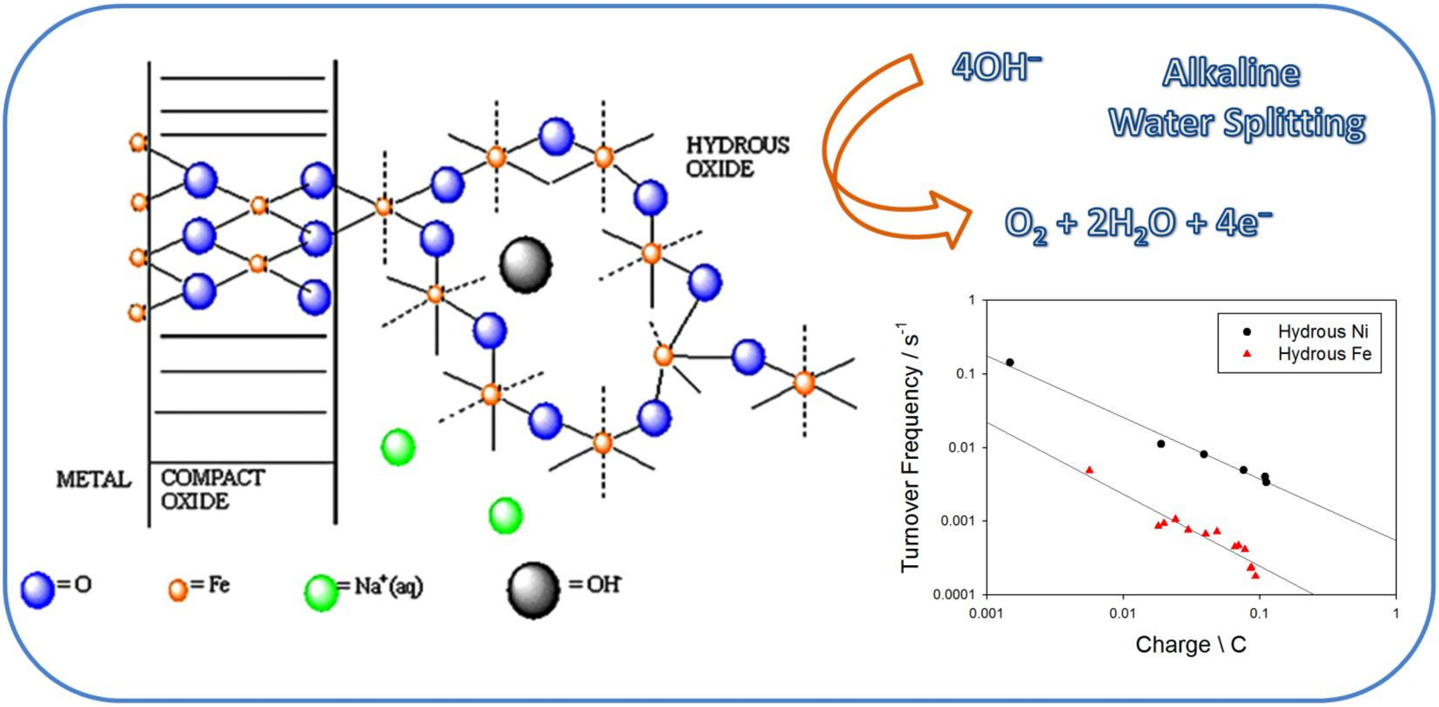
The Institute of Chemistry of Ireland

Irish Chemical News

Feature Articles:

Rusty Electrodes
Prof Mike Lyons

Monolayer-Protected Gold Nanoparticles
Elizabeth Guihen and Jeremy D. Glennon



2013 Issue 1

Editorial

Welcome to the new issue of Irish Chemical News. We have two feature articles in this issue. One is written by Prof. Mike Lyons, who is in the Physical Chemistry Section of the School of Chemistry at TCD. His article describes his recent work in electrochemical water splitting. The second article is authored by Elizabeth Guihen and Jeremy D. Glennon from Cork and Limerick. They discuss the use of gold nanoparticles in Capillary Electrochromatography. In addition to this the news section highlights a series of reports, written by members of the institute with an emphasis on Education in Ireland, and highlights of events to come.

One of the aims of this issue is that it can be distributed as widely as possible, to members and non-members alike, to highlight the activities of the Institute and hopefully to grow our membership. All our readers are encouraged to visit the website, http://www.chemistryireland.org/index.html, regularly. Details of membership rates can also be found there.

I am delighted to welcome two members to the editorial team at ICN; Dr Brian Murray (the immediate past president of the institute) and Margaret Franklin. However we still need volunteers for articles that can be featured in ICN. If you wish to contribute to the next issue, or have ideas of article types you wish to see, please do not hesitate to contact us.

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Introduction from the President of the Institute

When elected president at the AGM on April 11th 2013, I indicated three areas which need to be addressed in the next two years. These are:-

- The Membership Challenge.
- Publication of ICN
- Embracing Communication Technology

This is the second electronic issue. Publication of ICN continues to be difficult due to difficulties getting submissions of suitable articles. This is largely because of pressure on staff in academia with student contact hours, pressure to deliver research results, and the need to publish in international journals. Nor have our industrial partners been forthcoming in submitting publishable material.

Our editorial team are working to improve this situation. We still need more and updated email addresses to reach greater numbers of chemists across industry and academia. Nevertheless we have two substantive papers in this issue. The aim will be to have quarterly publications initially and eventually a monthly publication.

This year the Institute has supported a number of chemistry events which were a great success:-

Eurachem Analytical Measurement Competition held at DCU reported on in this issue.

Irish Universities Chemistry Research Colloquium held at TCD and the Institute's Graduate Member winner for best presentation was Laura Perdisatt DIT and her talk was "Systematic Study into substituent Effects on the Performance of a series of Ru (II) Complexes".

Claudia Coughlan was winner of the Best Oral Presentation in Section. Her talk "Systematic Study into the Synthesis and Shape development in Colloidal Culn^{x}Ga^{1-x}S^{2} Semiconductor Nanocrystals for Integration into Low-Cost Solar cells" MSSI, UL.

Winner of EYCN poster presentation was Michele Conroy UCC "Manipulation of threading dislocation densities within novel Nitride based UV Multiple Quantum Wells".

Preceding the AGM we had The Boyle Higgins Gold Medal and Lecture Award. This year Dr Sheila Willis of the Forensic Science Laboratory delivered an enlightening talk "Forensic Science - Fact or Fiction" at DIT Kevin Street.

The Schools Chemistry Newsletter Prize Winners 2012/13, Topic *'Chemistry for the Future'* winners were:-

First Prize

David A. Wacks and Lisa Lennon

Ballybay Community College, Carrickmacross Road, Ballybay, Co. Monaghan.

Joint Runners-Up

Kevin Finn, Conor Peppard and Sean Clancy
Christian Brothers Secondary School, Brigown, Mitchelstown, Co.Cork.

Amy O'Donoghue and Lee Boorman
St. Andrew's College, Booterstown Avenue, Blackrock, Co. Dublin.

Finally we had Eurovariety 2013 in UL with the theme "Smarter Teaching – Better Learning". I attended this event and was impressed with the commitment and dedication of chemistry lecturers worldwide and the novelty and innovation they bring to the teaching of chemistry.

Looking forward to the rest of this year we have two significant events in October and November. This year's ICI Annual Award for Chemistry will be given by Professor Herbert Roeskey's of Institute of Inorganic Chemistry, Gottingen a very well-known and published German inorganic chemist in late October at three locations. Our annual Congress will be held in Limerick Institute of Technology and the theme will be innovation in the pharmaceutical industry.

Returning to the membership issue. Membership is a challenge. Numbers are low and this limits what we can achieve. It directly impacts finance and sponsorship is difficult in these taxing times with companies implementing cost cutting measures. This is not unique to Ireland, its prevalent throughout EuCheMS. I hope to work with EuCheMS to attempt to address this issue. I will discuss this at the EuCheMS General Assembly in October.

Embracing Communication Technology. We live in a world of instant communication. We have Facebook, Twitter and LinkedIn, among others. How do we leverage advantage here? Most companies and organisations now use these technologies to communicate. This is a topic will try addressing in the coming months and hopefully generate a higher profile for our Institute.

Patrick Hobbs MSc, FICI, CChem, CSci, MRSC
President, Institute of Chemistry of Ireland

Awards 2013

Eva Philbin Award 2013 – Prof. Herbert Roeskey (University of Göttingen, Germany).

Prof. Roeskey is one of the formost inorganic chemists in Germany, with research mainly focussed upon main group organometallics. He has published over 1,500 papers and written a number of books, including “Chemische Kabinettstücke” and “Spectacular Chemistry Experiments”, which detail demonstartion experiments. He will delvier his lectures in late october and will also give a demonstration lecutre, for which he is well respected in Germany.

Boyle-Higgins Award 2013 - Dr Sheila Willis, (Forensic Science Laboratory).

Dr Willis is this year’s recipient of the Boyle-Higgins award. She delivered her lecture “Forensic Science – Fact and Fiction” in Dublin Institute of Technology, Kevin Street, on Thursday 11 April 2013.

Eurachem Ireland Analytical Measurement Competition – Dublin City University, March 22nd, 2013

Margaret Franklin

This year’s Eurachem competition was hosted by Dublin City University on March 22nd. The annual event, now in its 15th year, is a practical laboratory contest in analytical skills, which was initiated by Dr. Sean Cawley, former Head of School of Science at Carlow Institute of Technology. Through the Association of Heads of Science at the Institutes of Technology, he formed a committee composed of a number of chemistry lecturers from the Institutes and following a series of meetings during the 1997/98 Academic Year, the very first competition was hosted by IT Tallaght in 1999. The winning team that year came from Waterford Institute of Technology and in fact WIT has been more successful than any other college, having won the competition six times.

The main aim of the competition has been to raise awareness, among third level chemistry students, at an early stage in their studies, of the importance of being able to identify sources of uncertainty in their measurements and, as far as possible, to quantify the uncertainty. It also aims to raise the profile of Analytical Chemistry as a scientific discipline. The work of the analytical chemist often goes unnoticed, behind the closed doors of laboratories, yet it is of great importance in so many aspects of modern life. The skill and expertise of the analyst is crucial in ensuring that our food is safe and that our medicines contain the correct dose of the active ingredients. Analytical chemistry is an essential tool in environmental monitoring and, through forensic work, in the detection of crime. Almost all manufacturing industries employ chemists in quality assurance. But analytical measurements are meaningless unless the analyst can stand over them and express the results with an uncertainty estimate.

Eurachem is a network of European organisations dedicated to excellence in analytical chemistry and the Irish section has supported the competition from the start. The Environmental Protection Agency has also lent its support. Mason Technology has been the principal industrial sponsor in recent years. The Institute of Chemistry of Ireland offers prize money for the best team and also presents a plaque to the winning college. The judging panel is composed of experienced analytical chemists from outside the education system, who work in the chemical industry or in the Public Service.

The competition is restricted to students who have not yet commenced the third year of their course. In practice, most of the competitors are second years, though some brave first year students have participated over the years. It is open to full-time students studying laboratory sciences in any of the 3rd level colleges (Universities or Institutes of Technology) on the island of Ireland. There have been no participants from Northern Ireland to date, so perhaps some promotion north of the border needs to be done. The contestants work in teams of two and are selected by an internal competition within their own universities or Institutes.

In the early years of the competition, the standard displayed by the competitors was somewhat mediocre. However, over the first five or six years, there was a steady improvement in the practical skills element. This was largely due to the helpful feedback provided by the judges after each competition. The lecturers took the recommendations of the judges on board and passed them on to their students. The result has been an overall improvement in the practical laboratory training provided by the participating colleges. The internal competition motivates the students to take pride in their work and to develop their analytical skills. In recent years, most participants in the competition have shown excellent bench practice and safety awareness.

This year, the sample provided for analysis was in solid powder form. The students were told that it was a dietary supplement and they were required to determine the iron content, using both a volumetric method and a spectroscopic method. There was a record number of entries, with 26 teams competing, from 13 different institutions.

The competition required students to determine the percentage iron concentration in commercially available iron therapy tablets using both titrimetric and spectroscopic techniques. Twenty six teams were evaluated based on experimental data and associated data handling, bench practice, knowledge of background theory and adherence to health and safety guidelines. The purpose of this report is to summarise the overall results and document various observations noted in the course of the day.

The 2013 winning team came from the Dublin Institute of Technology. The winners are Damien Cooney and Siobhan Smith. Their mentor and lecturer Patrice Behan accepted The Institute of Chemistry of Ireland sponsored prize plaque on behalf of the winning college. The joint runners-up were Elgiva White and Hope Daly from UCD and Cheryl Hyland and Melissa McCrea from Dundalk Institute of Technology.

Each winner and runner up was presented with a replica of the 'Newgrange' trophy, a work of art designed by the Irish Pewtermill at Timolin, Co. Kildare. It depicts the Newgrange National Monument 'light box', which provides evidence of the scientific precision and skill that existed in ancient Ireland almost 5,000 years ago. The opening above the entrance of this ancient monument is so positioned that on the morning of the Winter solstice, the rays of the rising sun enter the 'light box' and the beam of light penetrates to the back of the chamber. This trophy represents a heritage of which we can be proud and which should inspire generations of scientists and analysts for years to come.

Patrice Behan (Chemistry Lecturer, DIT) with winning team members Damien Cooney and Siobhan Smith (students at DIT) displaying their Newgrange trophies.

Judges Report

Judges: Dr Ray Leonard, Dr. Thomas Hannigan, Dr. Darragh Cunningham

Overall team performance was evaluated based on the closeness of the reported result for each experiment to that of the "reference" result as measured by means of a "Z" score. A tolerance interval of [-1,1] was used to identify acceptable results – corresponding to approximately a 10% allowable error. Figure 1 attempts to summarise the overall individual performance of teams for the 25 teams that provided final results for each experiment (Z scores outside [-2,2] were set to either -2 or 2, such scores were typically the result of calculation rather than experimental errors).

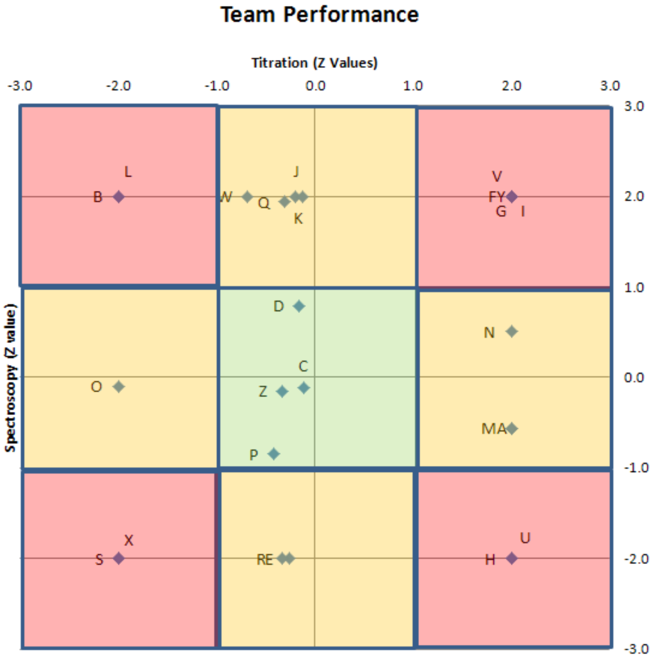


Figure 1: Overall Team Performance

Health and Safety

All teams showed good awareness of Health and Safety issues with regards to keeping the work area clean and the wearing of white coats, glasses and gloves. Bench practice was good and the majority of teams showed both good teamwork and organisation and were able to successfully complete the experimental work within the time allotted. General bench tidiness was of a high standard.

Experiments

The titration experiment consisted of three distinct stages namely:

- Preparation of Standard Ferrous Ammonium Sulphate (FAS) Solution
- Standardisation of Permanganate Solution
- Determination of % Fe II

Overall ten teams (~ 40%) successfully determined the correct % Fe in the "iron therapy" powder as measured by their Z score (|Z score| ≤ 1) (Figure 1), although one of the teams (W) arrived at the correct answer by making two off setting errors. There appeared to be a slight negative bias in the experimentally determined results relative to the reference result. Surprisingly, 25% of teams failed to correctly determine the Molarity of the FAS Solution, while nearly 60% failed to determine the Molarity of the permanganate solution. The vast majority of teams which did correctly determine the permanganate molarity went on to correctly determine the %Fe II.

The spectroscopy experiment consisted of the following stages:

- Preparation of Calibration Curve
- Reading Unknown
- Determination of % Fe II

Overall eight teams (~ 30%) successfully determined the correct % Fe in the "iron therapy" powder as measured by their Z score (|Z score| ≤ 1) (Figure 1) with acceptable scores distributed around the reference value.

The majority of teams (80%) developed a useable calibration curve. However, having developed the curve only 60% correctly read the molarity of the unknown sample (Sample C). In a number of cases this was as a result of incorrectly reading the unknown from the graph or as a result of a poorly drawn least squares line. It is debateable whether the response is still in the linear range for the high calibration standard and dropping this standard did generally improve all the correlation coefficients but did not materially affect the overall results.

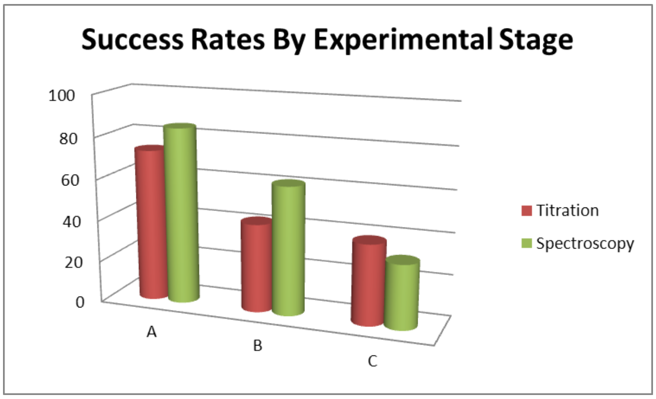


Figure 2: Experimental Stage Success Rates

The determination of the %Fe II in the sample appeared to present greater difficulty in the spectroscopy experiment likely as a result of the need to account for additional dilution steps.

Calculations and Reporting

The students were generally able to produce accurate titration figures and absorbance measurements. The main deficiency in the conduct of both experiments was the failure to process measurement data through the various stages and hence to arrive at the correct result although the design of the data sheet and the absence of a step involving a change of units probably helped students in the processing of data.

Some observations regarding data recording and calculations are noted in the table below along with a comparison from the previous year – a significant improvement in this area was noted.

Observation	Freq 2013	Freq 2012
Pencils and erasers being used rather than ink	Low	Medium
Inappropriate rounding of experimental and calculated data	Low	Low
Experimental results being recorded on rough work rather than directly onto provided analysis sheet	Low	Medium
Errors being scribbled out/erased rather than a line drawn through error.	Low	Medium

Questionnaire

As in recent years the questionnaire was an integral part in deciding overall positions and in the interests of feedback the breakdown of results is provided.

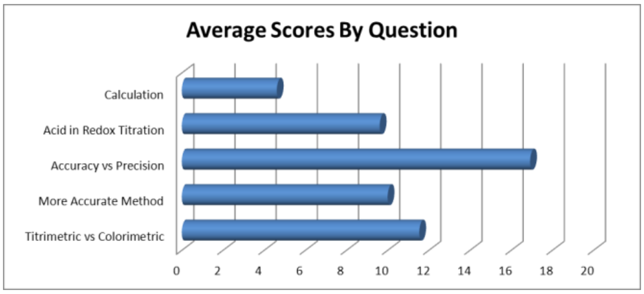
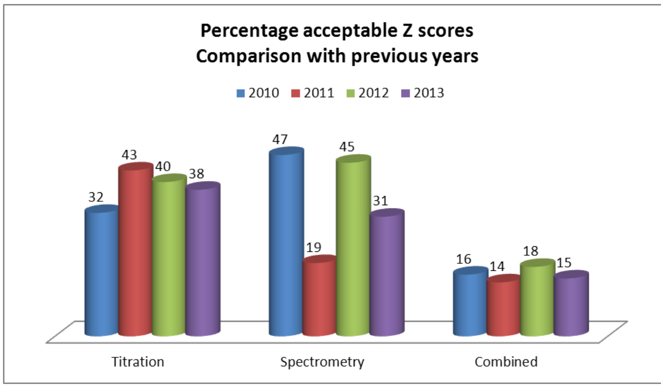


Figure 3: Questionnaire Results

From this analysis question 5, a calculation provided the greatest difficulty to students which is consistent with the observation that the greatest difficult remains the processing of data through each stage. Questions 1 and 2 were related and while most teams could identify some advantages/ disadvantages with a particular technique these were not used to support the teams answer of which technique gave the most accurate result. Question 4, caused some confusion as to the role of acid in the redox titration with some teams answering on the role of the buffer in colour development for the spectroscopic method.

Comparison with previous years

The number of teams participating, 26, was an increase over previous years which is encouraging. The format of the experiments was very similar to previous years with both a titrimetric and photometric experiment. The principal difficulty encountered by students in both years was the processing of data through the full procedure. Students fared slightly worse in this year's titration experiment relative to 2012 and significantly worse in the spectroscopy experiment. Looking at the previous four events, performance at the titrations has been relatively consistent varying between success rates of 32 to 43% with a much greater variability in the spectroscopy experiment, 19-47%. Overall the average number of teams obtaining a combined successful Z scores, remained relatively consistent with previous years. Overall, 4 teams managed to obtain satisfactory final Z scores for each of the experiments equating to an overall satisfactory rate of 15%.



Overall Result

Teams C,D,P and Z obtained correct results for all stages of the experiments and the final positions (winner and two run ups) were decided based on closeness to the true values as reflected in Z scores across the various stages of the experiment, a review of questionnaire answers and bench practice notes.

Team C were judged to be the overall winners based on having come closest to the expected answers in both experiments and the standard of their answers to the questionnaire. Teams D and Z were judged to be the runners up with team P narrowly losing out.

Concluding Remarks

The experimental data generated on the day by the majority of students was very good and within experimental error. Incorporating experimental data into the calculations so as to obtain an acceptable result continues to be a problem for many students. Many teams are so focussed on the experimental aspect that they fail to leave sufficient time for the calculations. Colleges are urged to emphasise to participants the importance of proper time management.

This year, each experiment posed equal difficulty to students with each being completed successfully by nearly 50% of teams. In general, teams performing the spectroscopy experiment in the morning and titration in the afternoon outperformed by a margin of 2:1 (13:6) those performing the experiments in the reverse order in terms of acceptable Z scores although no obvious external factor to explain this was identified.

Finally the judges wish to congratulate Pat O’Malley and the staff at DCU for a very well organised and efficiently run competition. From the judges perspective this made their task so much easier and meant that everything ran very smoothly on the day.

Report on the 17th European Carbohydrate Symposium

Professor Paul Murphy, FICI
NUI Galway

The 17th Meeting of the European Carbohydrate Symposium took place in Tel Aviv in Israel from the 7th-12th July 2013. The symposium was attended by 350 scientists from 33 countries who are working in carbohydrate synthesis, carbohydrate structural analysis, glycomedicine, glycobiology, glycomaterials, glycobiotecnology, glycosaminoglycans and glycomics. There were contributions from China, USA, Japan and other non EU countries. Two awards were presented at the symposium. Professor Xi Chen from UC Davis in the US obtained the Carbohydrate Research Award which was presented by Professor Stefan Oscarson (UCD), who represented the Editors of Carbohydrate Research. This prize lecture is given by a researcher in the field, who graduated with their PhD within the previous 15 years and who has made significant original contributions to the field. Professor Antoni Planas from the Universitat Ramon Llull in Barcelona, Spain gave the Emil Fisher Award Lecture which was established by the European Carbohydrate Organisation in order to honour active carbohydrate scientists distinguished with contributions of excellence. There was an enzyme theme to these two lectures with Professor Chen outlining the generation of sialic acid derivatives using chemoenzymatic methods whereas Professor Planis discussed mechanisms and applications of glycosidases, glycosyltransfereases and esterases. In addition to these two prize lectures there were an additional 8 plenary and 30 invited keynote lectures and 100 additional oral contributions and 160 poster presentations.

There was a significant contribution by Irish carbohydrate scientists at this meeting. Keynote lectures were given by Paul Murphy NUI Galway, Stefan Oscarson (UCD) & Pauline Rudd (NIBRT). There were additional oral contributions from Lorna Moynihan, Stephen Cunningham, Michelle Kilcoyne, Rob Woods (each NUI Galway), Lorenzo Guazelli (UCD) and Allesandro Ravido (DCU). In addition, posters were presented by Mark Farrell, Antony McDonagh, Louise Kerins, Lorna Moynihan, Marie Le Berre (each NUI Galway) and from Tamara Strebel and Aisling Ni Cheallaigh (each UCD). The contributions showed the activity of the Irish carbohydrate community in the areas of synthesis of biologically relevant carbohydrates as well as in glycoanalysis.

Some of the highlights of the meeting included presentations which showed the progress being made in the generation of glycoproteins both by biochemical and chemical methods as well in the (bio)synthesis of glycosaminoglycans. There was also updates on the development of synthetic carbohydrate based vaccines and adjuvants. All of these topics are very important for the pharmaceutical industry. It was apparent from discussions with industrial representatives at the meeting that the scale up of chemical synthesis of oligosaccharides may well become very important in the production of glycoprotein and related therapeutics.

The meeting organisation was considered excellent by Professor Timor Baasov and his local and international scientific committee. Due to the significant sponsorship generated the organisers were able to keep student registration fees low.

The delegates also heard from Professor Ehud Keinan, the current President of the Israel Chemical Society. Like Ireland, chemicals are important to Israel's economy. From a population of ~7.8 million the Israel Chemical Society has about 6000 chemists and chemical engineers as members, which interestingly also includes about 1000 chemistry teachers.

The next European Carbohydrate Symposium will take place in Moscow in 2015. In the meantime carbohydrate researchers will be able to attend the International Carbohydrate Symposium which will be held in Bangalore in 2014.

Chemical Education in the Republic of Ireland 2011–2012

Peter E. Childs

Adjunct Senior Lecturer, Department of Chemical and Environmental Sciences, University of Limerick, Limerick, Ireland

Major changes are underway in the second-level system in Ireland, with a major revision of the Junior Cycle which may mean that schools do not need to offer science to everyone. The senior cycle science syllabi are under revision and were sent out for consultation. There will be major changes in the way practical work and theory will be assessed, and it is intended to bring in assessment of practical work for the first time. The training of teachers at primary and secondary level is under review and there is a major discussion underway on entry to higher education. The economic cutbacks are taking their toll on schools, with the loss of teaching posts and potential loss of minority subjects like physics and chemistry. However, this year the numbers taking LC chemistry have increased again. Dublin was European City of Science in 2012 and hosted the Euroscience Open Forum. The first Chemistry for non-specialists courses was run and a new 3-year programme to train out-of-field maths teachers was launched by the government.

National educational policy

Ireland is in the middle of a major economic crisis and all levels of education have been affected: teacher's salaries have been reduced and jobs have been lost. It is reported that some schools will drop minority subjects like physics and chemistry because of this. The birth rate in Ireland has gone up and is now the highest in Europe and a bulge in numbers is starting to move up through the education system. In addition, Ireland now has over 10% of non-nationals in the population and the influx of non-native speakers into classrooms is creating problems, especially in some areas. Despite the poor economic situation, a programme of building new schools has been announced to meet this increase.

However, a number of educational initiatives have taken place at a national level over the last year or so.

Introduction of a National Literacy and Numeracy strategy 2011-2020 (http://www.education.ie/admin/servlet/blobservlet/lit_num_strat.pdf);

Introduction of bonus points for higher level mathematics (from Sept. 2012);

Major revision of the Junior Cycle to start in 2014, but at the moment Science is not a core subject (http://www.ncca.ie/en/Curriculum_and_Assessment/Post-Primary_Education/Junior_Cycle/junior_cycle_developments/);

Publication of draft syllabi for LC Biology, Chemistry and Physics and a consultation on them (available at http://www.ncca.ie/en/Consultations/Senior_Cycle_Science/Senior_Cycle_Science_Consultation.html);

New Maths syllabus; Project Maths, was rolled out across the country at junior cycle and senior cycle in 2011, in part to counter concerns of low numbers doing Higher Level mathematics, even though >95% of students staying on to the end of senior cycle take mathematics.

A new 3-year programme has been funded to up-skill out-of-field mathematics teachers and this project will be coordinated by the National Centre for Mathematics and Science Teaching and learning at the University of Limerick (www.nce-mstl.ie). However, concern continues to be expressed at the low numbers taking HL maths and the physical sciences. The National Council for Curriculum and Assessment (NCCA) has been working with teachers and science educators to develop new ways of assessing practical work and content for the new LC science syllabi.

A review is underway of teacher training at primary and second level. Initial Teacher training is being increased from 3 to 4 years at primary level and from 1 to 2 years for the consecutive Post Graduate Diploma in Education. Concern has been expressed at the amount of time spent in primary teacher training on religion at the expense of subjects like science.

A report on '*Entry to Higher Education in Ireland in the 21st Century entry*' was published in September 2011 as a discussion paper for a conference on entry into third level. (http://www.hea.ie/files/files/file/News/1335_HEA_Conference_01.pdf) Universities were asked to respond within 6 months with their proposals for revising the system of university entry.

A paper has been published by the Higher Education Authority on '*Towards a future higher education landscape'* and one of its proposals was for regional strategic groupings of higher education institutions, and a number of these have already been announced. (http://www.hea.ie/files/TowardsaFutureHigherEducationLandscape.pdf)

Criteria for the Institutes of Technology (IoT) to apply for Technological University status have been published, as a number of IoTs have been pressing for an upgrade to universities.

The 2012 figures for LC Chemistry have shown an increase to 15.45% of the LC cohort, an increase in numbers of 9.2%.

Events in chemical education for a range of audiences

There have been a number of science/chemical education conferences, often with a research theme:

For teachers:
The 30th ChemEd–Ireland Conference in Cork (October 2011), with the largest-ever attendance of over 140, was held in the new Eureka Science Education Centre at University College, Cork.

The 50th ISTA Annual Conference was held in Trinity College, Dublin, in April 2012.

The 6th Chemistry Demonstration Workshop was run at the University of Limerick, was held in June 2012, for a group of chemistry teachers and newly qualified science teachers.

The first Chemistry for Non-Specialists courses was run in June by the RSCs Education Division Ireland Region, modelled on the courses run in the UK, and it is hoped to run more in the 2012–13 school year.

For science education researchers:
The NW Europe IOSTE Symposium on *"Science and technology education research and its impact on practice"* in the University Limerick, was held in April 2012. The Proceedings are available on line at http://ioste-nwe.wikispaces.com/

SMEC 2012 conference, *'Teaching at the heart of learning'*, in Dublin City University, in June 2012, was combined with a meeting of European teachers working on the ESTABLISH project. (http://www4.dcu.ie/smec/2012/index.shtml)

For school pupils:
The BT Young Scientist and Technology Exhibition, was held in January 2012 – a major showcase for science projects by schoolchildren. (http://www.btyoungscientist.ie/)

SciFest is a national science fair for primary and second level students, was held around the country in May 2012. (www.scifest.ie)

Winners from these competitions have been unusually successful at European and International science fairs, considering the size of Ireland.

For the general public:
Dublin is the European City of Science in 2012, and a host of events has been arranged throughout the year, culminating in the Euroscience Open Forum (ESOF), in Dublin, in July 2012 (http://www.esof.eu/)

A Robert Boyle festival was held in Lismore, his birthplace, in November 2011 and there will be Robert Boyle Summer School in July 2012. (http://www.robertboyle.ie/robert-boyle-festival)

The 2012 Atlantic Corridor STEM Education conference, held in March 2012 (http://www.eventelephant.com/atlanticconference2012), included a workshop for school children.

Science Week Ireland in November each year is a national celebration of science. There is also an Engineering Week and a Mathematics Week. (http://www.scienceweek.ie/index.asp)

Publications

CRANN, a research centre for nanoscience in Trinity College, Dublin, has produced a teaching pack on Nanoscience for schools. (http://www.crann.tcd.ie/Education-Outreach.aspx)

The National Centre for Excellence in Mathematics and Science Teaching and Learning at the University of Limerick has continued to produce its series of 4-page Research and Resource Guides for teachers, which are available on-line (www.nce-mstl.ie)

The ISTA magazine *SCIENCE* is published three times a year and some back issues are now available on-line at http://www.ista.ie/publications/science-journal

Irish Chemical News is now only published on-line from 2012 (http://www.chemistryireland.org/docs/news/Irish-Chemical-News-2012-Issue-1.pdf)

Chemistry in Action! is aimed at Irish and UK chemistry teachers and is published three times a year. The Spring issue contains the Proceedings of the previous ChemEd–Ireland Conference, and it also publishes an annual review of results in the Leaving Certificate science and maths examinations.

Science Spin is a commercial science magazine for the general public and is available on-line. http://www.sciencespin.com/)

Liaison with the chemical industry

The previous President of the ISTA was Matt Moran, Director of Pharmachemical Ireland, and he was replaced in April by Charles Dolan, who works for Eli Lilly. Despite the health of Ireland's chemical industry, relatively little is invested in science education, except through local or small-scale initiatives.

The Eureka Centre in Cork received substantial funding from local pharmachemical industries.
Pharmachemical Ireland provided scholarships for 7 recently qualified science teachers to attend the 6th Chemistry Demonstration Workshop in Limerick.

Eli Lilly and Merck Sharpe and Dohme supported the *Organic Chemistry in Action!* action research project at the University of Limerick.

Dublin City University in conjunction with Amgen is running a series of IBSE workshops under the Amgen Science Teacher Training Initiative for teachers in the Dublin area.

Pharmachemical Ireland has an Education Officer and provides resources for teachers: http://www.pharmachemicalireland.ie/Sectors/PCI/PCI.nsf/vPages/Home~Education?OpenDocument.

International or European initiatives

Dublin City University is the coordinator for the ESTABISH project (http://www.establish-fp7.eu/) and in 2011 was also successful in a bid to coordinate the new SAILS project (http://www.sails-project.eu/). University College Cork is involved in the PROFILES project, St, Patrick's College, Dublin in the Fibonacci project (http://www.fibonacci-project.ie/) and the University of Limerick in the Tempus SALiS project (http://www.salislab.org/). Limerick Institute of Technology is a partner in the new 'Chemistry is all around' Life-Long Learning project (http://projects.pixel-online.org/chemistrynetwork/info/partnership.php).

Science/chemistry education research

The level of research activity in science/chemistry education has increased in the last few years, with major groups in: Dublin City University (CASTEL, www.castel.ie/), University of Limerick (NCE-MSTL, www.nce-mstl.ie, CERG), Waterford Institute of Technology (CALMAST, http://www.calmast.ie/), Dublin Institute of Technology (the Chemical Education Research Team (CERT), http://www.dit.ie/colleges/collegeofsciencesandhealth/chemistry/research/cert/#d.en.16764), and the Eureka Centre in University College Cork (http://www.ucc.ie/en/sefs/).

Three MSc courses for science teachers are currently running in Ireland.

The number of postgraduate awards, published papers, conference presentations at national and international meetings and involvement in EU projects have all increased.

Dr Michael Seery, from the Dublin Institute of Technology, won the RSC HE Award in 2012 for his work in bringing e-learning into 3rd level chemical education.

Eurovariety 2013

3-5 July University of Limerick

www.eurovariety2013.ul.ie

The 5th European Variety in Chemistry Education (EViCE) was held at the University of Limerick from 35 July 2013. Nearly 80 people attended from around Europe and further afield, mostly university lecturers in chemistry or science education lecturers preparing second-level chemistry teachers. It was encouraging to see a number of postgraduate students. The programme consisted of 5 plenary lectures, 4 workshops, 41 oral papers and 8 posters. There was a lively discussion at the poster reception and then at each coffee break. It was encouraging to see how many people stayed right to the end of the conference and the timing was designed to allow many people to arrive on the first day and leave after the final session. The conference was opened by welcome addresses from Professor Don Barry (President, UL), Pat Hobbs (President, Institute of Chemistry of Ireland), Professor Ilka Parchmann (Chair, EuCheMS, Division of Chemical Education) and Professor Kieran Hodnett (Dean, Faculty of Science and Engineering,UL).
The organisers were grateful for the sponsors who helped underwrite the costs of the conference and helped us keep the registration fee low (which included registration, meals and accommodation as a package). The major sponsors were: the Institute of Chemistry of Ireland; the RSCs Tertiary Education Group, Chemistry Education Research Group and Education Division Ireland Region, Merck Sharp and Dohme, and Aughinish Rusal. In addition there were a number of other industrial sponsors.

List of plenary lectures:
'Teaching college chemistry: context, collaboration and communication' Reiner Glaser (USA)
'Enhancing the Student Experience in Undergraduate Chemistry' David McGarvey (UK)
'Translating university chemistry for the classroom' Sabine Streller (Germany)
'Learning chemistry through inquiry' Natalie Rowley (UK)
'The more we do, the less they do..? Effective use of technology in chemistry education', Michael Seery (Ireland)

List of workshops:
‘ Wikis – what they are and how they are used to facilitate and assess group assignment ’, Claire McDonnell
‘Getting started in pedagogic research’, Tina Overton
‘Publishing in chemical education – research and popular’, Karen Ogilvie and Michael Seery
‘Promotion and outreach activities ’, Sylvia Draper and Tim Harrison

The program was very full (and is available on the website), as the conference only lasted for two full days (spread over three days). However, everything went smoothly and the proximity of the rooms made it easy for participants to move from one session to another. The number and quality of the talks was very encouraging and there were a good number of first time attendees at Eurovariety. There was some very positive feedback after the conference and the organisers hope that everyone took back something useful to their home institutions. The next Eurovariety conference will be held in Estonia in 2015.

The conference participants at Killaloe for the conference banquet

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Report on EC2E2N Meeting in Utrecht, 5-6/4/13

Peter E. Childs

Adjunct Senior Lecturer, Department of Chemical and Environmental Sciences, University of Limerick, Limerick, Ireland

The Institute of Chemistry of Ireland is a member of the ECTN Association and I attended the meeting in Utrecht representing the Institute. The EC2E2N pays for accommodation for the meeting for eligible participants. A number of Irish institutions are also members.

EC2E2N has been funded for a further 3 years by the EU but it is expected that this will be the last round of funding. After this project finishes in 2015 the ECTNA will have to raise its own funds for projects. This project is called:
EC2E2N-2 "Chemistry and Engineering Skills for Europe in 2020"
http://ectn-assoc.cpe.fr/network/ec2e2n/

Under the new round of funding there are 8 Working Parties. Further details of each WP and its membership is available at http://ectn-assoc.cpe.fr/network/ec2e2n/workpackage2.htm.

WP1 Towards excellence in school and university teaching
I am a member of this WP which will have a meeting later this year. Two projects are in preparation:

A book of best practice examples for teaching chemistry at second level
A database of expertise in teaching and learning at university level.

WP2 Enhancing professional capabilities
WP3 Sustainable entrepreneurship
WP4 Impact of chemistry on everyday life
WP5 Devlopment of a virtual educational community (VEC)
WP6 Broadening student horizons
WP7 Re-tuning competencies for Europe 2020

Each working group presented its work so far, met in a series of workshops and reported on their deliberations at the final meeting.

Official report on the ECTN Association General Assembly:

(http://ectn-assoc.cpe.fr/news/letter/2013/03/1403_201306.htm#2013_Plenary_meeting)

The ECTN Association General Assembly was held in Utrecht on 5th April 2013 in Utrecht, The Netherlands under the Presidency of Evangelia Varella (Thessaloniki).
In her report to the General Assembly, Evangelia Varella talked about the three flagships of the Association: the Eurolabels, Virtual Education including the EChemTest, and the Intensive Schools and related activities. She also reported that a Youth for Chemical Education group is being launched and invited all members to nominate two persons (doctoral candidates, post-docs or newly appointed teaching staff) to represent them in this new group.
The members were reminded that they can make use of the EChemTest suite of tests for free and are encouraged to use this important tool which provides a major advantage for ECTN Association members.

2013 Plenary meeting

The 2013 EC2E2N Plenary meeting was held at the Uithof campus of Utrecht University, The Netherlands; on 4 -6 April

2013. The meeting was brilliantly organised and hosted by Egbert Mulder and Iris Caris of the Utrecht University department of chemistry.

There were over 140 participants from 30 countries, representing 70 EC2E2N 2 member institutions.

The format of the meeting was changed from those of recent years to make this an essentially working meeting. This enabled the 7 working groups of the project to make significant advances in their work as we are near the beginning of this new project. There were no plenary lectures.

The meeting began with a reception in Aula of the 'Academiegebouw' of Utrecht University, a superb building in the centre of Utrecht, generously hosted by the university.

With ample time for working group sessions and for discussions with working group leaders at a 'market place' the meeting succeeded in allowing all working groups to move forward in their work and plan their future activities. Details will appear on the working group web pages.

There was also a meeting of national representatives for a European employment survey which is being planned in collaboration with EuCheMS, Cefic, and the European Commission Joint Research Centre.

Following the success of the student competitions last year, the contests were held again this year and there was a prize giving ceremony for the student winners. We send many congratulations to these winners, and to all those who participated in the competition. Given the continued success of this competition, we plan to make this an annual event.

Also, the newly appointed lecturers who successfully participated in the Eurolecturer programme (one of the EC2E2N project activities) were awarded Eurolecturer certificates at this meeting. Many congratulations to them all.

The EC2E2N 2 project includes 7 members from outside Europe and we were very pleased to welcome 4 of these members to the meeting. Participants from Canada (Brock Robertson - University of Calgary and Garry Hanan - University of Montreal), Kazakhstan (Irina Efimova and Lina Roessler - Auezov South Kazakhstan State University), and South Africa (Suresh Ramsuroop - Durban University of Technology) gave presentations about their universities and how they would contribute to the activities of the project.

Excellent presentations were made on how the universities of Utrecht and Krakow are making use of the EChemTest. We hope that this will encourage more universities to make use of this valuable and useful resource.

The meeting concluded with a brief presentation by Sanjiv Prashar (Madrid) on the 2014 annual meeting which will be held in Madrid.

2014 and 2015 Plenary Meetings

Following discussions and a vote by the Management Committee of the EC2E2N 2 project, it has been decided that the 2014 Plenary meeting will take place in Madrid, Spain (the provisional dates are **24 - 26 April 2014**) and the 2015 Plenary meeting will take place in Ljubljana, Slovenia. More information concerning the 2014 meeting will be published in October.

Report on Committee for Chemistry Education (CCE) meeting at IUPAC General Assembly, Istanbul 11-12/8/13

Peter E. Childs

Adjunct Senior Lecturer, Department of Chemical and Environmental Sciences, University of Limerick, Limerick, Ireland

Major activities of the CCE:

Young Ambassadors for Chemistry (YAC) Program – encouraging chemistry in developing countries by working with young people.

Flying Chemists Program (FCP) – providing visiting speakers for developing countries

http://old.iupac.org/standing/cce/FCP.html

See a recent report: http://www.iupac.org/publications/ci/2013/3503/pp1_CCE_projects.html

1st ACRICE – first chemical education conference in Africa 5-7/12/13 in Ethiopia (Dr Peter Childs is one of the invited plenary speakers). This is being organised by the Federation of African Chemical Societies with the help of IUPAC.

http://www.faschem.org/index.php?option=com_content&task=view&id=30

Sponsoring the biennial ICCE conferences:

Proceedings of the 22ICCE11ECRCE in Rome, July 2012 have been published at http://www.soc.chim.it/sites/default/files/users/div_didattica/PDF/2012-3.pdf

23rd ICCE – Toronto, 13-18 July 2014 – the biennial conference of CCE

http://www.icce2014.org/

Decision made on the 24th ICCE, 2016 – the bid from Malaysia was successful. Two strong bids were made by Malaysia and Sydney, Australia.

New projects:

Development of International Standards for Chemistry Education (ESCE) – analysis of national standards for content, practice and application from primary level upwards. This project aims to analyse the standards for chemistry in various countries from primary level upwards, covering content, practical work and application in order to come up with a set of recommended international standards.

Best practice in the use of learning outcomes in third level chemistry education

Best practice in the use of learning outcomes in chemistry education s being collected in order to develop a method of benchmarking to enhance learner-centred chemistry education at third level.

Work priorities

The six priorities that will lead the work of CCE for the 2012-2013 biennium were discussed at the meeting in Rome July 15 2012:

(a) To give priority to initiatives that highlight the relationship between chemistry and
sustainable development via working with divisions, also to extend the goals of the IYC
the UN Decade for Education for Sustainable Development.

(b) To maintain a primary focus on working with other partners, across divisions, and
stakeholders to maintain momentum of the International Year of Chemistry.

(c) To emphasize the importance of developing ALL students' inquiry competency and
learning outcomes of excellence in chemistry education, both in the developed and
developing world.

(d) To identify and communicate new learning and teaching practice in the areas of chemistry education throughout the world.

(e) To build chemistry education networks among and outside IUPAC, using fully the
multicultural capacity within CCE and chemistry to bridge people.

(f) To continue to support initiatives that raise awareness, social responsibilities, and
understanding of ethical issues that are important in chemistry education.

The biennial International Conferences on Chemistry Education (ICCE) is considered as a
major bridge for CCE to present the outcomes of CCE projects, to link chemistry educators
together to empower impact of chemistry education, and to implement CCE strategies for
making a valuable contribution to our society.
http://www.iupac.org/nc/home/about/members-and-committees/db/division-committee.html?tx_wfqbe_pi1%5Btitle%5D=Committee%20on%20Chemistry%20Education&tx_wfqbe_pi1%5Bpublicid%5D=050

Other items:
2014 will be the International Year of Crystallography UNESCO/IUCr There ae plans to have national and international crystal growing competition for schools.
IYCr2014 http://www.iycr2014.org/
Next meeting:
Toronto in conjunction with 23rd ICCE July 13-18 2014
2015 meeting will be held in Seoul in conjunction with the IUPAC General assembly.

Report on ISTA Quiz November 15th 2012

Dr Sean Reidy

Midlands Regional Representative

St Mel's College , Longford wins Regional Science Quiz (ISTA) in AIT

The ICI sponsored Midland Regional ISTA (Irish Science Teachers Association) science quiz was hosted by the Department of Life and Physical Sciences on Thursday 15th November. The venue was the Nursing and Health Sciences Building AIT. This was the Midlands round of the National Science table quiz for secondary school students of Science subjects Biology, Chemistry and Physics. Twenty one teams competed from across the Midlands. The top three teams competed in the National finals in TCD on Saturday 24th November. The following schools were represented and attended accompanied by their Science Teachers: Moate Community School, Athlone Community School, Our Lady's Bower, Marist College, Summerhill College, Athlone, St. Mel's College, Longford, Colaiste Mhuire, Mullingar, Wilson's Hospital, Mullingar, Colaiste Mhuire, Longford, Sacred Heart Convent, Tullamore, Mean Scoil Mhuire, Longford, Castlerea Community School, and Scoil Mhuire, Strokestown.

The winning team was from St Mel's College, Longford and included Andrew Halloran, Razi Ul-Munim and Turlough Mulligan. Coláiste Mhuire, Mullingar (CBS) supplied the second place team consisting of Pearse Murphy, Oisín Judge and Killian Daly. Third place also went to St Mel's, Longford and included Liam Twaddle, Luke Casserly and Dominic Sherry. 4th placed team were the local school Marist College team of Cian White, Eoghan O Reilly and James Flynn.

Other well placed Athlone teams included Marist College team of Daniel Boland, Sean Garvey, Niall McInerney, Our Lady's Bower team of Annette Benson, Katie Rock and Basola Salaja and Athlone Community School teams of Michael O Riordan, Rebecca Mahoney, Pierce Warwillow. (Joint 5th)

The main money prizes were very kindly sponsored yet again by the ICI (the Institute of Chemistry of Ireland) and Arran Chemicals, Monksland Industrial Estate, Athlone (Dr. Peter Cairns and Dr. Anthony Owens).

Many thanks to our two loyal sponsors who have sponsored the quiz each year since its inception over 10 years ago.

The winning team received a perpetual cup (the Midland region ISTA cup), a plaque and cash, with runners up and 3rd place teams receiving plaques and cash prizes. Interestingly until this year, a different school has won it each year. St Mel's are the first school to win it for a second time.

The quiz was run on the night by 2nd and 3rd year Science students from AIT, across a range of courses including the BSc (Ord.) in Pharmaceutical Science, and the Higher Cert. in Science

and the quizmaster was Dr. Sean Reidy. A page long report and photos was published in a number of local papers (Tullamore, Longford, Mullingar, Roscommon, Ballinasloe and Athlone).
Many thanks to Cynthia Coyne, Helen Bradley (AIT Science Staff), catering and caretaker staff including Pascal, for helping this Annual Science Week event to run smoothly as always.

Institute Events

2012

EAMC 2012

The 2012 Eurachem Analytical Measurement Competition (EAMC) took place in Galway-Mayo Institute of Technology on Friday 30th March.

Boyle Higgins Lecture

The recipient of the 2012 Boyle Higgins Award is Professor Malcolm R. Smyth, DCU. He will give a Boyle Higgins Lecture titled 'Sensors and Separations: A Journey Towards EMμ (and much more besides)', in Dublin City University, at 5.00pm on Thursday 12 April 2012. The lecture will be followed by a reception.

Annual General Meeting

The Sixty-third Annual General Meeting of the Institute of Chemistry of Ireland will be held in Dublin City University, on Thursday 12 April 2012 at 7.00pm. The meeting will be preceded by a reception.

From Alchemy to Chemistry

A half-day symposium titled "From Alchemy to Chemistry", co-sponsored by the Institute, will take place in the afternoon of Friday 13 April 2012, in the Dillon Theatre, Arts/Science Concourse, NUI Galway.

Irish Universities Chemistry Research Colloquium

The 64th Irish Universities Chemistry Research Colloquium under the auspices of the Institute of Chemistry of Ireland will be held from Thursday 14 to Friday 15 June 2012, in the University of Limerick.

Website: http://tinyurl.com/bt7xzva

Synthesis of Bioactive Molecules VII

A one-day Conference titled 'Synthesis of Bioactive Molecules VII' took take place on Thursday 5 July 2012, from 10.00am to 5.00pm, in Trinity College Dublin, College Green, Dublin 2. Contact: Mr Enda Bergin: ebergin@tcd.ie

Eva Philbin Lectures

The 2012 Eva Philbin Lectures and Receptions of The Institute of Chemistry of Ireland, 'Powering Ahead with Solar Energy' / 'Challenge Chemistry: Celebrating its Pivotal Role – Past, Present and Future', by Professor Lesley Yellowlees, University of Edinburgh, was given in three locations:

I. 'Powering Ahead With Solar Energy' in the National University of Ireland, Galway on 9 October 2012.

II. 'Powering Ahead With Solar Energy' in the National University of Ireland, Maynooth on 10 October 2012.

III. 'Challenge Chemistry: Celebrating its Pivotal Role – Past, Present and Future' in the Tercentenary Hall, Trinity Biosciences Institute on Thursday 11 October 2012.

ISTA Quiz

The ICI sponsored Midland Regional ISTA (Irish Science Teachers Association) Science Quiz was hosted by the Department of Life and Physical Sciences on Thursday 15 November 2012. The venue was the Nursing and Health Sciences Building, Athlone Institute of Technology.

Annual Congress.

The Annual Congress took place in University College Cork on Monday 26 November 2012. The theme of the congress was ‘Chromatography Ireland’. The Annual Dinner took place on the preceding evening.

Symposium on Inorganic Chemistry in Ireland

The third Irish Inorganic Chemistry Symposium was held for the first time at NUI Galway (School of Chemistry) on 7 December 2012 with financial support from The Institute of Chemistry of Ireland and others.

2013

EAMC 2013

The Eurachem Analytical Measurement Competition (EAMC) took place in Dublin City University on Friday 30 March 2013.

Boyle Higgins Lecture

The recipient of the 2013 Boyle Higgins Award is Dr Sheila Willis, Forensic Science Laboratory. She gave a Boyle Higgins Lecture titled Forensic Science – Fact and Fiction', in Dublin Institute of Technology, Kevin Street, on Thursday 11 April 2013 at 5.00pm.

Annual General Meeting

The Sixty-fourth Annual General Meeting of the Institute of Chemistry of Ireland was held in Dublin Institute of Technology, Kevin Street, on Thursday 12 April 2012 at 7.00pm. The meeting was preceded by a reception.

Irish Universities Chemistry Research Colloquium

The 65th Irish Universities Chemistry Research Colloquium under the auspices of the Institute of Chemistry of Ireland was held from Wednesday 27 to Thursday 28 June 2013, in Hamilton Building, School of Chemistry, Trinity College Dublin.

Other Events

EC2E2N Meeting 2012

This meeting marked the 15th anniversary and was the 16th annual conference of ECTN/EC2E2N, the European Chemistry Thematic Network. It was held in Milan from 26 to 28 April 2012.

4th EuCheMS Chemistry Congress

The 4th EuCheMS Chemistry Congress entitled ‘Chemistry” was held in Prague, Czech Republic, from 26 to 30 August 2012.

Website: www.euchems-prague2012.cz
Newsletter: http://www.czech-in.org/EUCHEMS/mailing/2012-03-26_mail.html

'Rusty' metal electrodes : redox chemistry and electrochemical water splitting catalysis

Michael E G Lyons*, Richard L. Doyle, Ian Godwin, Anja Cakara, Patrick O'Brien, Maria O'Brien and Lisa Russell

5

Trinity Electrochemical Energy Conversion & Electrocatalysis (TEECE)
Group, School of Chemistry & CRANN, Trinity College Dublin 2, Ireland
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Introduction

The oxygen evolution reaction (OER) is the anodic reaction that accompanies, in aqueous electrolytes, commercially important cathodic processes such as metal electrowinning[1] and hydrogen production via alkaline water electrolysis[2].The latter has been proposed as an environmentally inoffensive route to the production of large volumes of pure hydrogen gas required by a possible hydrogen economy[3] (see figure 1). For the latter process the anodic overpotential is the major factor in limiting operational efficiency[4]. Over the past 30 years, considerable research effort has been devoted to the design, synthesis and characterization of OER anode materials, with the aim of achieving useful rates of active oxygen evolution at the lowest possible over-potential, in order to optimize the overall electrolysis process. Currently, the optimal OER anode materials are RuO_2 and IrO_2 since these oxides exhibit the lowest overpotentials for the OER at practical current densities[5]. However the high cost of these materials and their poor long term stability in alkaline water electrolysis cells renders their widespread commercial utilization both uneconomical and impractical[6], however they have been shown to be quite stable in polymer electrolyte membrane (PEM) cells. In light of these limitations, the oxides of the first row transition metals offer a compromise solution. Iron and nickel electrodes are interesting candidates. Although they possess inferior electrocatalytic activity for the OER, their relatively low cost and long term corrosion resistance in alkaline solution make them attractive OER anode materials[7].

The mechanism of the OER at first row transition metal oxide surfaces remains controversial and the important question of whether a possible common mechanism can be formulated, which would facilitate a theory of electrocatalysis for oxygen evolution is currently unresolved. It is our opinion that a systematic and consistent study of the OER at the oxidized surfaces of electrodes of adjacent first row transition metals should prove useful in eluciding whether a common reaction mechanism prevails.

In the present paper we report on recent studies performed within the TEECE Group on examining the mechanism of oxygen evolution at iron and nickel oxyhydroxide film coated electrodes in aqueous base. We propose a mechanism for the OER reaction which specifically takes into account the nature of the electrochemically generated hydrous metal oxide film present on the metal surface during active oxygen evolution.

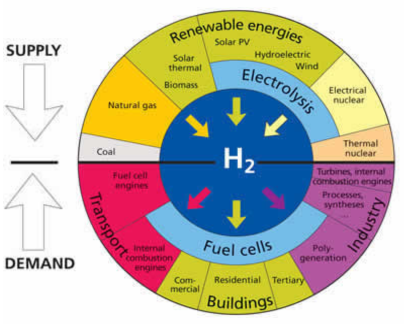


Figure 1. Electrochemical Ying/Yang. Schematic representation of hydrogen used as energy vector. Hydrogen can be generated via water electrolysis, and consumed as a fuel in a fuel cell for electricity generation.

Electrochemically induced generation of metal oxy-hydroxide thin films on electrode surfaces

We classify metal oxides into two groups[8]. The first are termed compact, anhydrous oxides such as rutile, perovskite and spinel in which oxygen is present only as a bridging species between two metal cations and ideal crystals constitute tightly packed giant molecules. The second class are dispersed, hydrous oxides where oxygen is present not just as a bridging species between metal ions, but also as O^-, OH and OH_2 species in co-ordinated terminal group form. In many cases, the latter materials when in contact with aqueous media, contain considerable quantities of loosely bound and trapped water plus, on occasion electrolyte species. It should be noted[8] that with microdispersed species the boundary between the solid and aqueous phase may be nebulous as the two phases virtually intermingle. This will be important when a simple physical model is developed to aid the understanding of the redox switching behaviour observed in thin films of the latter materials[9].

Furthermore, while compact oxides are usually prepared by thermal techniques such as for example decomposition of an inorganic salt precursor in air at elevated temperatures (RuO_2 and IrO_2 are typically formed at 450ºC), the dispersed oxides are almost invariably prepared in an aqueous environment using base precipitation of electrochemical techniques. We focus attention on the latter preparation methods here. In the latter methodology, the potential applied to the parent metal (or indeed to an inert metal support if film formation is accomplished via electro-precipitation from a metal salt solution) is cycled (or pulsed) in a repetitive manner between suitable upper and lower limits in an aqueous solution of appropriate pH. It is important to emphasise here that the oxide materials deposited via such procedures are deposited in the kinetically most accessible, rather than the thermodynamically most stable form. As a consequence the redox behaviour of the film will exhibit time varying effects. The deposited films are often amorphous or only poorly crystalline and will be prone to rearrangement in a manner that is directly influenced by factors such as temperature, pH and ionic strength. Microdispersion is usually due to the presence of strand, layer, tunnel or cage structures which facilitate not just small ions, but also in many cases solvent molecules to permeate the oxide or oxy-hydroxide phase.

One of the most versatile and convenient techniques used to generate hydrous metal oxy-hydroxide modified electrodes in a form suitable for the real time determination of their redox switching and electrocatalytic behaviour is that of repetitive potential multicycling (RPM). Here the electrode of the parent metal is cycled repetitively between suitable lower and upper limits in an aqueous alkaline or indeed acid solution. The RPM technique has been used to form oxide layers on many metals such as Fe, Ni, Co, Rh, Ir, Pt, Pd, Mn, and Cu. The type of potential perturbation used for oxide growth –sinusoidal, square or triangular wave- apparently makes little difference. Indeed the triangular wave is the most convenient, as changes in the current vs potential response profile (termed the cyclic voltammogram) can be employed during the oxide deposition reaction to monitor changes in redox behaviour associated with the latter as illustrated below in fig.2 for the growth of hydrous oxy-hydroxide films on Fe electrodes in aqueous 0.5 M NaOH.

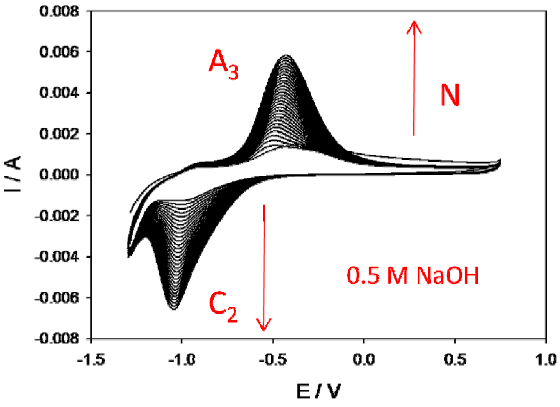


Figure 2 Growth of hydrous iron oxy-hydroxide thin film on Fe support electrode monitored via analysis of the real time voltammogram in 0.5 M NaOH. Potential swept between – 1.30 V and 0.75 V (vs Hg/HgO) at a sweep rate of 400 mV/s.

The growth of the hydrous oxide film on the Fe electrode can be readily monitored by following the development of the set of redox peaks labelled A_3,C_2 as a function either of the time or the number of potential cycles N. The variation of the integrated redox charge capacity Q (the latter is directly related to the hydrous oxide layer thickness L) as a function of number of cycles N is outlined in fig.3 below.

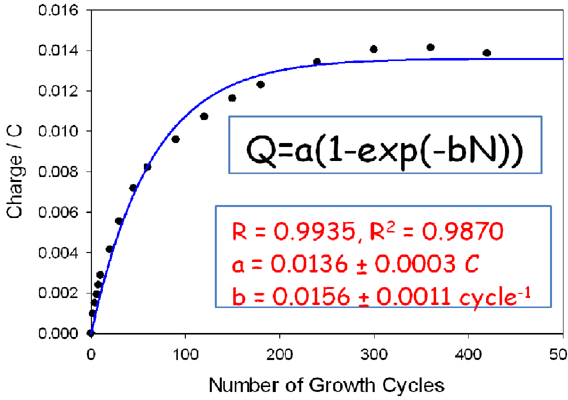


Figure 3 Growth of hydrous iron oxy-hydroxide thin film on Fe support electrode monitored via analysis of the real time voltammogram in 0.5 M NaOH. Potential swept between – 1.30 V and 0.75 V (vs Hg/HgO) at a sweep rate of 400 mV/s.

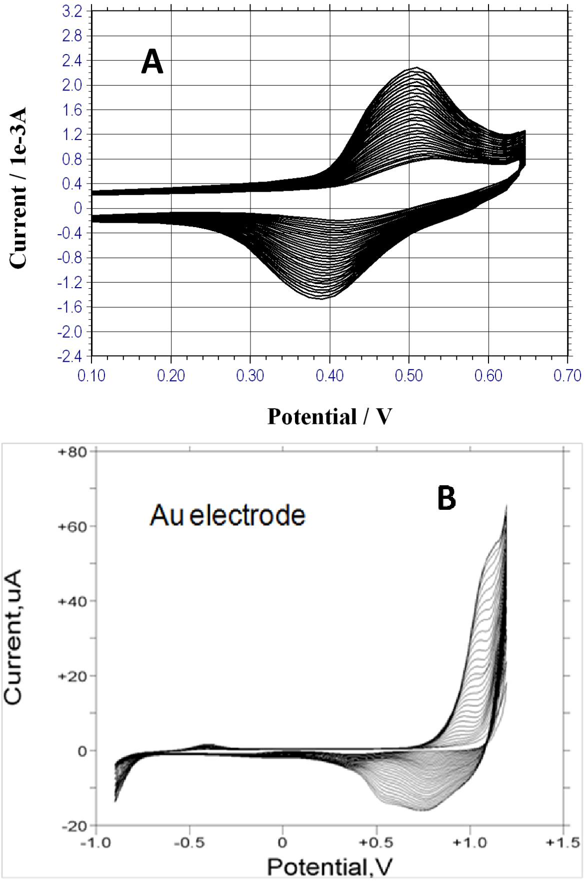


Figure 4 (a) Growth of nickel oxy-hydroxide thin film on Ni metal support electrode in 1.0 M NaOH. Growth potential limits: - 1.45 V to 0.65 V (vs Hg/HgO), sweep rate 150 mV/s, N = 30 cycles. (b) Growth of nickel oxy-hydroxide thin film on Au support electrode monitored via analysis of the real time voltammogram in Ni^{2+} containing aqueous acetate buffer solution, pH 7.6. The potential was cycled from – 900 mV to + 1200 mV (the latter potentials were measured with respect to a SCE in the acetate buffer medium) at a potential sweep rate of 50 mV/s.

In fig.3 the data can be fit adequately to the latter expression

$$Q = a\left\{1 - \exp\left[-bN\right]\right\} \qquad (1)$$

This expression implies that as N → ∞, Q → a which is a constant limiting value. Furthermore the rate of increase of oxide growth dQ/dN decreases in a regular manner with increasing number of cycles N.

As illustrated in fig.4 the RPM technique can also be applied to deposit a hydrous nickel oxy-hydroxide thin film on either a Ni metal electrode in aqueous base or on a Au support electrode from a buffer solution containing Ni^{2+} ion (Pt and GC electrodes are also good supports). The developing redox behaviour of the immobilized nickel ion sites in the film can be readily monitored in real time by examination of the developing voltammograms.

The mechanism of hydrous oxide growth via RPM is now reasonably well understood, at least at a qualitative level[10,11]. It may be assumed that the initial oxidation process involves the formation of reversibly adsorbed OH and O moieties on the metal surface. With increasing degree of surface coverage adsorption assumes a more irreversible character accompanied by the formation, via a place exchange mechanism, of a thin, largely anhydrous, compact passivating phase oxide layer. Under conventional steady state anodization conditions where a steady oxidizing potential is applied to the metal surface such layers are of limited thickness as the activation energy for atom or ion migration in the compact film is usually quite large.

Even though it is directly produced in the initial electrochemical oxidation process, the anhydrous film is probably not the most stable metal oxidation product in the aqueous medium, but it may be regarded as an intermediate or metastable product in the formation of the hydrous oxide layer. In the anhydrous film ions are held in a rigid manner in an extended network of polar covalent bonds which drastically reduce ion transport through (and consequently extension of) the surface layer. The next stage of the film thickening reaction is the hydration process, and is generally very slow. This is because as in phase transformation reactions, it involves rupture of primary coordination metal-oxygen bonds. We have established in previous studies that the extent of hydrous oxide growth depends on the value chosen for the upper and lower limit of the potential sweep. As well as on the cycling frequency adopted and the solution temperature and pH employed during the RPM procedure.

The chemistry involved in film formation can be complex. For example referring to the data outlined in fig.4 for nickel oxy-hydroxide film deposition in aqueous buffer We note that the electro-deposition process may proceed as follows:

$$Ni^{2+}\,(aq) + 2\,OH^- \rightarrow Ni(OH)_2 \qquad (2)$$

The following process may also occur as the applied potential becomes more anodic:

$$OH^- \rightarrow OH_{ads} + e^- \qquad (3)$$

$$Ni^{2+}\,(aq) + H_2O + OH_{ads} \rightarrow NiOOH + 2\,H^+\,(aq) \qquad (4)$$

The following process may also occur in the solution:

$$Ac^- + H_2O \rightarrow HAc + OH^- \qquad (5)$$

$$Ni^{2+}\,(aq) + OH^- \rightarrow NiOH^+(aq) \qquad (6)$$

$$NiOH^+ + OH_{ads} \rightarrow NiOOH + 2\,H^+ \qquad (7)$$

Hence we infer that both $Ni(OH)_2$ and NiOOH may well be formed during the course of the potential sweep perturbation. Unravelling the details of the redox chemistry which underlie the oxide film deposition can indeed be complex, and one needs to apply a combination of gravimetric and spectroscopic techniques to fully elucidate the mechanism[12].

Hence under conditions of thick film growth produced via potential cycling the interfacial region may be represented by the following: $M/MO_x/(MO)_a(OH)_b(OH_2)_c$/aqueous phase, as outlined in fig.5 below. This is the Duplex Layer Model of the oxide/solution interface region first proposed by Burke et al[13] some time ago.

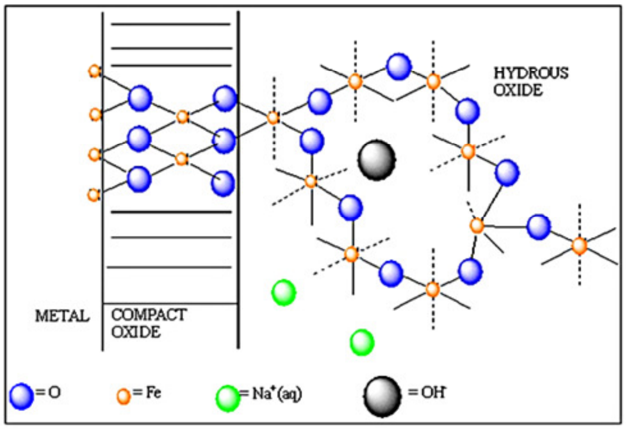


Figure 5 Schematic representation of Duplex Layer Model of oxide/solution interface.

The inner compact oxide layer is usually extremely thin, typically 1-5 monolayers in extent. The outer hydrous layer is regarded as extensively hydrated with both bound and trapped water present, as well as anions and cations. Hence we conclude that the hydrous oxide film can be regarded as an extended surface bonded polynuclear species. Metal cations in the polymer network are held together by a sequence of oxy and hydroxyl bridges. In short we can regard the microdispersed hydrous oxide layer as an open porous mesh of interconnected octahedrally coordinated surfaquo metal oxy groups. Burke and O'Sullivan[13] have suggested that the compact film component of the duplex oxide is highly conducting, with little potential drop across the inner layer. The major potential drop is assumed to occur at the outer surface of the compact film where the hydrous oxide is located (fig.5). As noted in fig.2 and indeed in fig.3 the growth of the hydrous oxide layer on cycling is not accompanied by any notable increase in charge associated with the double layer region. This suggests that the electrode area remains constant despite the formation of a thick, quite visible porous oxide film.

A possible explanation of the observed constancy of the double layer currents exhibited in fig.2 and fig.3 is that the compact oxide/hydrous oxide interface (the region of maximum potential drop) is the only region where a faradaic electron transfer reaction occurs. The material in the hydrous layer is so dispersed that it does not behave as a separate bulk phase distinct from the electrolyte solution. Hence the hydrous oxide strands and solution do not form separate phases. The oxide might well not exhibit such bulk characteristics as a distinct three dimensional electronic band structure or a well defined oxide/solution phase boundary. This concept is borne out by ellipsometric measurements where the apparent refractive index exhibits a very low value and the film density is low.

The marked dependence of oxide growth rate on the lower limit of the potential sweep is indicative of the essential role that partial reduction of the anhydrous oxide plays in the production of a thick deposit. Partial reduction of the compact oxide layer apparently facilitates rearrangement of oxy-cation species at the metal surface, leaving it in a somewhat disrupted state. It has been established for a number of metals that the anhydrous film is reduced much more readily than the hydrated film. The greater stability of the latter is probably due to reasons such as (i) lower repulsion between cations owing to greater separation, (ii) decreased net charge arising from hydroxyl ion coordination by cations present and (iii) polymer formation. On subsequent re-oxidation of the partially reduced metal surface the compact layer is restord but the outer region of the compact film is present in a more dispersed form. On further reduction the latter material becomes incorporated into the outer hydrated layer. It is not clear whether this rearrangement process involves the detachment of oxycations, i.e. a dissolution/re-precipitation mechanism, or a certain weakening, with only a partial detachment of oxy-cation binding in the compact oxide layer. In the latter case the partially reduced cations are assumed to be displaced from normal lattice sites, and, as such, are more susceptible to oxidation in the subsequent anodic sweep during which they complete their oxygen coordination shell of six oxygen atoms to form a rather open polymeric inorganic bronze or zeolite type structure.

The upper limit of the potential sweep also has an important effect on the rate of oxide growth. The importance of this parameter lies in the fact that it extends oxygen penetration into the outer regions of the metal lattice, and may also help to generate a slight expansion and stress associated disruption of the metal/oxide interface. The upper potential limit may also facilitate uptake of a slight excess of oxygen by the oxide phase. A common observation in our studies is that there is an optimum value of upper limit. The fall of in oxide growth efficiency at more anodic values of applied potential may be associated with the increasing difficulty of reduction of the passivated surface film at lower potentials when the potential sweep is subject to reversal. Hence the optimum upper limit corresponds to a potential which represents the best compromise between two opposing effects. In short the compact layer must attain a reasonable thickness (hence the need for a relatively high anodic potential), but too high an upper limit results in a very un-reactive layer which does not reduce readily at the lower potential limit. Hence for most metals, but especially for the noble metals such as Au, Pt, Ir and Rh, extension of oxide growth beyond the monolayer level under conventional galvanostatic or potentiostatic (constant current or potential) conditions is usually quite slow. This is obviously due to the presence of the initial compact oxide product layer which acts as a passivating diffusive barrier to further growth via ion migration (such compact oxides often exhibit parabolic growth kinetics). In contrast under potential cycling conditions the upper limit plays a significant role. There is probably a combination of thermodynamic and kinetic factors involved, but evidently the upper limit must be sufficiently anodic that compact oxide formation exceeds significantly the single monolayer level so that on subsequent reduction, a disturbed, highly disordered layer of metal atoms is prepared on the metal surface (see fig.5). Thus with Pt and Au, two metals where oxide monolayer behaviour is well defined[14], the optimum lower limit lies at a potential value at, or below, the value of the monolayer oxide reduction peak. On subsequent re-oxidation the disturbed layer of metal atoms is converted to hydrated or partially hydrated oxide – complete hydration under these circumstances may involve several redox cycles- with a fresh inner compact layer being regenerated at the metal surface on each anodic sweep. On repetitive potential cycling the porous outer layer increases in thickness at the expense of the underlying metal.

Finally the decrease in oxide growth rate with number of cycles, time (or equivalently with increasing film thickness expressed quantitatively via $dQ/dN = ab\exp[-bN]$, can be attributed to the increasing inhibition of water and hydroxide ion transfer to the inner region of the oxide layer, with increasing hydrous oxide thickness. We have observed that this effect is more marked with increasing base concentration. Evidently, increased hydroxide ion activity suppresses hydroxide ion dissociation and/or favours adsorption of this species. This will result in the inhibition of crystallization of the hydrous oxide layer, and the resulting more amorphous film will be more effective in excluding water from the inner region of the oxide film, thereby inhibiting growth of the microdisperse hydrous layer.

Redox switching in multilayer hydrous oxide films

We now describe the electrochemical properties of hydrous oxyhydroxide thin film modified electrodes which are formed via potential cycling in aqueous base. We focus particular attention on nickel oxy-hydroxide films in which the metal oxide is deposited electrochemically on either a Ni or Au support surface. The discussion will focus on the redox switching reaction within the hydrous oxide layer in which the oxymetal sites charge oxidation state via potential induced topotactic redox reactions involving electron transfer between adjacent metal ion sites along the polymeric oxide strand and charge compensating counter ion transport within the solution region between the oxide strands. We focus attention on the latter process since it defines many of the practical applications of the oxide electrode such as its capacity to store charge (useful in supercapacitor applications), to change colour when the oxidation state is changed (electrochromic behaviour) and to serve as an effective pH and chemical sensor.

Typical cyclic voltammetric profiles recorded for multicycled (N = 30 cycles in both cases) Ni and Au electrodes modified with a nickel oxy-hydroxide film in contact with aqueous 1.0 M NaOH are outlined in fig.6. In fig .6(a) the oxide layer was grown on a Ni electrode in 1.0 M NaOH by cycling the potential between limits of – 1.45 V to 0.65 V (vs Hg/HgO) at a sweep rate of 150 mV/s. In fig.6(b) the oxide layer was deposited on an Au support surface from a deposition solution of 0.1 M $NiSO_4$, 0.1 M NaAc and 0.001 M NaOH between limits of – 0.90 to 1.20 V (vs SCE) at a sweep rate of 20 mV/s.

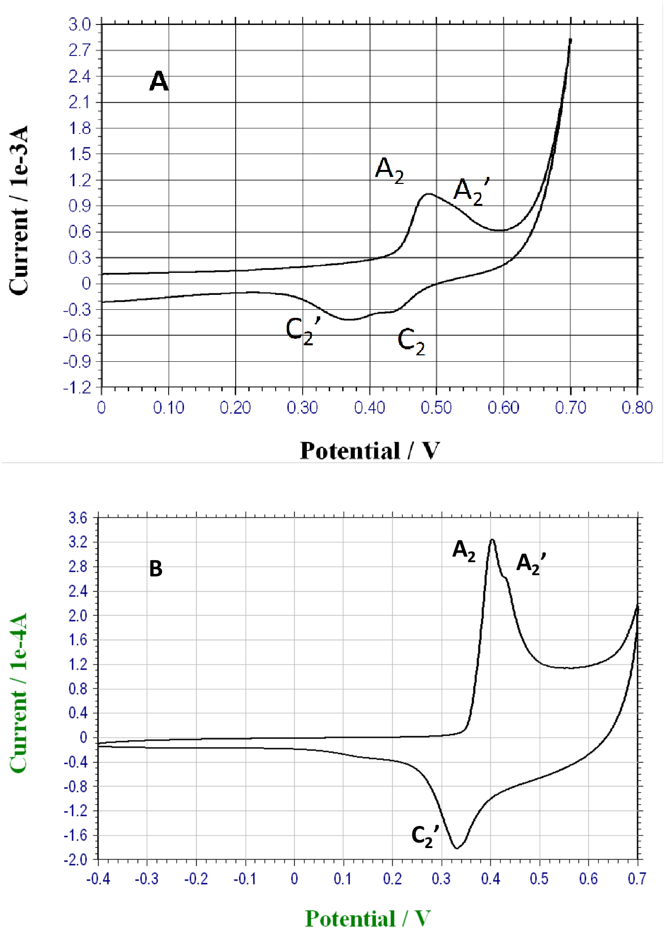
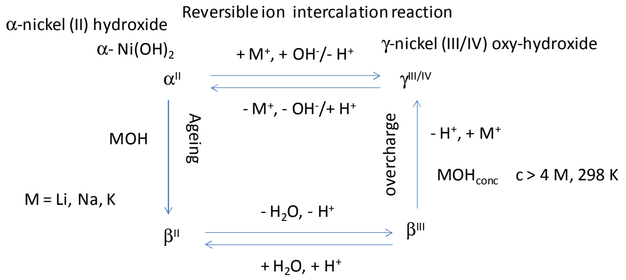


Figure 6 (a) Typical voltammetric response recorded for a hydrous nickel oxy-hydroxide thin film on Ni support electrode in 1.0 M NaOH. Sweep rate, 40 mV/s. Layer grown for N = 30 cycles. (b) Voltammetric response recorded for an electroprecipitated nickel oxyhydroxide modified Au electrode in 1.0 M NaOH. Sweep rate, 40 mV/s.

It is clear from fig. 6 that the voltammetric behaviour recorded for the nickel oxy-hydroxide thin films grown both on Ni and Au support electrodes is similar in that two sets of peaks may be observed in the potential region 0.30 – 0.60 V (vs Hg/HgO) prior to the onset of active water oxidation to generate molecular oxygen. These peaks correspond to redox reactions involving the transfer both of electrons and ions within the microdispersed oxide film. The interfacial redox chemistry of the multicycled nickel oxide electrode in aqueous alkaline solution can be readily understood in terms of the Bode scheme of squares[15] as presented in scheme 1 and fig.7 below.



Scheme 1. Bode square scheme for redox switching in nickel oxy-hydroxide thin films .

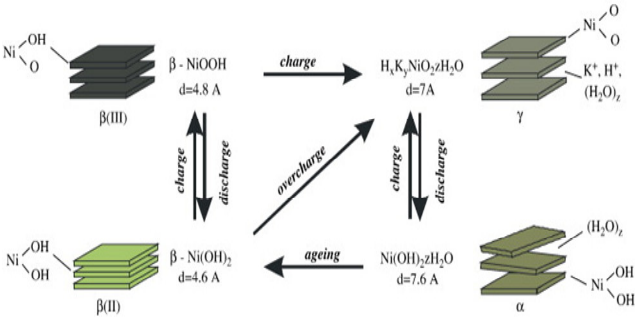


Figure 7. Structural representation of Bode square scheme.

The redox chemistry has been largely elucidated using electrogravimetric methods such as the Electrochemical Quartz Crystal microbalance which enables tiny mass changes which occur in the deposited thin film during redox switching to be monitored in real time[16]. Here the redox switching behaviour of electrochemically generated nickel oxide films was rationalized in terms of four phases as outlined in fig. 7. The discharged or reduced $Ni(OH)_2$ material can exist either as a largely anhydrous phase designated as β – $Ni(OH)_2$ (denoted β-Ni(II)) or as a hydrated phase denoted as α-$Ni(OH)_2$ (in short represented as α-Ni(II)). Oxidation of the β-Ni(II) material is envisaged to produce a phase referred to as β-NiOOH or β-Ni(III). In contrast oxidation of the α-Ni(II) material produces γ-Ni(III) or γ-NiOOH. Hence one expects two distinct redox transitions : α(II)/γ(III) which we label RT1 and β(II)/β(III) which is RT2. The corresponding redox peaks are designated A_2'/C_2' and A_2/C_2 respectively. A general representation of the RT1 and RT2 stoichiometry are outlined below.

We note that the redox potentials of RT1 is typically some 60-100 mV less positive than those of RT2. It can be noted from fig. 8 that upon ageing the α-$Ni(OH)_2$ can dehydrate and re-crystallize as β-$Ni(OH)_2$. This is especially prevalent in more concentrated alkali solution. In addition, overcharging β-NiOOH (which occurs at more elevated potentials) can convert it to γ-NiOOH. The non-stoichiometric nature of both the discharged and charged material is indicated by the average oxidation state of Ni in each phase as indicated in the structural representation of the various phases in fig. 7. It is important to note that while there is a general acceptance for the general features of the Bode scheme, one must understand that it is inappropriate to think about the formation of a compound or a phase with definite stoichiometry during the chemically complex $Ni(OH)_2$/NiOOH transformation. Instead the four phases mentioned in the Bode scheme should be considered as the limiting forms of the divalent and trivalent materials – the actual composition of the oxide at a given potential depending on a range of factors including its history, method of preparation, degree of hydration, defect concentration etc.

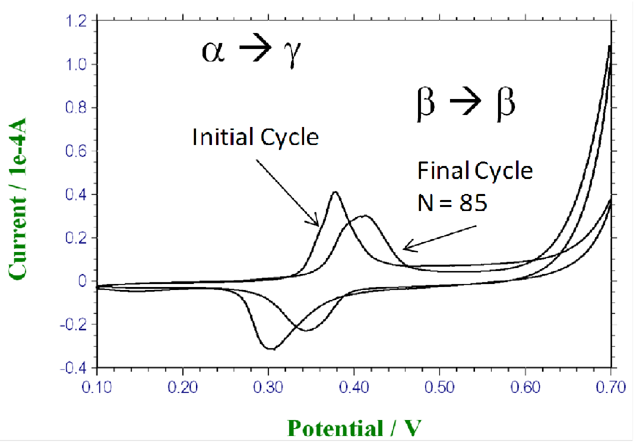


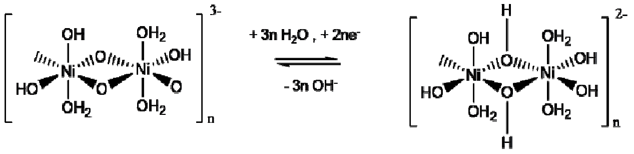
Figure 8. Typical voltammetric response recorded for an electroprecipitated nickel oxide film deposited on a polycrystalline gold substrate subjected to slow multicycling (sweep rate 10 mV/s) between 0.1 and 0.7 V (vs Hg/HgO) in 5.0 M NaOH. The initial and final response profiles are presented.

Burke and Lyons[17] and more lately, Lyons et al [18] have shown that, for an ideal oxide electrode system in aqueous solution at 25ºC, the potential decreases with increasing pH by ca. 59 mV/pH unit with respect to a pH independent reference electrode such as the NHE or the saturated calomel electrode (SCE). Such a potential-pH shift is referred to as a *Nernstian shift*, since it is predicted by the Nernst equation. Alternatively, if the reference electrode is pH dependent, such as the reversible hydrogen electrode (RHE) or the Hg/HgO electrode, no potential pH shift will be observed, since the potential of this type of electrode also alters by ca. 59 mV per unit change in pH at 25ºC. Furthermore, Burke and Lyons[17] have discussed super-Nernstian shifts that have been observed for various hydrous oxide systems – in these cases the potential/pH shift differs from the expected 0.059V/pH unit at 25°C. The mathematical treatment of this situation is beyond the scope of the present paper, but suffice to say, the phenomena have recently been qualitatively summarized[18]. Thus, a zero potential shift (with respect to a pH dependent reference electrode) implies that both the reactants and the product possess the same net charge. A positive potential shift with pH, is indicative of an oxidised state that is more positive than the reduced state, whereas the converse is true in the case of an observed negative potential/pH shift.

As previously shown[17,18] that the anhydrous A_2'/C'_2 peaks exhibit a regular Nernstian shift whereas the hydrous counterparts A_2/C_2 exhibit the characteristic of a hydrous or hyper-extended oxide i.e. *a super-nernstian potential-pH shift*, which typically has the value of $dE/dpH = -2.303(3RT/2F) = -0.088$V/pH unit at T = 298 K. Accordingly, by analogy with a scheme produced by Burke and Whelan[19] for redox switching of iridium oxide films, it has been proposed that the main redox switching reaction (corresponding to the peak set A_2/C_2) may be written as:

$$[Ni_2(OH)_6(OH_2)_3]_n^{2-} + 3nOH^- \rightarrow [Ni_2O_3(OH)_3(OH_2)_3]_n^{3-} + 3nH_2O + 2ne^- \quad (8)$$

corresponding to an Ni(II)/Ni(III) redox transition in a polymeric microdispersed hydrous oxide layer. This redox switching reaction is illustrated schematically in scheme 2.



Scheme 2. Redox switching in hydrous nickel oxy-hydroxide matrix involving electron/ion exchange.

The redox switching reaction (associated with the A_2/C_2 voltammetric peaks) reflects the change in oxidation state of the film as a result of a potential perturbation. Redox centres immediately adjacent to the support electrode are directly affected by the electrode potential, whereas charge is further propagated along the oxy-nickel polymer strands in the hydrous layer via a sequence of electron self exchange reactions between neighbouring oxy-metal sites. This process is envisaged to be analogous to redox conduction exhibited by electroactive polymer films. In the simplest terms this electron "hopping" may be modelled in terms of a diffusional process, and so the charge percolation rate may be quantified in terms of a *charge transport diffusion coefficient*, D_{CT} or in terms of a diffusive frequency $\tau = D_{CT}/L^2$ where L denotes the thickness of the oxide film. . In the case of hydrous nickel oxide, the latter may reflect either the electron hopping rate or the diffusion of of OH^- (or equivalently H_3O^+) ions via a rapid Grotthuss type mechanism. The charge transport diffusion coefficient may be quantitatively estimated using cyclic voltammetry [20]. The important point to note is that redox switching in the oxide involves electron and ion transport. The Ni(II)/Ni(III) redox transition occurs within a polymeric microdispersed oxide consisting of polymer strands comprising of interlinked octahedrally coordinated surfaquo groups. The assembly can be regarded as a dual rail electrical transmission line of the type presented in fig.9 for porous modified electrodes[21]. Hence the charge transport through the layer can be characterized in terms of characteristic resistances for electron and counter-ion motion along the oxide polymer strands and within the solution filled pores between the oxide strands. This type of conductivity characterization can be best accomplished using Electrochemical Impedance Spectroscopy[21]. The latter technique is very powerful and has been applied to mixed conducting systems in thin film form such as metal oxides and electronically conducting polymers[22].

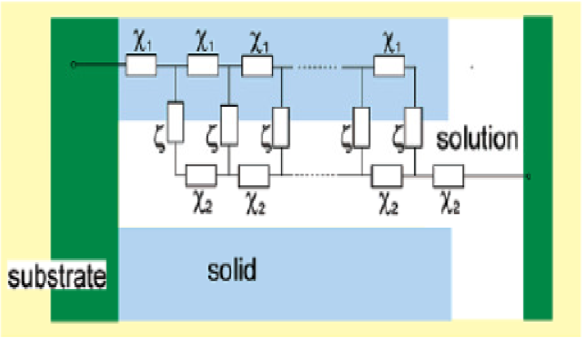


Figure 9 Dual rail transmission line model for porous thin film mixed electronic/ionic conductor. Note that χ_1 and χ_2 corresponds to the specific conductivity of the solid oxide phase and electrolyte solution respectively and ζ represents the specific polarization/charge transfer element at the solid/solution interface.

Multilayer hydrous oxide films as potential pH sensors

The fact that nickel oxy-hydroxide films exhibit a Super-Nernstian decrease in the peak potential associated with the Ni(II)/Ni(III) surface redox switching with increasing solution pH is significant for two reasons. The first signifier is that the oxy metal species must be anionic [17,18]. The second is that the oxide film may prove useful for pH detection. The variation is open circuit potential with solution pH for an electroprecipitated nickel oxy-hydroxide film on a gold substrate is presented schematically in figure 10. The open circuit potential was recorded for a range of time scales varying from 200 to 15,000 seconds. A good linear response of potential to changes in solution pH was recorded. The slope or super-Nernstian with $dE_{OC}/d\text{ pH} = -0.080$ V/dec and $r^2 = 0.95$. The behaviour of the oxide pH sensor was examined by monitoring the response of the latter to the rapid changes in solution pH encountered during the course of a pH titration. The titration of 1M sulphuric acid H_2SO_4 with a strong base (50 mL 1 M NaOH) was monitored in real time using both a conventional glass electrode and the metal oxide modified electrode. The open circuit of the latter was determined as a function of volume of strong acid added to the reaction mixture.

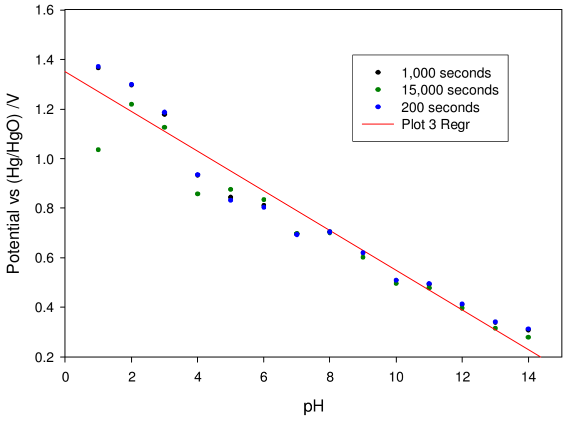


Figure 10 Variation of open circuit potential recorded at an electroprecipitated nickel oxyhydroxide modified gold electrode as a function of solution pH (the latter measured using a glass electrode).

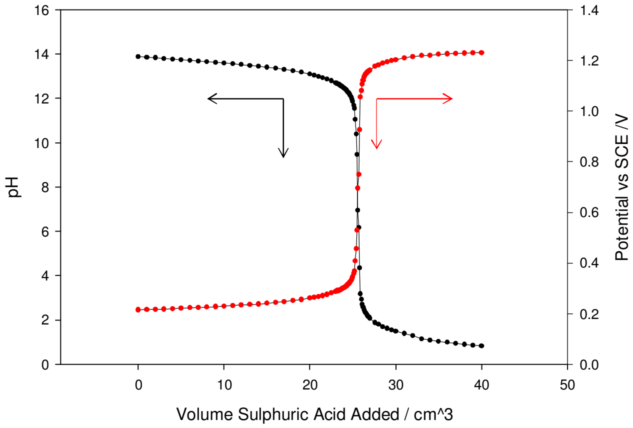


Figure 11 Variation of open circuit potential recorded at an electroprecipitated nickel oxyhydroxide modified gold electrode as a function of solution pH (the latter measured using a glass electrode) during the course of a strong acid/strong base titration.

It is indeed gratifying to note that the metal oxide wire electrode potential (measured with respect to a SCE reference electrode) monitors accurately the change in solution pH (measured using a commercial glass electrode system). The solid state pH sensor responds very rapidly to the rapid changes in pH recorded near the equivalence point. As the solution becomes more alkaline the open circuit potential of the oxide electrodes increases in a well defined manner. The metal oxide electrode accurately predicts the position of the equivalence point. Furthermore we have shown that an excellent correlation exists between the pH value calculated from the E_{OC} magnitude and that experimentally measured using a commercial glass electrode. Hence we conclude that electro-precipitated nickel oxyhydroxide thin film electrodes offer potential as novel pH sensors[23] .

The kinetics and mechanism of electrolytic water oxidation to generate molecular oxygen

The generation of molecular oxygen via electrolysis of water (OER) is a complex and energetically demanding reaction. The reversible potential in alkaline solution is 0.303 V (vs Hg/HgO). However in order to generate oxygen at an appreciable rate an overpotential of several hundred millivolts may be required. The net reaction takes the following form

$$O_2 + 2H_2O + 4e^- \leftrightarrows 4OH^- \qquad (9)$$

Hence the process may be regarded as a proton coupled electron transfer process which occurs over a number of steps which will include both electron transfer and chemical steps, and will also involve adsorbed intermediates. The surface coverage of reaction intermediates may well vary with electrode potential. Consequently the analysis of the oxygen evolution reaction thermodynamics and kinetics is challenging. In recent years the TEECE group at Trinity College have made significant progress in the understanding of the OER. First it must be noted that the OER at oxidized metal and metal oxide electrodes involves the active participation of the oxide. Second, the acid/base behaviour of the oxide layer is an important factor : the oxide is anionic (as noted previously when discussing super-Nernstian behaviour (see fig. 12 for nickel oxy-hydroxide thin films grown on Ni metal support surfaces), and, as illustrated in fig.13 for nickel oxy-hydroxide thin films grown on nickel electrodes in aqueous base the OER onset potential decreases in a linear manner to less positive potentials with increasing solution pH which mirrors the variation of the redox switching peaks. Third, the activity of the oxide film can be ascribed to the presence of active surface or surfaquo groups which are octahedrally co-ordinated and interlinked throughout the hydrous oxide matrix. Hence the catalysis of oxidative water splitting is three dimensional. These ideas have been recently reviewed by Lyons and co-workers[24].

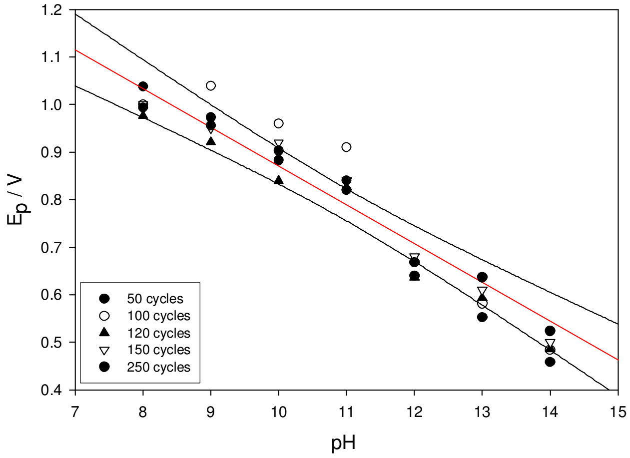


Figure 12 Variation of anodic A_2 peak potential with solution pH. Slope = - 0.082 V, r^2 = 0.96. Data measured for layers of various thickness. Nickel oxy-hydroxide layer grown via potential cycling in 1.0 M NaOH on Ni support electrodes.

The classic approach adopted to examine the kinetics of the OER at metal oxide and oxidized metal electrodes has been the use of an ensemble of steady state and transient electrochemical techniques such as Tafel Plot Polarization, Open Circuit Potential Decay (OCPD) and Electrochemical Impedance Spectroscopy[22]. These measurements yield key parameters such as the Tafel slope b and the reaction order m of the mechanistically significant reactant such as the hydroxide ion when studies are conducted in alkaline solution. The latter data are of mechanistic significance and can be used to propose a chemically meaningful step by step mechanism for the multistep OER . Electrochemical impedance spectroscopy data can be directly fitted to a proposed electrical equivalent circuit which is developed from a mathematical analysis of the proposed OER mechanistic sequence. The components of the equivalent circuit (resistors, capacitors etc) can in many cases be assigned to physically meaningful parameters and processes such as rate constants (via Faradaic impedance), film resistances, and ionic and electronic transport rates.

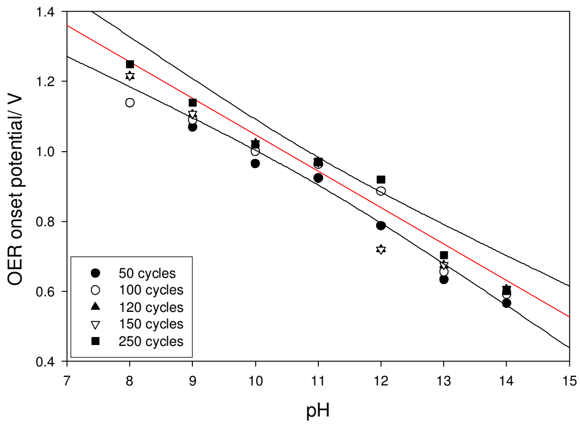


Figure 13 Variation of oxygen evolution onset potential with solution pH. Slope = - 0.104 V/dec, r^2 = 0.97. Data measured for layers of various thickness. Nickel oxy-hydroxide layer grown via potential cycling in 1.0 M NaOH on Ni support electrodes.

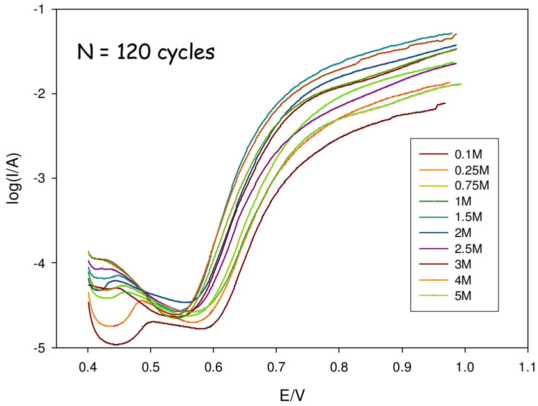


Figure 14 Typical Tafel plots for OER at multicycled nickel oxy-hydroxide thin films grown for N = 120 cycles in 1 M NaOH. Plots were recorded as function of base concentration.

Typical Tafel plots for oxygen evolution at hydrous nickel oxy-hydroxide thin films grown via potential cycling (N = 120 cycles) on Ni support electrodes are presented in fig.14. The latter data is expressed in conventional Tafel format where the OER rate is expressed as the logarithm of the current and the reaction driving force is the electrode potential. According to the Tafel equation the OER rate is exponentially dependent of the applied potential. The Tafel slope b is given by b = dE/d log i. We note dual Tafel slope behaviour with a slope of 60 mV/dec at low potentials and 120 mV/dec at higher potentials. The latter values are mechanistically significant. The reaction order is obtained by plotting the logarithm of the oxygen evolution current density recorded at a fixed electrode potential as a function of the logarithm of the hydroxide ion activity. This was done for potentials located in the low and high Tafel slope region at typical values of reaction order were $m_{OH^-} \approx 0.9$. Similar results were obtained for electro-precipitated nickel oxy-hydroxide films grown on gold support electrodes.

We have recently proposed[25] that the following set of reaction steps may be proposed to account for the mechanism of electrochemical oxygen evolution at nickel oxy-hydroxide electrodes in aqueous alkaline solution. Our mechanistic thinking is guided by the earlier work of Kobussen and Broers[26] . The mechanism is presented in schematic form in scheme B. Note that octahedrally co-ordinated oxy-nickel surfaquo groups are identified as the catalytically active species and are located within the hydrous layer. The following reaction sequence based on scheme B may be outlined:

$$SOH_2 + OH^- \rightarrow SOH^- + H_2O \qquad (10)$$

$$SOH^- \rightarrow SOH + e^- \qquad (11)$$

$$SOH + OH^- \rightarrow SO^- + H_2O \qquad (12)$$

$$SO^- \rightarrow SO + e^- \qquad (13)$$

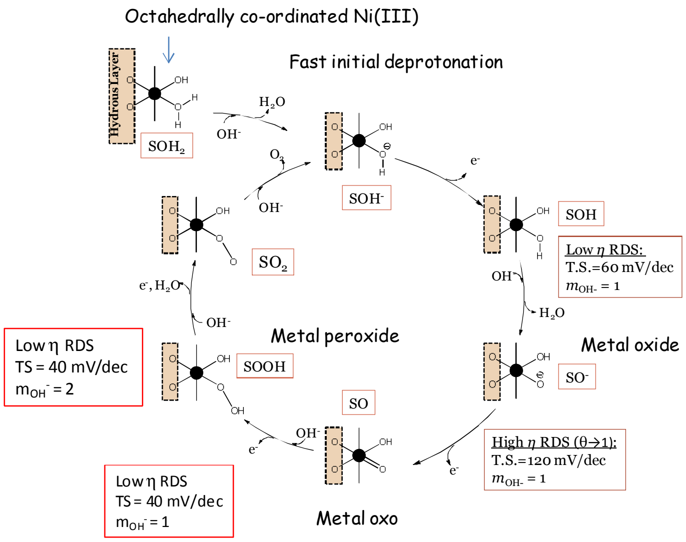
$$SO + OH^- \rightarrow SOOH + e^- \qquad (14)$$

$$SOOH + OH^- \rightarrow SO_2 + H_2O + e^- \qquad (15)$$

$$SO_2 + OH^- \rightarrow SOH^- + O_2 \qquad (16)$$

In the latter scheme S represents the surfaquo group which is attached to the hydrous oxide surface by bridging oxygen ligands.

The Lyons-Doyle reaction sequence[25] is presented schematically in scheme 3 The initial deprotonation step involves a bound water molecule attached to an octahedrally co-ordinated Ni(III) surfaquo group located within the hydrous layer. A common feature of these schemes is that the starting point for the OER catalytic cycle is usually represented as a metal coordinated water molecule. However, in the strongly alkaline conditions used in this system it is likely that a significant proportion of these coordinated water molecules will be deprotonated. The pK_a value for a water molecule coordinated to a highly charged metal atom is generally in the range pK_a 5-9 [27]. In light of this, it is more reasonable to assume that the initial deprotonation step expressed in eqn.10 is facile and will occur outside of the catalytic cycle.



Scheme 3. Lyons Doyle reaction sequence for electrolytic generation of molecular di-oxygen at nickel oxygroups located within the hydrous oxide layer in aqueous alkaline solution.

Hence, the initial deprotonation step is depicted as a pre-step in Scheme 3 and the OER catalytic cycle begins with the resultant coordinated OH^- ion which we label SOH^-. A second point of note regarding Scheme B is that the formation of the metal oxide SO^- (eqn.12) and metal oxo SO (eqn. 13) species are designated as rate determining. Interestingly, in a recent theoretical study Muckermann *et al.* [28] showed, through the use of DFT calculations, that for a GaN/ZnO surface with high coverage of adsorbed OH^- ions the intermediate associated with the highest energy was an oxide radical. Similarly, Rossmeisl *et al.* [29] performed a DFT study of the OER at RuO_2 surfaces. They too found, for a surface saturated with adsorbed OH, that the highest energy intermediate was a surface oxygen species, in this case an oxo species. Considering these studies, the present mechanistic interpretation brings together a number of strands in the current understanding of the OER at metal oxides, and resonates with recent work proposed for water oxidation using transition metal complexes in homogeneous solution. The 60 mV/dec Tafel slope and associated reaction order of unity is associated with rate determining generation of metal oxide species (eqn.12) whereas the Tafel slope of 120 mV/dec observed for all base concentrations at high potentials and associated unity reaction order with respect to hydroxide ion activity is rationalized by assuming that the decomposition of metal oxide to form metal oxo species is slow and rate determining (eqn.13). We also note from scheme 3 that rate determining decomposition of the nickel oxo species or indeed rate determining decomposition of the nickel peroxide moiety would suggest a different set of diagnostic parameters, namely low potential Tafel slope values of ca. 40 mV/dec for both options and reaction orders wrt hydroxide ion activity of 1 and 2 for oxo decomposition (eqn.14) and peroxide decomposition (eqn.15) respectively. The catalytic cycle illustrated in scheme 3 has been used to rationalize the OER kinetics and mechanism both at hydrous Fe and Ni oxy-hydroxide thin film modified electrodes. One of the key steps in our proposed mechanism involves the formation of a surface bound metal oxo species (SO). In scheme 3 above this species is depected as M=O suggesting a M(V) metal centre. However, this species could also be represented as a metal oxyl moiety M(IV)-O· . Indeed the degree of radical character has been shown to depend on the length of the metal oxo bond with M(V)=O being more stable for shorter bond lengths[30]. In the case of Fe the metal oxo species possibly involves Fe(V) [31] as inferred from recent variable temperature mass spectrometry data obtained for a biomimetric non-heme Fe complex with an Fe(V) oxo as the catalytic centre. The situation in the case of Ni is less clear. The Ni-O bond may be longer and have a greater radical character and a Ni(IV) oxyl intermediate may be the better descriptor of the situation.

The important point to note is that the surfaquo group structures outlined in the catalytic cycle presented in scheme 3 reflects current thinking in the allied field of water oxidation in homogeneous solution via molecular catalysts [32]. This is not unexpected given the very dispersed and somewhat tenuous nature of the catalytically active hydrous oxide layer which we postulate to be formed electrochemically on the electrode surface after cyclic polarization of the support electrode in aqueous alkaline solution.

Concluding Remarks and Future Outlook

In this paper we have presented a survey of some recent work on electrochemically prepared nickel oxy-hydroxide materials deposited as thin films on conductive gold and nickel support surfaces. The redox chemistry of the latter materials has been described in terms of electron transfer along connected surfaquo groups located within a microdispersed polymeric matrix of oxide strands immobilized on the support electrode surface. The application of these films as new generation solid state pH sensors and as efficient electrocatalysts for the electrolytic generation of molecular di-oxygen gas has been demonstrated. We have noted that the acid/base behaviour of the electrochemically prepared films is an important factor to take into account when considering the mechanism of oxygen evolution. An important new mechanism has been proposed for the OER at nickel oxide modified electrodes based on electrochemical, spectroscopic and DFT studies both in our laboratory and in others. We conclude that metal oxide and oxo species are active intermediates in the multistep OER under electrochemical conditions in aqueous solution. Indeed we can conclude that the chemistry of the surfaquo group determines the chemistry of the OER catalytic cycle.

Acknowledgements

This publication has emanated in part from research conducted with the financial support of Science Foundation Ireland (SFI) under grant number SFI/10/IN.1/I2969. The authors would like to thank Dr Michael Brandon and Prof Paula Colavita for useful discussions MEGL would like to acknowledge the late Prof. L.D. Burke for introducing him to the fascinating and important topic of metal oxide electrochemistry many years ago. For information regarding postgraduate and postdoctoral research opportunities please do not hesitate to email melyons@tcd.ie

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IRISH CHEMICAL NEWS

Research Article

Monolayer- Protected Gold Nanoparticles in Etched Open-Tubular Capillary Electrochromatography

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Introduction

Open-tubular capillary electrokinetic chromatography (OTCEC) has shown great potential for high efficiency and resolution coupled with short separation times compared with conventional liquid chromatography. However the OT format has always suffered from low phase ratio limitations, which has sometimes resulted in the adoption of alterative phases, such as monolithic or packed beds for separation. In response to this, Pesek *et al.* has published a number of works highlighting the potential of chemical etching to overcome these low phase ratio challenges. Also this work has shown that proteins and peptides are ideal candidates for separation on chemically etched capillary columns. In earlier work, Pesek showed the separation of lysozyme (turkey), angiotensin III, bradykinin, ribonuclease A and angiotensin I in less than 10 min, and the effects of pH and percentage organic modifier (MeOH) were studied to optimize the separation [1]. The same group [2] investigated the effects of various chemical modification methods on etched capillaries, using basic molecules and proteins and peptides: tryptamine, cytochrome c, and lysozyme as target analytes.

In OTCEC the stationary phase can be easily tailored to suit many kinds of analytes being separated, because of its unique separation properties, (electrophoretic mobility and hydrophobic interaction), unwanted adsorption effects associated with protein and peptides can be at least partially eliminated. In packed CEC, surface silanols can interact with the basic functional groups present on proteins and peptides, whereas, in a typical etched capillary the number of accessible silanol groups is quite small, so this kind of interaction is significantly minimized [3]. Some other advantages of the OT approach is the elimination of the need for tedious and irreproducible frit formation, also simple instrument handling eliminates the need for high pressure capillary packing equipment, and pressurization of vials is not necessary.

Two strategies have been devised to overcome the low phase ratio challenges: firstly the extended light path (ELP) capillary which has a bubble cell at the detection point is used to improve sensitivity. Li and co-workers showed that on using a 20 µm internal diameter capillary in conjunction with a 150 µm bubble cell, peak height was enhanced by a factor of 4-10 fold, however peak efficiency and resolution suffered [4]. Secondly, as mentioned earlier, etching can counteract effects associated with the small amount of stationary phase present and the large distance that solutes must travel to interact with the phase [5]. The etching process involves exposing the inner walls of a fused silica capillary to a corrosive agent such as ammonium hydrogen-difluoride at elevated temperatures (300-400 ^oC), usually for three to four hours. This results in dissolution of the inner walls, followed by redeposition of these inner capillary walls, resulting in changes in inner wall morphology, in turn increasing the surface area. The new surface, now in the form of a series of hills and sand dunes or large silica pieces, can also have radial extensions of up to 5 µm, which reduce the distance necessary for solute-bonded phase interactions. This has shown to increase the surface area as great as 1000 fold or more, and much of the literature is dominated by reports of Pesek and co-workers advocating this approach towards OT based separations for protein and peptide applications [1, 6].

With regards to characterization, Scanning electron microscopy (SEM) and atomic force microscopy (AFM) can provide valuable topographical but not chemical information about the surface [7]. Pesek and co-workers observed a tendency of EOF reversal in etched capillaries at low pH. At a pH below ~ 4.5, a small anodic EOF was attributed to an impurity in the etching agent or the ammonium ion being incorporated into the silica matrix [7]. The same group concluded that elements from the etching agent, nitrogen and fluoride form part of the new surface, which at low pH; the nitrogen's become protonated and give a net positive charge to the inner wall. When the pH is raised, nitrogen is deprotonated, the silanols ionize, and in conjunction with the negatively charged fluoride species give a cathodic EOF [2]. This interesting feature greatly reduces unwanted adsorption interactions between silanols and basic species such as pharmaceuticals, peptides and proteins.

To date, micro- and nanotechnology have had a major impact on biomedical applications, some application areas include, aerosol sprays, anti-cancer treatments, drug loaded micro-fabricated particles, with specific ligands linked to the surface to improve oral bioavailability of peptides and protein drugs. In separation science, nanoparticles have been most widely used in capillary electrophoresis and CEC. As previously mentioned, Pesek *et al.* has shown that peptides and protein are ideal hosts for separation on etched chemically modified capillaries. Other authors such as Kleindienst *et al.* [8] showed the use of polystyrene particles in OT separation of basic and acidic proteins with efficiencies up to (1,900,000 theoretical plates/m). We previously reviewed the role of nanoparticles in separation science [9], more recently Liu [10] reviewed applications and analysis of gold nanoparticles in separation science.

In this work, fused-silica capillary was etched with ammonium hydrogen difluoride to the increase surface area, prior to derivatization with MPTMS and octadecanethiol gold nanoparticles. The electrochromatographic properties were investigated with regard to pH, applied potential, organic modifier and temperature. Efficient separations of a reversed phase test mixture and PAHs are presented. This study shows some new results using octadecanethiol gold nanoparticles and a more in depth characterization, as opposed to our previous work, which focused on dodecanethiol gold nanoparticles [11].

2.0 Results and discussion

2.1 Fourier transform infrared (FTIR) spectrum of octadecanethiol gold nanoparticles

The main objectives of obtaining IR spectra were to establish that the S-H bond of the alkanethiol had been broken due to the newly formed S-C linkage as part of our in depth characterization study. Also to confirm the presence of the octadecanethiol-gold nanoparticle ligand. The strong intensity of the methylene groups present in the C-H stretching region (2800-3000 cm^{-1}) suggests the presence of the alkanethiol ligand. Strong intensity symmetric and asymmetric CH_2 stretching bands are readily observable at wavenumbers of 2857 and 2923 cm^{-1}, with an obscured and less intense asymmetric band also present at a wavenumber of 2955 cm^{-1}. In figure 1, antisymmetric (d^-) and symmetric (d^+) stretches are evident. The bands of weak intensity at (2955 cm^{-1}), strong intensity at (2923 cm^{-1}), and medium intensity at (2857 cm^{-1}), are entirely consistent with those reported in the literature. Hostetler and co-workers [14] attached different straight alkyl straight chain lengths to gold clusters, and studied the effects of attachment using FTIR. They reported bands at (2954, 2918, 2848 cm^{-1}) of weak, strong and medium intensity, for dodecanethiol-stable gold cluster compound. They observed that with increasing the number of carbons on the alkyl chain, the intensity of these bands changed.

In the region (1400-1500 cm^{-1}), the literature reports four bands associated with straight alkane chains. For alkanethiols larger than C_3, (1463 cm^{-1}) is due to methylene scissoring, the weak band at (1466 cm^{-1}) in the spectrum below could be due to this behaviour. Other bands in this region have proven difficult to interpret but could be assigned to methylene scissoring and CH_2-S methylene scissoring. The more pronounced percentage transmittance was observed by Hostetler and co-workers [14] on increasing the carbon chain. As more functional groups of the same kind are present, there must be more vibrational movement taking place. The bands occurring in the region (1400-1500 cm^{-1} are most likely attributable to methyl antisymmetric bending ~ (1463 cm^{-1}). The band at (1387 cm^{-1}) could be due to methyl symmetric bending vibration which occurs ~ (1375 cm^{-1}). Both the C-S and S-H bonds are often too weak to observe, but the presence of the ligands were confirmed and the absence of the S-H bond was noted. It can be concluded that the FTIR spectrum of the nanoparticles beared close resemblance to the alkanethiols from which they were synthesized.

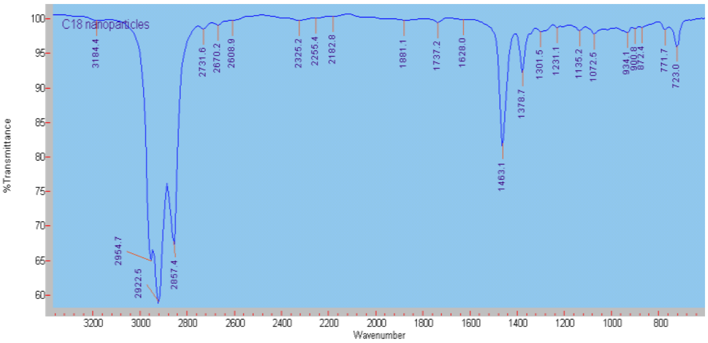

Figure 1. FTIR spectrum of octadecanethiol gold nanoparticles dispersed in hexane.

2.2 Investigation of electroosmotic flow characteristics with inner wall modification

In order to investigate changes in the electoosmotic flow (EOF) accompanying etching, chemical derivatization and immobilization of the nanoparticle stationary phase, EOF velocity was studied as a function of separation voltage. As expected, the bare fused silica capillary (figure 2) displays the highest EOF velocity. The capillary with an etched inner surface shows a significantly lower EOF velocity, due to the reduction in the number of silanol groups. The capillaries derivatized with the organosilane coupling agent MPTMS, and chemisorbed with gold nanoparticles display lower EOF velocities. The MPTMS provides further shielding of surface silanols which further reduces the EOF, while the gold nanoparticles assembled on the thiol moieties provides even more silanol shielding showing the lowest EOF velocity.

2.3 Effect of variation of percentage organic modifier on reversed-phase behaviour

The dodecanethiol and octadecanethiol gold nanoparticles act as novel stationary phases for OTCEC, by imparting hydrophobicity to the surface. It is apparent from figure 3 that on increasing the percentage methanol, there was a linear decrease in log *k′* for neutral solutes naphthalene and biphenyl. In this case, as the percentage methanol was increased, the retention times of naphthalene and biphenyl decreased while efficiency increased. In order to confirm that electrochromatographic

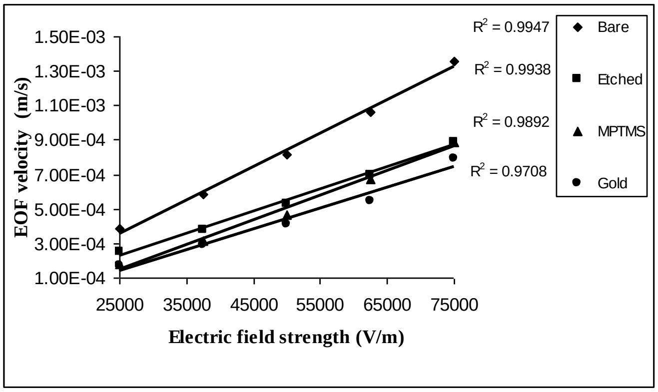

Figure 2. Effect of applied electric field strength on EOF flow velocity in various capillaries (bare, etched, etched-MPTMS, and etched-MPTMS-gold nanoparticles in hexane). Conditions: 40 cm (L_{tot}), 31.5 cm (L_{eff}) x 50 µm I.D., MeOH-25 m*M* Na_2HPO_4 pH 7.0 (60:40). Sample: 3 m*M* thiourea methanol- water (70:30)). Injection: 34.5 mbar for 4 s. UV detection 214 nm.

retention was due solely to the presence of the gold nanoparticles, separation of these neutral solutes was attempted on an etched-MPTMS capillary column. The results of which showed that little separation, but no effective separation occurred, and naphthalene and biphenyl eluted much faster, and unresolved close to the EOF marker.

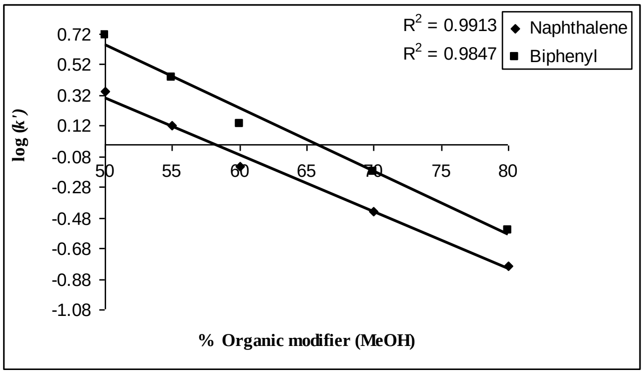

Figure 3. Plot of the logarithm of capacity factor, (*k'*) versus percentage organic modifier for naphthalene and biphenyl (0.1 g/L) in methanol-water (70:30) on an etched-MPTMS-gold nanoparticle coated capillary 39 cm (L_{tot}) 30.5 cm (L_{eff}) x µm 50 I.D. Conditions: MeOH-25 m*M* Na_2HPO_4 pH 7.0. Injection: 50 mbar for 15 s, separation voltage 25 kV, UV detection 214 nm.

2.4 Effect of variation of pH on EOF characteristics with inner wall modification

The pH of the buffer was varied between (pH 3.1 and 9.0) and studied for its effect on electroosmotic mobility. As expected, the bare capillary displayed the highest EOF mobility, due to having the greatest number of ionized silanol groups present. There were significantly lower mobilities after etching, derivatizing and stationary phase bonding, with the gold nanoparticle coated capillary showing greatest silanol shielding effect. As mentioned earlier, the anodic pH effect observed by Pesek *et al.* was not seen here. Interestingly after etching, chemical derivatization and stationary phase immobilization, there is still a small but adequate EOF to allow solutes to reach the cathode.

2.5 Effect of column temperature on retention characteristics of OT octadecanethiol gold nanoparticle coated capillaries

To examine the effect of temperature on resolution, separation speed, along with chromatographic retention, the capillary column temperature was varied in the range (10 °C - 30°C). As figures 4 and 5 illustrate, resolution (R_s=6, 3) for naphthalene and biphenyl was higher at (10°C) as opposed to a column temperature of (20°C). Temperature influences EOF velocity through affecting the zeta potential and the mobile phase viscosity. Figure 6 shows a pronounced increase in resolution accompanying a decrease in column temperature. It has been concluded here, that temperature affects the EOF velocity and solute-bonded interactions and is a quick and easy way of manipulating resolution and selectivity.

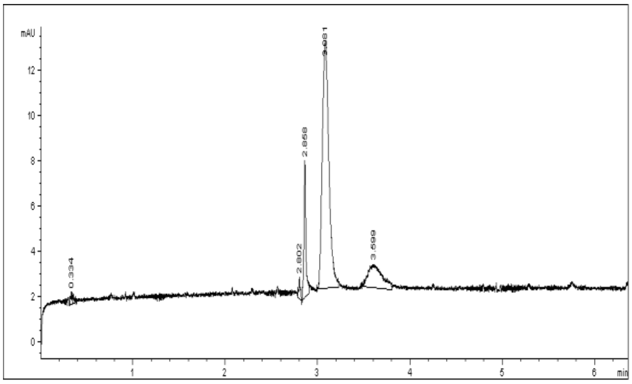

Figure 4. Electrochromatogram showing thiourea, naphthalene, biphenyl (0.1 g/L) in methanol-water (70:30) on a etched- MPTMS-octadecanethiol-gold nanoparticle coated capillary 39 cm (L_{tot}), 30.5 cm (L_{eff}) x 50 µm I.D. Conditions: MeOH-25 m*M* Na_2HPO_4 pH 7.0 (30:70).Injection: 50 mbar for 2s, separation voltage 30 kV, UV detection 214 nm, column temperature (20°C).

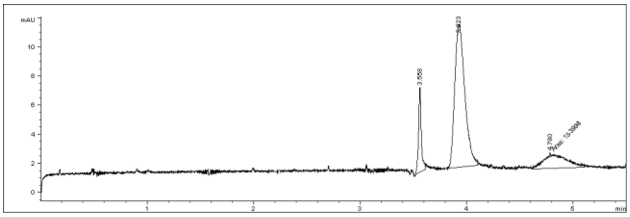

Figure 5. Electrochromatogram showing thiourea, naphthalene, biphenyl (0.1 g/L) in methanol- water (70:30) on a etched- MPTMS-octadecanethiol-gold nanoparticle coated capillary 39 cm (L_{tot}), 30.5 cm (L_{eff}) x 50 µm I.D. Conditions: MeOH-25 m*M* Na_2HPO_4 pH 7.0 (30:70).Injection: 50 mbar for 2 s, separation voltage 30 kV,UV detection 214 nm, column temperature (10°C).

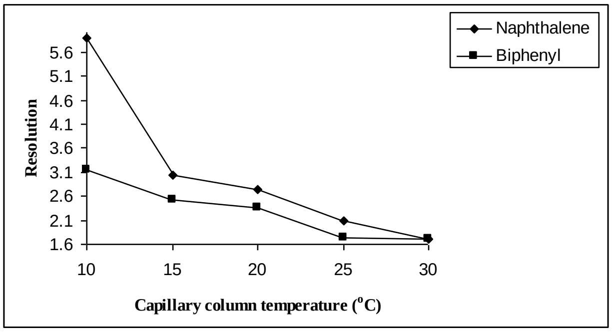

Figure 6. Effect of variation of column temperature on resolution. Conditions: etched- MPTMS-octadecanethiol-gold nanoparticle capillary 39 cm (L_{tot}) 30.5 cm (L_{eff}) x 50 µm I.D. MeOH-25 m*M* Na_2HPO_4 (30:70). Sample: thiourea, Naphthalene, biphenyl (0.1 g/L) methanol- water (70:30)). Separation voltage 30 kV, injection: 50 mbar for 2 s. UV detection 214 nm.

2.6 Electrochromatographic retention characteristics of loosely coated OT-dodecanethiol- gold nanoparticle coated capillaries

The electrochromatographic retention ability of a loosely coated alkylthiol gold nanoparticle capillary in the absence of the etching step was investigated. The loosely coated capillary displayed theoretical plates of (49,000/m and 16,000/m) for naphthalene and biphenyl respectively at a separation voltage of 25 kV. However after performing 25 consecutive injections, the separation performance deteriorated rapidly. A probable explanation for this loss in separation performance may be due to the absence of the organsilane coupling agent MPTMS which allowed for chemisorption of the gold nanoparticles onto the thiol functionality. After 25 replicate injections of the neutral solute mixture, there was a tendency for the retention times to become shorter. This is in agreement with the explanation that as the stationary phase is being slightly washed off, more silanol groups are being exposed and the EOF is becoming stronger. These shorter retention times of the neutral solutes, however may be primarily a result of the decrease in the solute-bonded interactions, due to the fact that the stationary phase is being progressively washed away.

2.7 Applications of OT etched octadecanethiol gold nanoparticle coated capillaries

An obvious application of this novel etched-MPTMS-alkylthiol gold nanoparticle capillary column is in the separation of peptides, proteins, pharmaceuticals and polyaromatic hydrocarbons (PAHs). The etched octadecanethiol-gold nanoparticle capillary column gave a partial separation of PAHs: naphthalene and phenacetin as shown in figure 7. The number of theoretical plates obtained for phenacetin and naphthalene were 141,000/m and 16,000/m respectively. The separations were achieved in less than 6 minutes. This highlights the potential for future application of these etched gold nanoparticle stationary phases.

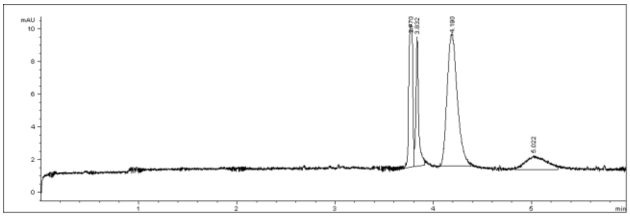

Figure7.Electrochromatogram showing thiourea, phenacetin, naphthalene, biphenyl, (0.1 g/L) in methanol-water (70:30) on a etched-MPTMS-octadecanethiol-gold nanoparticle coated capillary 39 cm (L_{tot}), 30.5 cm (L_{eff}) x 50 µm I.D. Conditions: MeOH-25 m*M* Na_2HPO_4 pH 7.0 (30:70).Injection: 50 mbar for 2 s, separation voltage 30 kV,UV detection 214 nm, column temperature (10°C).

Concluding Remarks and Future Outlook

OT capillary columns were etched to increase the surface area, which increased solute-bonded interactions between the nanoparticle stationary phase and the neutral analytes. This preliminary work showed that these novel capillary columns were capable of resolving neutral solutes with relatively high efficiency using dodecanethiol or octadecanethiol gold nanoparticles. This is great potential here for further studies using these etched nanoparticle coated capillaries for separation of a range of proteins and peptides. The silanol shielding due to the etching process should greatly decrease unwanted adsorption effects associated with basic functional groups on protein structures.

By way of in-depth characterization, the reversed-phase properties of these etched-MPTMS-alkyl-thiolated-gold nanoparticle capillary columns were confirmed by changes in capacity factor with organic modifier composition, and by variation of column temperature. The EOF properties of these capillary columns were further investigated by the effect of variation of voltage on EOF velocity and also a column reproducibility study. For nanoparticle characterization, FTIR confirmed the successful synthesis of the nanoparticles. The changes in inner wall morphology as a result of etching were observed by SEM analysis. The resolution of selected neutral solutes demonstrated the potential of these etched nanoparticle capillary columns as a suitable alternative to the more conventional octadecylsilica bonded columns. In separation science, the fact that nanoparticles can be easily functionalized with a range of stationary phase chemistries, while simultaneously possessing the ability to form self-assembled monolayers (SAM) has been readily exploited. Once these nanomaterials have been functionalized with a stabilizing ligand, no signs of agglomeration are obvious and the particles appear stable for very long periods and can be easily re-suspended in organic or aqueous solution. It is envisaged that nanoparticle interest will continue to flourish in separation science, with special emphasis on different functionalities, and smaller sizes for particles and column.

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