications. *Thobeka Adonisi and Lindiwe Khotseng*

Electrochemical Kinetics and Sensing of Conjugated Dienes in Acetonitrile

Noluthando Myedi, Tesfaye Waryo, Emmanuel Iwuoha*

Sensor Lab, Department of Chemistry, University of the Western Cape, Bellville 7535 Cape Town,
South Africa

Tel; 021-959 3079; email; nmyedi@uwc.ac.za

The study focuses on the electroanalysis of some dienes (2-methyl-1,3-butadiene (MBD), tran-1,3-pentadiene (PD), 1,3-cyclohexadiene (CHD) and 3-cyclooctadiene (COD)) found in gasoline and the development of simple electrochemical diene sensors. The detection of dienes in fuels is important as they readily polymerise and form gum in fuel tanks. The electroactivity of the dienes was studied with glassy carbon electrode (GCE) and Pt electrode in tetrabutylammonium perchlorate (TBAP)/acetonitrile solution. Polyaniline-polystyrene sulfonic acid (PANi-PSSA) composite films were electro-deposited or drop-coated on GCE, with and without gold nanoparticles (AuNPs) and characterized by cyclic voltammetry (CV), high resolution transmission electron microscopy (HRTEM) and ultraviolet-visible (UV-vis) spectroscopy. Both composite polymers were found to be of nanofibril structure, and the spherical gold nanoparticles were dispersed uniformly within the polymer. The dienes exhibited no redox peaks on GCE/PANi-PSSA and GCE/PANi-PSSA/AuNPs electrode systems from -1.0 V to +1.5 V, beyond which PANi would overoxidize and lose its electroactivity. Therefore, cyclic voltammetry and steady state amperometry of the four dienes (MBD, PD, CHD and COD) were studied with unmodified Pt and GCE electrodes. Subtractively normalised interfacial-fourier transform infra-red (SNIFTIR) spectroscopic studies of the dienes were performed with Pt electrode. SNIFTIR data showed that there was a definite electro-oxidation of 1,3-cyclohexadiene as electrode potential was changed from $E = 770$ mV to $E = 1638$ mV. Severe electrode fouling was observed when steady state amperometric detection of CHD, as a representative diene, was performed on Pt electrode. Randel-Sevčik analysis of the CVs of the dienes on Pt electrode gave diffusion coefficient (D_{ox}) values of 10.65 cm^2/s , 9.55 cm^2/s , 3.20 cm^2/s and 3.96 cm^2/s for CHD, COD, PD, and MBD, respectively. The corresponding detection limits ($3\sigma_{n-1}$) were 0.0106 M, 0.0111 M, 0.0109 M, and 0.0107 M.

Transition Metal Alloy-Modulated Lithium Manganese Oxide Nanosystem for Energy Storage in Lithium-Ion Battery Cathodes

Natasha West, Kenneth Ozoemena, Emmanuel Iwuoha

SensorLab, Department of Chemistry, University of the Western Cape,

Private Bag X17, Bellville, South Africa

Email: 2505812@uwc.ac.za

This presentation contains the synthesis, characterization and testing of high performance $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$ ($M = \text{Fe-Au}$) as a novel lithium ion battery material. The synthesis involved the incorporation of bimetallic Fe-Au nanoparticles into the spinel phase LiMn_2O_4 . This study addressed the issue of lithium ion battery capacity loss by introducing the synthetic route that oxidized Mn^{3+} to Mn^{4+} in $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$ that was produced. This conversion was confirmed by ^7Li solid state NMR, XRD, SEM, AFM and electrochemical analyses.

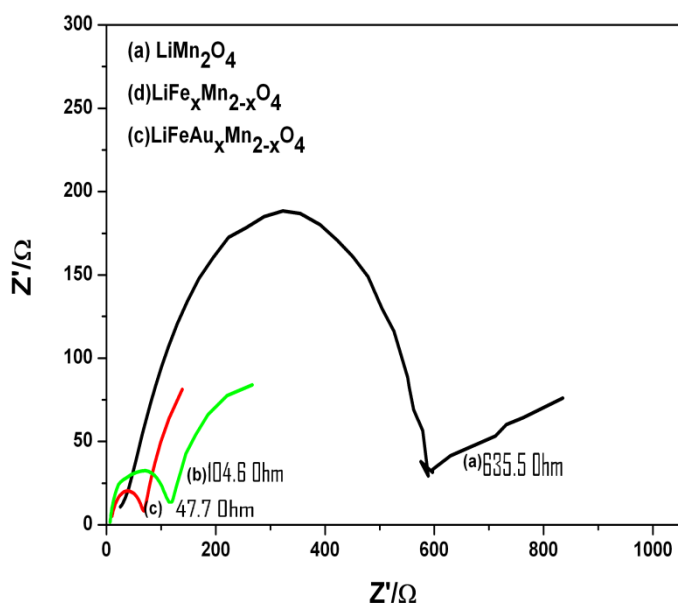


Figure 1. Electrochemical impedance spectra (Nyquist plot) of LiMn_2O_4 and $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$.

PRELIMINARY INVESTIGATION OF ANTI CANCER POTENTIAL OF ETHANOLIC EXTRACTS OF NAUCLEA LATIFOLIA AND PLEIOCARPA PYCNANTHA LEAVES

O.A. Omoyeni I.R.Green and E. I. Iwuoha

Sensorlab, Department of Chemistry, University of Western Cape, Private Bag X17, Bellville, 7535, South Africa

Corresponding author email : nikxyglo@yahoo.com, oomoyeni@uwc.ac.za

Two medicinal plants used in Nigerian and South African ethnomedicine were subjected to phytochemical and preliminary anticancer studies using established standard procedures. The result of the study revealed the presence of phytochemical constituents such as saponins, flavonoids and terpenes. *Nauclea latifolia* and *Pleiocarpa pycnantha* crude extracts and the semi purified extracts were active against colon and Hela cancer cell lines at different concentrations. It is anticipated that these potential drugs would serve as new 'leads' in phytomedicine.

Structure and Electrochromism in thin films of Urchin-like WO₃ microspheres prepared by Aqueous Chemical Growth

B.T. Sone^{1,2,3}, T. Malwela⁴, R. Bucher¹, E. Iwuoha³ and M. Maaza¹

¹Materials Research Department, iThemba LABS, P.O. Box 722, Somerset West, 7129, South Africa.

²NANOAFNET-Materials Research Department, iThemba LABS-NRF, Somerset West, South Africa.

³Chemistry Department, University of the Western Cape, Bellville, South Africa.

⁴National Centre for Nanostructured Materials, CSIR, P.O. Box 395, Pretoria, South Africa.

Aqueous Chemical Growth (ACG) is a low cost, low temperature, wet-chemistry method that has been used to synthesize thin films of multi-functional semiconductor metal oxides [1,2] in large-arrays that may find application in electrochromic devices, batteries, photoelectrochemical cells, etc. Through this method, crystalline thin solid films of WO₃ (2-3 μm thick), were grown at 80-95°C for a period of 18-24 h on un-seeded F-doped SnO₂-coated glass (FTO). SEM showed that the thin films produced contained a variety of WO₃ forms among which were nanoplatelets, nanorods and urchin-like microspheres made up of a central core 1-2 μm thick, on which grew hair-like protrusions 200-400 nm long and 50-100 nm thick. X-ray Diffraction analysis carried out post calcination of the films at 500°C revealed WO₃ to be in the hexagonal and cubic phase. TEM and HRTEM confirmed the existence of WO₃ hexagonal phase showing evidence of the existence of lattice fringes in the hair-like protrusions. FT-IR and EDX confirmed the purity of WO₃ with EDX suggesting the presence of Sn within the thin films. For electrochromism the WO₃ thin films showed fairly fast, reversible, optical switching speeds of less than 20 seconds upon H⁺ intercalation, from a semi-transparent colour to deep blue. H⁺ intercalation of the WO₃ films in 0.1-0.5M H₂SO₄ was carried out through Cyclic Voltammetry (CV) with bleaching and coloration potentials occurring at +0.5 V and -1V. The presence of WO₃ on FTO when compared to bare FTO allowed for higher charge density, at 50 mV/s. This could be ascribed to the fast ion diffusion and charge transfer that occurred in the semi-porous WO₃ thin films. Increase in the scan rates from 50-200 mV/s resulted in an increase in the area of the voltammograms albeit irreversibly suggesting that the semi-porous WO₃ films were unstable. Cyclic Voltammetry followed by UV-Visible-NearIR Spectrophotometry was used to evaluate the change in optical densities (ΔOD) and the Coloration Efficiency (CE) in the thin films. WO₃ thin films produced by ACG that have improved adhesion could find applications in smart windows which would be employed in energy-efficient buildings of the future.

References

- [1] L. Vayssieres, "On the design of advanced metal oxide nanomaterials", *Int. J. Nanotechnology*, **1(1-2)** (2004) 1-41.
- [2] Lionel Vayssieres and Arumugam Manthiram, *J. Phys. Chem. B*, **107** (2003) 2623-2625.

SYNTHESIS AND CHARACTERIZATION OF Pt-Sn/C CATHODE CATALYSTS FOR USE IN DIRECT METHANOL FUEL CELLS

Lynwill G Martin^{a,b*}, Ivan R Green^b and Bruno G Pollet^a

^aHySA Systems Competence Centre, South African Institute for Advance Material Chemistry,

^bDepartment of Chemistry, The University of the Western Cape, Private Bag X17, Bellville, 7535, South Africa

Corresponding Authour email: lynwillm@gmail.com Tel: +27-21-959-2158

An effective method was developed for preparing highly dispersed nano-sized Pt-Sn/C electrocatalyst synthesized by a modified polyol reduction method. From XRD patterns the Pt-Sn/C peaks shifts slightly to lower 2θ angles when compared with commercial Pt/C catalyst, suggesting that Sn is alloying with Pt. Based on the HR-TEM data the Pt-Sn/C nanoparticles show small particle sizes well dispersed onto the carbon support with a narrow particle distribution. The Methanol Oxidation Reaction (MOR) on the *as*-prepared Pt-Sn/C catalyst appears at lower currents (+680 mV vs. Ag/AgCl) compared to the commercial Pt/C suggesting that the Pt-Sn/C catalyst has ‘methanol tolerance capabilities’.

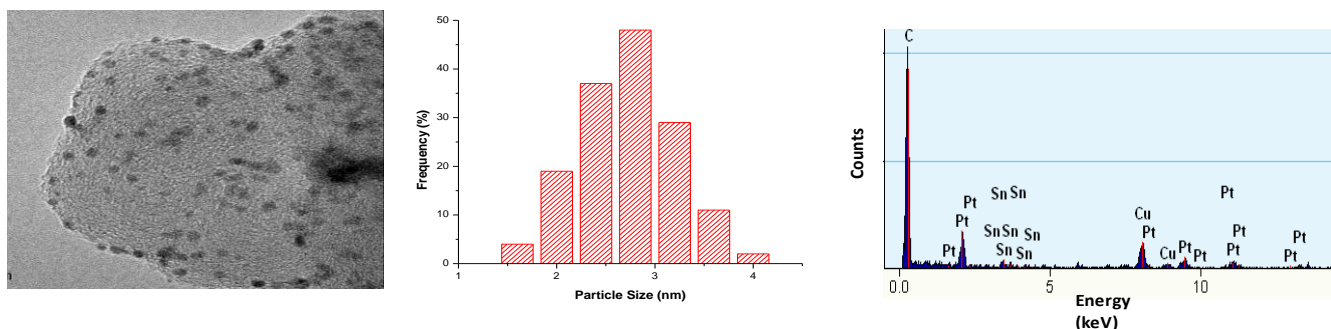


Figure 1. HR-TEM image of Pt-Sn\C HA Slurry pH3 catalyst.

Pt-Sn/C HA Slurry pH3 shows better activity towards the ORR than commercial Pt/C which could be attributed to smaller particles. The Pt-Sn/C catalyst appears to be a promising methanol tolerant catalyst with activity towards the ORR in the DMFC.

References

1. F. Colmati, E. Antolini, E.R. Gonzalez, *Electrochim. Acta*, (2005), **50**, 5496.

Screen-printed carbon electrodes modified with a bismuth film for stripping voltammetric analysis of environmental samples

B. Silwana^{a,b}, C. van der Horst^{a,b}, E. Iwuoha² and V. Somerset^{a*}

^a*Council for Scientific and Industrial Research (CSIR), NRE, PO Box 320, Stellenbosch, 7599, South Africa. vsomerset@csir.co.za*

^b*SensorLab, Chemistry Department, University of the Western Cape, Bellville, South Africa, South Africa.*

The increasing use of platinum group metals, PGMs (e.g. platinum, palladium and rhodium) in catalytic converters and the increasing mining activities for these metals in South Africa, has increased the presence of these metals in the aquatic environment. For this reason, the development of sensitive detection techniques for metal ions in environmental samples have been proposed [1,2]. The work reported in this paper describes the development of an adsorptive differential pulse stripping voltammetric procedure for the determination of palladium (Pd), platinum (Pt) and rhodium (Rh) in the presence of nickel (Ni) and cobalt (Co), using standards and environmental samples [3]. A screen-printed carbon electrode coated with a bismuth film, SPCE/BiFE was constructed. The optimisation of the experimental conditions performed, included an appropriate buffer solution for coating and the supporting electrolyte solution. The voltammetric procedure included pre-concentration of the metals using dimethylglyoxime (DMG) as chelating agent, followed by adsorptive differential pulse stripping voltammetry (AdDPSV) at appropriate deposition potentials for each of Pd, Pt and Rh. Other essential stripping voltammetric parameters optimised included the DMG concentration, composition of the supporting electrolyte, pH, deposition time, and deposition potential. Interference studies in the presence of Ni and Co have also been conducted and showed promising results. Application of the assay using the SPCE/BiFE sensor on standards and environmental samples has shown excellent linear behaviour in the concentration range from 0.01 to 0.1 µg/L, with good detection limits obtained after a 120 s deposition time. The voltammetric analysis has further been applied to the determination of Pd, Pt and Rh in river water and sediment samples.

References:

- [1] Ramírez and Gordillo. (2009). *Journal of Electroanalytical Chemistry*, 629: 147–151.
- [2] Mandil et al. (2010). *Microchimica Acta*, 170: 299–305.
- [3] Locatelli (2006). *Analytica Chimica Acta*, 557: 70–77.

Electrophoretic deposition of Pt/C nanocatalysts onto gas diffusion layers for MEAs in HT-PEMFC applications.

C. Felix*, S. Pasupathi, B. Pollet, V. Linkov

South African Institute for Advanced Materials Chemistry, Department of Chemistry,

University of the Western Cape, Private Bag X17, Bellville, 7535, South Africa

Tel: 021 959 4208

**Corresponding author email: cecilfelix09@gmail.com*

Electrophoretic deposition (EPD) is a process where charged particles are moved to and deposited onto a target substrate by an applied electric field. Compared to other coating processes, EPD has many advantages such as the high uniformity and easy control of the deposited layer. In polymer electrolyte membrane fuel cells (PEMFC), the electrode reaction(s) are usually catalysed by expensive platinum group metal catalysts. Active research is being carried out on alternative, less expensive catalytic materials as well as attempts to improve the efficiency of utilisation of the noble metal catalysts. The EPD process has already been used for the deposition of catalytic layers in membrane electrode assemblies (MEA) for low temperature PEMFC applications [1, 2]. In this study we applied the EPD process to fabricate MEAs for high temperature PEMFC applications. Catalyst suspensions were investigated by zetasizer equipment. Zetapotential and particle size were optimised as a function of suspension pH, catalyst particle volume fraction, and suspension ionic strength to produce very stable catalyst suspensions. EPD process parameters i.e. deposition time and applied electric field strength was optimized for fabricating the MEAs. MEAs were characterised by polarisation and impedance measurements. Deposited catalyst layer morphologies were characterised by scanning electron microscope (SEM). MEAs prepared by EPD gave better performance than both the hand and machine sprayed MEAs.

References

- [1] H. Morikawa, T. Mitsui, J.-I. Hamagami, K. Kanamura, *Electrochemistry (Tokyo)* (2002), 70, 937 – 939.
- [2] R.F. Louh, H. Huang, F. Tsai, *Journal of Fuel Cell Science & Technology* (2007) 4, 72 – 78.

Stripping voltammetric determination of palladium, platinum and rhodium in freshwater and sediment samples from South African water resources

C. van der Horst^{1,2}, B. Silwana^{1,2}, E. Iwuoha² and V. Somerset²

¹*SensorLab, Department of Chemistry, University of the Western Cape, Bellville, 7535, South Africa.*

²*Natural Resources and the Environment (NRE), Council for Scientific and Industrial Research (CSIR), Stellenbosch, 7600, South Africa. vsomerset@csir.co.za*

The development of an analytical sensor for the detection and characterisation of PGMs were investigated, since there is an ongoing need to find new sensing materials with suitable recognition elements that can respond selectively and reversibly to specific metal ions in environmental samples [1-3]. The work reported shows the successful application of another mercury-free sensor electrode for the determination of platinum group metals in environmental samples. The work reported in this study entails the use of a glassy carbon electrode modified with a bismuth film for the determination of platinum (Pt²⁺), palladium (Pd²⁺) or rhodium (Rh²⁺) by means of adsorptive cathodic stripping voltammetry. Optimised experimental conditions included composition of the supporting electrolyte, complexing agent concentration, deposition potential, deposition time and instrumental voltammetry parameters for Pt²⁺, Pd²⁺ and Rh²⁺ determination. Adsorptive differential pulse stripping voltammetric measurements for PGMs were performed in the presence of dimethylglyoxime (DMG) as complexing agent. The glassy carbon bismuth film electrode (GC/BiFE) employed in this study exhibit good and reproducible sensor characteristics. Application of GC/BiFE sensor exhibited well defined peaks and highly linear behaviour for the stripping analysis of the PGMs in the concentration range between 0 and 3.5 µg/L. The detection limit of Pd, Pt and Rh was found to be 0.12 µg/L, 0.04 µg/L and 0.23 µg/L, respectively for the deposition times of 90 s (Pd) and 150 s (for both Pt and Rh). Good reproducibility was also observed and the practical applicability of the sensor was demonstrated with the analysis of environmental water and sediment samples.

References

- [1] Locatelli, C. (2007). *Electroanalysis*, 19: 2167-2175.
- [2] Bobrowski, A., Gawlicki, M., Kapturski, P., Mirceski, V., Spasovski F., Zarebski, J. (2009). *Electroanalysis*, 21: 36-40.
- [3] Locatelli, C. (2006). *Analytica Chimica Acta*, 557: 70-77.

Design and Synthesis of Highly Active Platinum Group Metal Electrocatalysts Using Organometallic Chemical Vapour Deposition Method

Q Naidoo^a, S Naidoo^a, L Petrik^a, A Nechaev^a and P Ndungu^b

^a*Environmental and Nanosciences Research Group, Department of Chemistry, University of the Western Cape, Bellville, South Africa, +27 219593878*

^b*School of Chemistry, University of KwaZulu-Natal, Westville Campus, Durban, South Africa.*

E-mail: qiling.naidoo@uct.ac.za

Fuel cells are new clean energy for power to be generated at the point of use utilizing a variety of fuels. Benefits arising from the use of fuel cells include efficiency and reliability, as well as economy, unique operating characteristics, planning flexibility and future development potential. In the context of fuel cell engineering, platinum is the most popular electrocatalyst for fuel cells. When this platinum electrocatalyst is in contact with one of the electrodes in a fuel cell, it increases the rate of oxygen reduction to water (or hydroxide or hydrogen peroxide). Currently, many studies have been devoted to liquid-phase methods to prepare supported catalysts. However, the required steps by liquid method such as adsorption, drying, calcinations and reduction would significantly alter and sinter the catalyst structure and consequently reduce the active surface area of the catalyst. Contrary to the liquid impregnation method, the proposed platinum Organometallic Chemical Vapour Deposition (OMCVD) method is fast and the stages of impregnation, washing, drying, calcinations, activation, surface poisoning and material transformations activated during drying are avoided. The performance of the CVD process can be affected by the choice of metallic precursors, nature of the substrate, design of the system and the system parameters, operating pressure (vacuum), deposition time and temperature, etc. According to these criteria, it is very important to reach performance optimization by controlling synthetic procedures and conditions. In this study, a series high active platinum group metal nanocatalyst was successfully synthesized by OMCVD and characterized by XRD, HRTEM and CV. The results catalysts showed high methanol oxidation activity.

Determination of the antioxidant potentials via electrochemical and spectro-photochemical methods of a selection of South African medicinal plants

O. J. Babajide^a and O.O. Babajide^{a,b}

^a*Department of Chemistry, ObafemiAwolowo University, Adeyemi College Campus, P.M.B 520, Ondo, Ondo State, Nigeria.*

^b*Department of Chemistry, University of the Western Cape, Private Bag X17, Bellville 7535, Cape Town, South Africa*

E-mail: obabajide@uwc.ac.za

A wide range of ethno-medicinal uses and anti-oxidative spectrum reported for two South African medicinal plants – *Cissampeloscapensis* and *Geranium incanum* motivated this study. A comparison of antioxidant potentials of different extracts and isolates of these medicinal plants were evaluated using both electrochemical and spectro-photochemical methods. The methanolic extract of both plants showed a distinct presence of polyphenols, and flavonoids with the methanolic extract of *G. incanum* exhibiting higher oxidation potentials. The cyclic voltammetry method was applied for both qualitative and quantitative purposes. By measuring the cyclic voltammetry activities using quercetin, catechin, rutin and gallic acid as reference standards for detecting the antioxidants components, results showed a parallel correlation between the components detected which was also confirmed by spectrophotocemical method. This study proved the applicability of cyclic voltammetry method in identifying anti-oxidant components present in these medicinal plants rapidly and accurately.

POLYANILINE COMPOSITE: POTENTIAL APPLICATION IN ELECTROCHEMICAL SENSING OF POLYCHLORINATED BIPHENYLS

F.O. Okumu, M.C. Matoetoe

Department of Chemistry, Faculty of Applied Science, Cape Peninsula University of Technology, Cape Town 652, South Africa

Corresponding author email: MangakaM@cput.ac.za

Hybrid material was investigated through preparation of a composite material possessing excellent characteristics in terms of mechanical, chemical and electrochemical properties. Polyaniline (PANI) and Polyaniline-titanium dioxide (PANI/TiO₂) composite were investigated by spectroscopic methods where UV-vis and FTIR studies showed that TiO₂ particles affect the quinoid units along the polymer backbone and indicate strong interactions between TiO₂ particles and quinoidal sites of PANI with minimum interaction on the benzenoid units. Spectroscopic spectral comparison of PANI/TiO₂ hybrid material with (PANI) of UV-visible, FTIR, Scanning electron microscopy (SEM) and X-ray diffraction was undertaken together with thermogravimetric analysis (TGA). All spectra showed the characteristic PANI peaks, indicative of the intact PANI structure. However there were observable peak shifts, indicating possible chemical environmental changes experienced by PANI functional groups. TGA showed an initial degradation at 160 °C and 380 °C for PANI and PANI/TiO₂ respectively. SEM micrographs indicated that the materials are porous and the porosity increased in the hybrid. The composite film exhibited an increase in electrochemical sensing over neat PANI. By using electrochemical polymerization, PANI and its composite were fabricated in bulk form. Electrochemically deposited PANI on chemically deposited TiO₂ showed better electrochemical properties on the glassy carbon electrode where the electrocatalytic properties of PANI/TiO₂/GCE toward the electrocatalytic reduction of PCBs were investigated using cyclic voltammetry (CV) and square wave voltammetry (SWV) techniques. The potential application of PANI/TiO₂ hybrid materials in electrochemical studies of selected PCBs congeners in waste waters was investigated with respect to measurable range, detection limit, reproducibility and suitability for in field use.

Development of L-phenylalanine biosensor and its application in the real samples

ZA Mangombo*, EI Iwuoha, PGL Baker.

SensorLab, Chemistry Department, University of the Western Cape, Private Bag X17, Bellville 7535, South Africa

**Corresponding author. Tel.: +27 21 466 0251. E-mail address: zmangombo@gmail.com*

Electrochemical biosensor based on boron-doped diamond (BDD) electrode modified with the enzyme tyrosinase (Tyr), obtained from mushrooms (Sigma-Aldrich), immobilized in polyaniline (PANI) doped with polyvinyl sulfonate (PVS) composite films were studied and offered many advantages for new possibilities to be used as biosensors to detect L-phenylalanine in the real samples. The biosensor response to its natural substrate, L-phenylalanine, prepared in the aqueous solutions using voltammetric methods and the results obtained were plotted as Lineweaver-Burk plots in order to determine apparent Michaelis-Menten constants. The biosensor was also applied to certain commercially available real sample to assess its performance. The enzyme catalysed the oxidation of L-phenylalanine was measured as the formation of L-3,4-dihydroxyphenylalanine (L-dopa) at peak potential around 800 mV (vs. Ag/AgCl). The linearity response of the biosensor to L-phenylalanine (L-Phe) has shown in the concentration range between 2–10 μM ($r = 0.999$, $n = 6$). The apparent Michaelis-Menten constants (K_m) of the immobilized tyrosinase onto PANI-PVS modified BDD electrode for L-Phe detection was 1.39 μM . The detection limit for L-phenylalanine was $1.0 \times 10^{-2} \mu\text{M}$ and for real samples such as lipoprotein and lemonade were respectively found to be $(1.0 \times 10^{-3} \pm 0.1 \mu\text{M})$. The sensitivity of the biosensor towards L-phenylalanine as a substrate was $7.19 \text{ Amol}^{-1} \cdot \text{dm}^3$.

Electrochemiluminescence of Poly(8-anilino-1-naphthalenesulfonic acid) Derivatised with Novel Ruthenium(II)phenanthroline Complex

**Kerileng M. Molapo¹, Anitha Venkatanarayanan², Ciaran Dolan³,
Tia E. Keyes^{2,3}, Robert J. Forster^{2,3}, Emmanuel I. Iwuoha¹**

¹SensorLab, University of the Western Cape, Cape Town, South Africa; ²Biomedical Diagnostics Institute, Dublin City University, Glasnevin, Dublin 9, Ireland; ³National Centre for Sensor Research, Dublin City University, Glasnevin, Dublin 9, Ireland

Ruthenium(II)(bis-2,2-bipyridyl)-2(4-carboxylphenyl)imidazo[4,5-f][1,10]phenanthroline (RuBP) was incorporated into polyaniline (PANI) or poly(8-anilino-1-naphthalene sulfonic acid) (PANSAs) by electrosynthesis on an indium tin oxide (ITO) glass electrode. The voltammetry, luminescence and electrochemiluminescence (ECL) of PANI-RuBP and PANSAs-RuBP were studied. Analysis of the UV-vis data showed that PANSAs exhibited lower band gap and higher conductivity than PANI. Co-reactant ECL of PANI-RuBP and PANSAs-RuBP using tri-n-propylamine (TPA) showed that PANI-RuBP was in the penigraniline (P) state and PANSAs-RuBP in the leucoemeraldine radical cation (LRC) state.

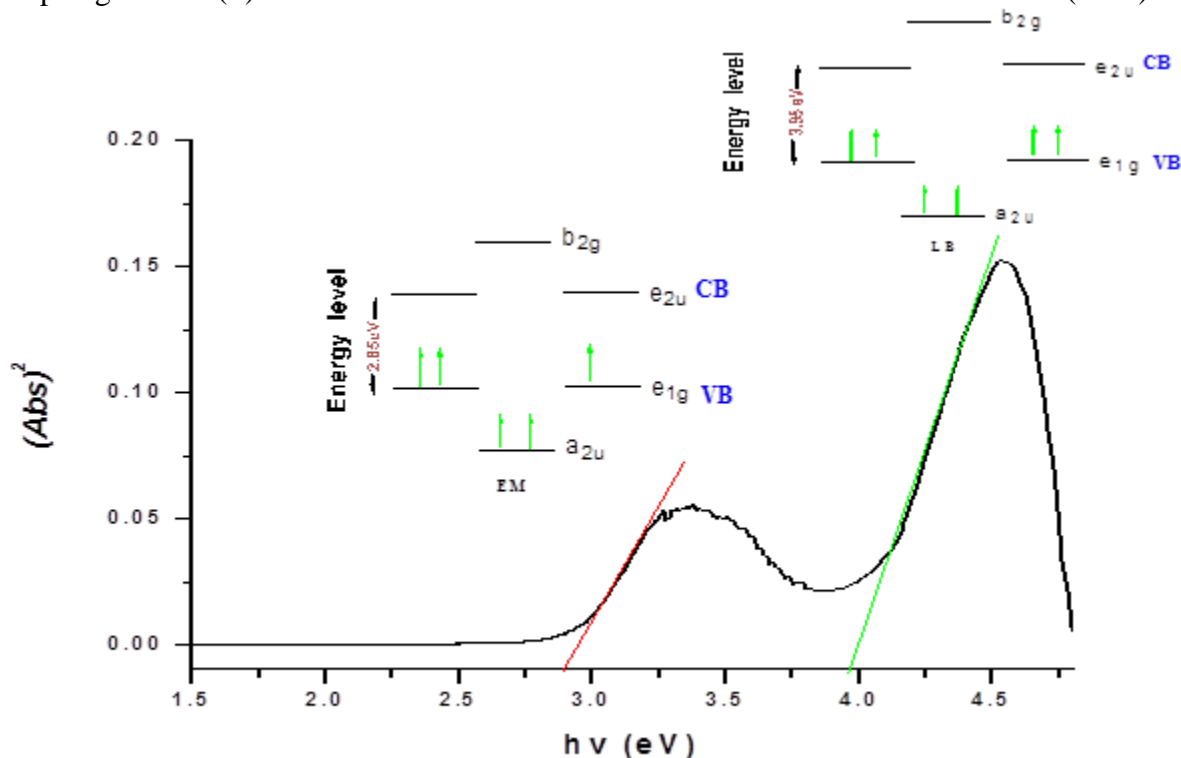


Figure 1: Absorbance and photon energy of undoped PANSAs, and the band gaps (inset) for polyleucoemeraldine (LE) and polyemeraldine (EM).

Synthesis and Electrochemistry of Novel Conducting Dendrimeric Star Copolymers on Poly(propylene imine) Dendrimer

A. Baleb, N. Jahed, E. Iwuoha, P. Baker

SensorLab, Department of Chemistry, University of the Western Cape, Private Bag X17, Bellville, South Africa, 7535

Novel star copolymers based on a poly(propylene imine) (PPI) dendrimer core (generations 1-4) and a polypyrrole (PPY) shell were prepared both chemically and electrochemically. The procedure for the synthesis of the star copolymers involves a condensation reaction between the diamino functional dendrimer and 2-pyrrole aldehyde to give the pyrrole functionalized PPI dendrimer. Chemical oxidative polymerization of the pyrrole functionalized dendrimer (PPI-2Py) with additional pyrrole monomer in the presence of ammonium persulfate gave poly(propylene imine)-co-polypyrrole (PPI-co-PPY). The (PPI-co-PPY) was electrochemically prepared by polymerization of the functionalized dendrimer using a platinum electrode in (0.1M LiClO₄) electrolyte solution. The star copolymers were characterized using analytical techniques such as FTIR, TGA, XRD, SEM as well as cyclic voltammetry and Hall Effect measurements.

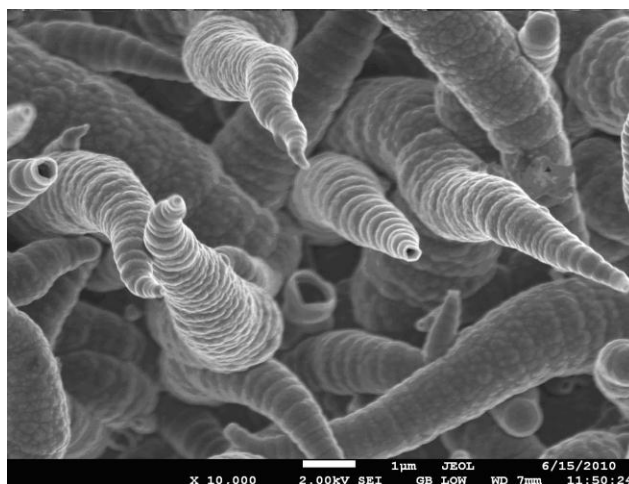


Figure 1. The SEM image of electrochemically prepared generation 1 (G1) poly(propylene imine)-co-polypyrrole star copolymer on platinum electrode surface.

Cytochrome c biosensor for determination of trace levels of cyanide and arsenic compounds

Xolile G Fuku, Priscilla GL Baker and Emmanuel I Iwuoha

*SensorLab, Chemistry department, University of the Western Cape, PB X17,
Bellville 7535, South Africa*

Boron Doped Diamond (BDD) electrode was used as a transducer, onto which cyt c was immobilised and used for direct determination of Prussian blue, potassium cyanide and arsenic trioxide by inhibition mechanism. The sensitivity as calculated from cyclic voltammetry (CV) and square wave voltammetry (SWV), for each analyte in phosphate buffer (pH= 7) was found to be (1.087- 4.488 ×10⁻⁹ M) and the detection limits ranging from 0.0043- 9.1 μM. These values represent a big improvement over the current Environmental Protection Agency (EPA) and World Health Organisation (WHO) guidelines. The protein binding was monitored by SWV and electrochemical impedance spectroscopy (EIS) at peak potential of -300mV (vs. Ag/AgCl). EIS also provided evidence that the electrocatalytic advantage of BDD electrode was not lost upon immobilisation of cytochrome c. UV/vis spectroscopy was used to confirm the binding of the protein in solution by monitoring the intensity of the solet bands and the Q bands. FTIR was used to characterise the protein in the immobilised state and to confirm that the protein was not denatured upon binding to the pre-treated bare BDD electrode. SNFTIR of cyt c immobilised at platinum electrode, was used to study the effect of oxidation state on the surface bond vibrations. The spherical morphology of the immobilised protein, which is typical of native cyt c, was observed using scanning electron microscopy (SEM) and confirmed the immobilisation of the cyt c without denaturation.

Hydrogel Systems based on Polysulfone and Polyvinyl alcohol

Gcineka Mbambisa, Priscilla Baker, Emmanuel Iwuoha

Department of Chemistry, University of the Western Cape, Bellville, Cape Town, South Africa; email: 3158082@uwc.ac.za

Hydrogels are materials that can absorb a large amount of water without itself dissolving. They are chemically and thermally stable materials. They have been used in applications such as electronics, sensors, biomedical applications. Sampath et al has reported the potential use of polyvinyl alcohol (PVA) based hydrogels as electrolytic materials for capacitors. In biomedical applications, hydrogels are seen as potential molecules for drug delivery. Synthesis of hydrogels can be achieved by polymerising the monomeric units.

The current study involves the synthesis of hydrogel based on polysulfone (PSF) and polyvinyl alcohol utilising N-hydroxy succinimide (NHS) as a crosslinker. Spectroscopic characterisation is done in order to deduce the mechanism of formation of the hydrogel. The FTIR spectroscopy showed that the hydrogel formed using PSF, PVA and N-hydroxy succinimide showed most of the characteristic vibrations due to the starting materials, except for the -OH stretching vibration from the PVA, indicating that the interaction of the PVA with the crosslinker was through the hydroxyl bond. The hydrogel absorption maximum was observed at 256 nm, within the ultraviolet region where absorption of molecules with some degree of π bonding is found. The SEM image of the hydrogel shows an intertwined branched network with very small pores. Spectroscopy and morphology characterisation confirm that a hydrogel material was formed.

Gas diffusion electrodes for high temperature PEMFCs

O. Barron*, S. Pasupathi, B. Pollet, V. Linkov

SAIAMC Innovation Center, University of the Western Cape,

Modderdam Road, Bellville 7535

email: 2233175@uwc.ac.za

This work focuses on the development of the Gas Diffusion Electrode (GDE) specifically for use in high temperature polymer electrolyte membrane fuel cells (HT-PEMFC), that leads to the optimisation of the membrane electrode assembly (MEA) for HT-PEMFC. Developing gas diffusion electrodes, will involve looking at the most suitable materials for operation at high temperature, particularly various proton conductors suitable for HT-PEMFC operation. Commercial GDLs (Elat, Freudenberg, SGL) were coated with a catalyst layer and the prepared GDEs were tested in MEAs for durability and reproducibility. The best commercial GDL was coated with catalyst layer where the PTFE binder in the catalyst layer was replaced with a CsHSO_4 proton conductor and tested for its suitability in HT-PEMFCs. Toray carbon paper was coated with a microporous layer (Carbon Black, Vulcan XC 72) and a catalyst layer. The produced MEAs were electrochemically evaluated by polarisation studies in a HT-PEMFC test-bench as well as undergoing EIS. The MEAs were physically characterised using SEM.

Electrochemical characterization of Platinum based catalysts for fuel cell applications.

Thobeka Adonisi and Lindiwe Khotseng

South African Institute for Advanced Materials Chemistry, Department of Chemistry,

University of the Western Cape, Private Bag X17, Bellville, 7535, South Africa

Although Pt-based electrocatalysts have been commonly used in commercial fuel cells owing to their relatively low overpotential and high current density, they still suffer from serious intermediate tolerance, anode crossover, sluggish kinetics, and poor stability in an electrochemical environment. This, together with the high cost of Pt and its limited nature reserves, has prompted the extensive search for alternative low-cost and high performance ORR electrocatalysts. Among all pure metals, Pt exhibits the highest catalytic activity for the ORR. However, to further reduce the voltage losses associated to the cathode performance, it is necessary to develop ORR electrocatalysts more active than Pt. This research is focusing on electrochemical characterization of several Pt-based carbon supported catalysts synthesized in-house which are 10% Pt/C, 20% Pt/C, 40% Pt, 20% Ru/C and 30% Pt 15% Ru/C and compared with the commercial 10% Pt/C, 20% Pt/C, 20% Pt 10% Ru/C which are used as bench-marks. Properties like oxygen reduction reaction (ORR), Electroactive surface area (ECSA), Mass activity (ma) and Specific activity (sa) were determined using CV. From the ORR it was observed that the in-house 10% Pt/C has the highest activity towards ORR compared to the commercial 10% Pt/C followed by the commercial 20% Pt/C, compared to other catalysts. The lowest activity of the commercial 10% Pt/C towards ORR, was attributed to the fact that on comparing the particle size of the two catalysts the In-house one was found to be lower compared to the commercial 10% Pt/C (3.398 nm, 3.06 nm). X-ray diffraction (XRD) and transmission electron microscopy (TEM) techniques were also used that to determine information on particle size distribution, aggregate morphology, metal crystalline size and degree of alloying. The particle size of the catalysts determined using XRD are Commercial catalysts (10% Pt/C, 20% Pt/C, 20% Pt 10% Ru/C and In-house (10% Pt/C, 20% Pt/C, 30% Pt 15% Ru/C, 40% Pt 20% Ru/C) were found to be, 3.398 nm, 3.349 nm, 3.391 nm, 3.06 nm, 2.937 nm and 2.976 nm, respectively.

2nd International symposium on Electrochemistry

19-20 July 2012

List of delegates

ADONISI, T

BABAJIDE, O

BAKER, P

BALEG, A

BARRON, O

BILLIBANA, M

BOTHA, S

FELIX, C

FUKU, X

GOUWS, S

GUISEPPI, A

HENDRICKS, N

HESS, E

IKPO, C

IWUOHA, E

JJANA, A

LEKITIMA, J

MAILU, S

MAKELANE, H

MAKGOPA, K

MANGOMBO, Z

MARTIN, L

MASIKINI, M

MBAMBISA, G

MOLAPO, K

List of delegates

MPHAHLELE, N

MYEDI, N

NAIDOO, Q

NGQONGWA, L

NJOMO, N

NOHAKO, K

NXUSANI, E

OKUMU, F

OLIVIER, T

OLOWU, R

OMOYENI, O

PARSUPATHI, S

SILWANA, B

SONE, B

SUNDAY, C

TOVIDE, O

TSEGAYE, A

TSHIKALAHA, P

VAN DER HORST, C

WARYO, T

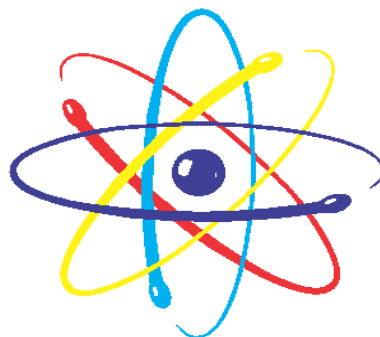
WEST, N

THANK YOU



UNIVERSITY of the
WESTERN CAPE

KIMIX
Chemical and Laboratory Suppliers



SensorLab

 **Metrohm**

WISAM
SCIENTIFIC & PRECISION EQUIPMENT (PTY) LTD.