Research on Electrochemistry

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Preamble:

The present article is focused on providing a perspective of the activities on electrochemistry and electrochemical science and technology carried out in Analytical Chemistry Division towards the work program of the department. The electrochemistry related activities started in 1950s in the Chemistry Group. In the absence of modern spectroscopic techniques during the initial period, the electrochemical techniques provided the required insights for the development of analytical chemistry in the Centre. In addition to the analytical supports to the departmental work program, the activities have important contribution in solving vitaltechnical issues of analytical and materials sciences. Present article outlines some of the activities since the inception of electrochemical research under the broad umbrella of the chemistry activities of the Atomic Energy Commission. The progress towards setting up of various electrochemical instrumentation facilities along with the scientific contributions from 1950s to the recent time are briefed. The article is a tribute to all the scientists and technicians contributed to build the legacy in this interesting branch of science.

Introduction:

The research on electrochemical techniques has started in 1950s under the leadership to Dr. V T Athawale and Dr. A K Sundaram along with the inception of Analytical Chemistry Section in Chemistry Division in 1953, which subsequently become Analytical Division in 1956. The technique has been extensively used in the determination of uranium, thorium, several rare earth elements and transition metal ions and halides to support the activities of the department. The activities are well documented in terms of publications, internal reports and analysis reports. In ahistorical perspective,the electrochemical techniques are evolved internationally to determine the composition of gun powder during the worldwar one in consequence of the discovery of polarography by Dr. Jaroslav Heyrovský in current days Czeck Republic. The technique has been very well incepted in the electrochemistry activity of the Analytical Division for the determination of metal ions. Electrochemical techniques were having unique advantage of low-cost instrumentations and their capability of generating kinetic and mechanistic information of the chemical systems. The contribution of the electrochemical techniquestowards the Chemistry activities in the Centre has been presented

in the present article with subdivision of the progress in three different categories indicating the time frame of the progress since its inception.

Electrochemistry activities during its inception:

During its inception in late 1950s the electrochemical experiments were carried out using potentiometer, pH meter and conductivity meters. Later, the current measurements were carried out using thelamp and scale galvanometer with the application of potentials through analogue potentiometers. The dropping mercury electrode was used in the analytical measurements. Some of the works which has been carried out during the early days of developments are discussed here.

A method for selective extraction of Beryllium was developed,extensive work on the effect of pH of the media and solution compositions on the extraction efficiency was carried out and the efficient extraction of Beryllium with extraction efficiency of 70 to 80 % could be attained. The polarography of uranyl ion was recorded and published way back in 1959 using the manual set up and homemade electrochemical cell. The two-wave pattern of the reduction of uranyl ion was obtained in ammonium thiocyanate media along with perchloric acid. The reversible nature of the reduction pattern was established with first reduction as two electron transfer process and the second reduction as the single electron transfer process, the mechanism of the electrochemical process was proposed to be due to the reduction of U(VI) to U(IV) and reduction of the U(IV) to U(III). Information about the disproportional nature of the reduction wave of U(IV) to U(III) was observed and discussed. The analytical method was established from the reduction peaks of uranium. Polarography of uranium was also investigated in several other media.

Electrochemical work contributed well to the thorium extraction research. The complexation of Th and the mechanism of the complexation with EDTA were established using conductometric titration. The conductometric titration along with polarographic measurements were extended for other metal ions as well for their determination and also investigation of basic kinetic parameters.In addition to conductometry, the potentiometry and potentiometric titration was used in analytical determination and also obtaining basic kinetic information of redox systems.Voltammetry was introduced with solid electrode systems as alternate to mercury electrodes.The cathode ray polarography was available during that time using bimetallic electrode system was investigatedusing inhouse developed micro cell for electrochemical measurements. In order to avoid the oxidation of mercury, the Ag as the indicator electrode and the Mo as the reference electrode was employed for the measurements in aqueous and also in non-aqueous solutions.

Zinc has been one of the important transition metal elements, very well studied using polarographic measurements. The element was investigated for its complexation in several different matrices pertaining to its determination and the investigation of its toxicity.Meanwhile, with the advancement of instrumentation facilities the electrokinetic parameters of several chemical systems were investigated.Important contributions were made in relation with analytical determination and solving the problem of materials science with strong interaction with the materials science activities of the Centre.

Activities during 1980s and 1990s:

During this period the instrumentations have been improved with the availability of potentiostat and associated automated dropping mercury electrode systems along with the facility to fabricate several customized electrodes. Electrochemical systems and controlled power sources were fabricated in-house during this period for different customized measurements in addition to the use of commercial instrumentations. In 1989, several groups have started to work on the low energy nuclear reaction (LENR) or popularly known as the cold fusion. Scientists of Electrochemical Methods Section of Analytical Chemistry Division also have contributed in this activity, this activity continued for several years. The cylindrical Pd electrode was used as cathode and Pt as anode for the electrolysis experiments in D_2O media with LiOD as the electrolyte. Tracks over the stainless-steel surface and presence of the tritium activity was reported by confirmation through several control experiments.

The analysis of minerals was one of the important activities for their metal ions content, polarographic techniques were adopted for the analysis of metal ions like, Pb, Cu, Cd, Zn, and Ni in the minerals like monazite and zircon. In one of the developments, the analysis of Pb in zircon sample has been reported through improvised dissolution and selective voltametric determination procedure.

The determination of impurities in ultrapure gallium has been an important activity on electrochemistry where several transition metal elements as impurities were determined. The development of method and determination Cr in ultrapure Ga sample was reported.

Hydrogen charging and permeation of hydrogen through different nuclear structural material was taken through the fabrication of permeation cells. Hydrogen was charged using the material of interest as cathode. The correlation of hydrogen charging current, hydrogen concentration in structural material were investigated to ascertain the detrimental effect of hydrogen in structural stability.The permeation experiments were carried out with different current density and the presence of Arsenic on the permeation current has been investigated. The permeation current density has strong dependency with the charging current and the presence of arsenic in the charging media. Additionally, Important analytical methods were developed for quantitative determination and investigation of kinetic parameters of metal ion and biological systems during this two decades.

Activities in the last two decades:

In the last two decades, significant uplift of the activities on electrochemistry in Analytical Chemistry Division has been carried out using modern electrochemical facilities and newly introduced activities for the analytical measurements, investigation of corrosion and their inhibition and investigation of the interfaces. Determination of Pd, Cr, nitrites, halides, Pt, Rh, Hg, U, As, peroxides etc. in complex matrices for the important applications in departmental and societal requirements are developed and the methods were utilisedfor analytical measurements.

The potential of the electrochemical techniques in the investigation of the interfacial processes have been carried to its outmost capacity. The corrosion aspects of cold rolled and heat treated SS304 was investigated in 2001. The hydrogen uptake and the related corrosion property of zircaloy-2 and zircaloy-4 were investigated, indicating impervious passive films and their possibility of bleaching under different solutions and polarization conditioning.The inhibition of corrosion and the binding mechanism of the inhibitors with active functional groups for binding with metal and alloy surfaces were investigated with thermodynamics and kinetics parameters.

The scientific and technical expertise were rendered in the deposition of Mn, Fe, Ni films for the selective and impervious depositions of radioisotopes in several application using radionuclides. Cd was deposited over copper discs for the generation of ^{111}In radioisotopes in the medical cyclotron program. Important process chemical parameters were optimized for the deposition and recovery of several important metals for the departmental interests. The electrochemical research in the molten salt electrolyte media has been introduced which has implications in recovery of important elements and also for the generation of electrokinetic data of the structural materials under molten state.

The electrochemical instrument, potentiostat and galvanostatic with features like, linear sweep and pulse voltametric techniques was developed and used in the Division in several important electrochemical analysis. The photograph of the in-house developed electrochemical system (2001) is shown in Fig.1.

Fig. 1: The in-house developed computer controlled electrochemical system equipped with linear and pulse voltametric techniques

Instrumentations and related technologies are developed for the determination of dissolved oxygen (DO) in water required in nuclear and in several chemical industries and environmental monitoring. It requires continuous monitoring of DOto keep the corrosion of the structural material under control and thus to improve the life of the plant. In nuclear industry, the specification of dissolved oxygen in coolant water is as low as 5 ppb. Determination of the DO is also important in industrial waste, sewage and water bodies, DO concentration in potable water is an important water quality parameter. The DO meter has been designed for the continuous monitoring of dissolved oxygen under flow condition.The reduction current of oxygen is the measurable parameter for the determination of dissolved oxygen. The current flows due to this process is measured using the electronics device and the measured current is calibrated with respect to the dissolved oxygen concentration. Sensor displays the reading of DO concentration in ppm/ppb units, the instrument can be used for continuous monitoring and also batch mode of applications. It has been developed with completely indigenous materials and technology. The system has been tested in the secondary coolant circuit of the Madras Atomic Power Station (MAPS) and Tarapur Atomic Power Station (TAPS) for continuous monitoring of dissolved oxygen in the coolant water. The photographof the dissolved oxygen sensor is shown in Fig.2. The technology has been published over BARC website, and the technology has been transferred to four companies so far.

Fig. 2: Photograph of the dissolved oxygen monitor which has been developed and technology has been transferred to several companies, Technology code: CH32ACD, Website, http://barc.gov.in/technologies/dom1/index.html

Electrochemical measurements in hyphenation with the spectroscopic and microscopic techniques are utilised in characterization of biological interfaces, bacteria, antibiotics, glucose, anticancer drugs etc.

Electrochemical science is an important thrust area in utilization of alternate energy through developing supercapacitor electrodes and efficient catalysts for electrochemical and photoelectrochemical generation of hydrogen and oxygen from water. The metal oxides and sulphides, Prussian blue analogues, along with the graphene oxides (GO), reduced graphene oxides (rGO), 3D-graphene oxide and carbon quantum dots composites were synthesised. The electron transport from the active redox system of the metal chalcogenides are enhanced and transported to the current collectors through the different forms of carbon for the supercapacitor electrodes with enhanced capacity.

Nano phases and composites of MoS_2, 3D graphene/noble metals, cobalt oxide, Ni oxide, bismuth vanadate, hematite etc. were synthesised through hydrothermal, electrochemical and metal organic frame work route for the electrochemical and chemical splitting of water to generate hydrogen. The kinetics of the interfaces were probed through several conventional electrochemical technique and scanning electrochemical microscope.The fabricated electrodes have shown performances similar to the international reports. The activities have strong linkages with the hydrogen generation program of the Centre through exchange of materials and testing of different engineering developments along with the Chemical Engineering Group. The new strategy of experimentation and some representative results used in the characterization of the interfaces used in energy harvesting, storage and sensing substrates are documented in several important publications.

Currently electrochemical activity of Analytical Chemistry Division has expertise to resolve complex scientific and technical issues of the department. The Section is carrying out research in the field analytical and materials electrochemistry at per with the international peers. The research is being carried out in the interfacial processes in materials, biological systems with focusing towards energy materials and investigations in cellular level and detection of single molecular species due tothe events of molecular collision.

Way forward:

Electrochemical research in the chemistry group has poised towards the development of newer analytical methods in challenging matrices. Some of the new activities include: supporting the departmental work program for the recovery of important elements, development of electrochemical methods for the determination of analytes at single molecular level, determination of drugs to support health care and cancer research of the department, in biological media and also in cellular level through ultra-micro and nano electrodes, noninvasive sensing of metabolites for disease diagnostics, development of wearable sensor, research and technology developments towards photoelectrochemical generation of green hydrogen using solar energy and scale up through collaboration with engineering Divisions and development supercapacitor and redox flow battery system for efficient storage of alternate energy.