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ELECTROANALYTICAL AND ELECTROCATALYTIC
APPLICATIONS OF ZEOLITE-MODIFIED ELECTRODES

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ELECTROANALYTICAL AND ELECTROCATALYTIC APPLICATIONS OF ZEOLITE-MODIFIED ELECTRODES

The growing interest of zeolites in electrochemistry arises from the synergistic combination of their attractive characteristics like size, shape and charge selectivity, cation exchange capacity and inherent catalytic behaviour that are likely to affect the electron transfer processes at the electrode/solution interface. This has led to the design and preparation of zeolite-modified electrodes (ZMEs) for various applications in electroanalysis, electrocatalysis, charge and mass transport characterization, molecular recognition and power sources.

The research work described in the present thesis pertains to the studies on some electroanalytical and electrocatalytic applications of ZMEs. Although ten commercially available zeolites of different framework types including FAU, LTA, MFI and MOR have been chosen for preliminary investigations, the major results have been obtained with zeolite Na-Y and zeolite NH\textsubscript{4}-Y due to their manifestation of advantageous electrochemical properties in electroanalytical and electrocatalytic processes. Potentiometry, chronoamperometry, cyclic and square wave voltammetry are the techniques employed to follow the electrochemical processes. Powder X-ray diffraction (XRD), solid state nuclear magnetic resonance (NMR) spectroscopy, scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM) and energy dispersive X-ray analysis (EDX) have been employed for the characterization of ZMEs.

The main focus of the electroanalytical study has been to develop electrochemical sensors for Cd\textsuperscript{2+}, Pb\textsuperscript{2+} and Cu\textsuperscript{2+} ions based on ZMEs. The optimum conditions with respect to the choice of zeolite, electrode composition, preconcentration time, electrolyte
and scan rate required to maximize the sensitivity have been investigated. For
electocatalytic studies, oxygen, methanol and hydrogen peroxide are employed as the
substrates.

The thesis contains eight Chapters. Chapter I presents a brief summary of the
classification, salient properties and applications of zeolites. The literature on the
methods available for the preparation of ZMEs is also presented. The recent advances on
the use of ZMEs in electroanalytical and electrocatalytic applications are highlighted.
The general mechanisms involved in electrochemical reactions with ZMEs are discussed.

Chapter II gives the experimental details of the present study. A brief description
of the principle and theory of the electrochemical, powder XRD, solid state NMR
spectroscopy, SEM and HRTEM, inductively coupled plasma-optical emission
spectrometry (ICP-OES) and atomic absorption spectroscopy (AAS) techniques used in
the present study is given in this Chapter.

A novel healing procedure for the preparation of a free-standing and coherent
zeolite Na-Y membrane is discussed in Chapter III. The method involves the synthesis of
SiO₂ in situ at the intercrystalline regions of the zeolite Na-Y pressed disk.
Tetraethylorthosilicate is used as the source of silica. The membrane characterization by
powder XRD, solid state NMR spectroscopy and SEM techniques confirms the formation
of amorphous silica and also that the zeolite structure is preserved during the healing
process. A possible mechanism for the healing process is also proposed. The coherent
nature of the membrane is ascertained by its size selective exclusion of the TBA⁺. For the
first time, the free-standing zeolite Na-Y membrane has been used in the potentiometric
sensing of Cd²⁺ and Pb²⁺ ions. The estimated detection limits for Cd²⁺ and Pb²⁺ ions are
4×10⁻⁵ M (4.5 ppm) and 1×10⁻⁴ M (20.7 ppm), respectively.
Chapter IV deals with the modification of the interface between two immiscible electrolyte solutions (ITIES) with zeolite Na-Y membrane. Cyclic voltammetric results at the zeolite Na-Y membrane for the size and charge selective ion transfer across the resultant zeolite Na-Y modified ITIES (ZM-ITIES) are discussed. Tetrabutylammonium (TBA\(^+\)), tetrafluoroborate (BF\(_4^-\)) and perchlorate (ClO\(_4^-\)) ions are excluded from zeolite Na-Y membrane because of either molecular size (TBA\(^+\)) or charge (BF\(_4^-\) and ClO\(_4^-\)) of the ions. From the size and charge selective ion transfer data, the maximum pinhole area is estimated to be about 5% for a total geometric area of 0.39 cm\(^2\) of the membrane. However, the transfer of TEA\(^+\) ion is observed across the ZM-ITIES. The peak current values observed for the transfer of TEA\(^+\) ion across the ZM-ITIES are directly proportional to the concentrations of TEA\(^+\) in the range between 2\(\times\)10\(^{-4}\) M and 1\(\times\)10\(^{-3}\) M. The diffusion coefficient of TEA\(^+\) ion within the zeolite Na-Y membrane is of the order of 10\(^{-8}\) cm\(^2\) s\(^{-1}\).

Chapter V describes an electrochemical procedure for the incorporation of Pt nanoclusters within the free-standing zeolite Na-Y membrane. Cyclic voltammetry and chronoamperometry techniques are used for the electrodeposition of Pt nanoparticles. HRTEM image reveals that the size of Pt nanoclusters present in the zeolite Na-Y membranes is less than 1 nm. The procedure appears to give a direct link between the inner diameter of zeolite Y pore (1.12 nm) and the metal deposit size (< 1 nm). The EDX spectrum confirms the presence of Pt particles within zeolite Na-Y membrane. The Pt-loaded membrane has shown good response to the oxygen reduction and methanol oxidation reactions suggesting that it can be used in other electrochemical applications.

Chapter VI discusses the voltammetric sensing of Cd\(^{2+}\) and Pb\(^{2+}\) ions using zeolite-modified carbon paste electrodes (ZMCPEs). Ten commercially available zeolites
including faujasite, zeolite Na-Y, zeolite NH$_4$-Y, zeolite 13X, molecular sieve 3Å, molecular sieve 4Å, molecular sieve 5Å, molecular sieve 10Å, mordenite and ZSM-5 are used to identify the best one for the detection of Cd$^{2+}$ and Pb$^{2+}$ ions. Among the various types of zeolites used, zeolite NH$_4$-Y is found to show the best performance in terms of the voltammetric peak current magnitude and reversibility. The following optimum conditions are found to result in maximum sensitivity at an analyte concentration of $1\times10^{-3}$ M using zeolite NH$_4$-Y-modified carbon paste electrode (ZYMCPE): zeolite NH$_4$-Y to graphite ratio: 1:1; preconcentration time: 30 min; electrolyte: 0.1 M KCl and scan rate: 0.01 V s$^{-1}$. The reproducibility of the results reveals that the methodology employed for the preparation of ZYMCPE is highly reliable. A single ZYMCPE can be replenished and reused in six experiments, and the results indicate that the electrode is mechanically stable. The performance of the ZYMCPE is compared with that of some unmodified electrodes including carbon paste, bare ITO and Pt disc electrodes. The enhancement factors for Cd$^{2+}$ ion at ZYMCPE with respect to carbon paste, bare ITO and Pt disc electrodes are 10, 4 and 5, respectively, and for Pb$^{2+}$ ion, the enhancement factors are 32, 6 and 8, respectively. The several-fold current enhancement at ZYMCPE can be attributed to the accumulation of metal ions at the electrode surface by simple ion-exchange behaviour of zeolite, resulting in large local analyte concentration. The sensor calibration curves constructed for the detection of Cd$^{2+}$ and Pb$^{2+}$ ions show a detection limit of $8.9\times10^{-9}$ M (1.0 ppb) and $1.7\times10^{-8}$ M (3.6 ppb), respectively. The interference effects due to the presence of other metal ions such as Hg$^{2+}$, Cu$^{2+}$ and Fe$^{3+}$ ions which are some of the other possible contaminants in waste water streams and industrial effluents have been investigated. The mutual interference effects between Cd$^{2+}$ and Pb$^{2+}$ ions have also been studied. The maximum threshold limit of interference for Cd$^{2+}$ ion sensing is due to the presence of Fe$^{3+}$ ions at $1\times10^{-9}$ M (0.056 ppb), whereas for Pb$^{2+}$ ion, Hg$^{2+}$ ion
upto $1 \times 10^{-9}$ M (0.2 ppb) shows least interference effects. The utility of ZYMCPE and the validation of the methodology developed in the present study are tested with two real samples viz. a well water sample and an industrial effluent sample, and the results obtained at the ZYMCPE agree very well with those obtained by AAS. The several-fold current enhancement for the detection of both Cd$^{2+}$ and Pb$^{2+}$ ions at the ZYMCPE compared to CPE along with the high reproducibility of the results provide good scope for developing commercial sensors based on ZYMCPE.

Chapter VII provides the application of zeolite-MWCNT nanocomposite modified glassy carbon electrode (zeolite-MWCNT/GCE) in the electroanalysis of Cu$^{2+}$ ion. Here also all the ten types of zeolites have been investigated to find out the best choice of zeolite. The cyclic voltammograms for Cu$^{2+}$ ion show two one-electron redox processes at all the ten zeolite-MWCNT/GCEs and among the electrodes investigated zeolite NH$_4$-Y-MWCNT/GCE shows the best performance in terms of the first cathodic process ($E_{pc(1)} = 13$ mV) in the detection of Cu$^{2+}$ ion. In order to bring out the unique advantages of the zeolite NH$_4$-Y-MWCNT/GCE, experiments have been carried out at the graphite/GCE, MWCNT/GCE and zeolite NH$_4$-Y-graphite/GCE. For the same surface area, the magnitude of first cathodic peak is nearly 4 times higher for MWCNT/GCE than for graphite/GCE. Likewise, the first cathodic peak current value at zeolite NH$_4$-Y-MWCNT/GCE is about 7 times larger than that at MWCNT/GCE, and 2 times larger than that at zeolite NH$_4$-Y-graphite/GCE. The combination of zeolite NH$_4$-Y and MWCNT as a nanocomposite has resulted in a synergetic effect. Also, in order to bring out the significance of the Cu$^{2+}$ ion exchange in zeolite NH$_4$-Y in the current enhancement, direct experiments without any preconcentration are carried out at graphite/GCE, MWCNT/GCE, zeolite NH$_4$-Y-graphite/GCE and zeolite NH$_4$-Y-MWCNT/GCE. It is found that the preconcentrated zeolite NH$_4$-Y-MWCNT/GCE shows a superior
performance in the determination of \( \text{Cu}^{2+} \) among the modified electrodes investigated. Square wave voltammetry (SWV) is employed to obtain the sensor calibration plot. The SWV response is linear in the concentration range between \( 1 \times 10^{-5} \) and \( 5 \times 10^{-8} \) M giving the slope and regression coefficient values of \( 1.69 \mu \text{A} / \mu \text{M} \) and 0.99, respectively. The detection limit of \( \text{Cu}^{2+} \) ion is \( 1.12 \times 10^{-8} \) M (0.716 ppb), and this value is found the lowest among the values reported so far in literature for various ZMEs.

The results obtained on the performance evaluation of the zeolite \( \text{NH}_4\text{-Y-MWCNT/GCE} \) compared to zeolite \( \text{NH}_4\text{-Y/GCE} \) and MWCNT/GCE in the electrocatalytic reduction of \( \text{H}_2\text{O}_2 \) using an organic mediator \( \text{MV}^{2+} \) and an inorganic mediator \( [\text{Ru(NH}_3)_6]^{3+} \) are presented in Chapter VIII. The electrodes are preconcentrated in the mediator solution for 20 min prior to the cyclic voltammetric measurement in 0.1 M phosphate buffer. The peak current magnitude for the reduction of \( \text{H}_2\text{O}_2 \) at \( \text{MV}^{2+}\text{-zeolite Y-MWCNT/GCE} \) is found to be about 15 times higher than that at \( \text{MV}^{2+}\text{-zeolite Y/GCE} \). It is inferred that the MWCNT acts as an electron relay between the \( \text{MV}^{+} \) and \( \text{H}_2\text{O}_2 \), i.e., MWCNT is capable of accepting and storing electrons from \( \text{MV}^{+} \), then the stored electrons are readily discharged on demand by the electron acceptor, \( \text{H}_2\text{O}_2 \). Similarly, the peak current magnitude for the reduction of \( \text{H}_2\text{O}_2 \) at \( [\text{Ru(NH}_3)_6]^{3+}\text{-zeolite Y-MWCNT/GCE} \) is found to be 19 and 3 times higher than that at \( [\text{Ru(NH}_3)_6]^{3+}\text{-zeolite Y/GCE} \) and \( [\text{Ru(NH}_3)_6]^{3+}\text{-MWCNT/GCE} \), respectively. The enhanced electrocatalytic effect has been attributed to the adsorption of \( [\text{Ru(NH}_3)_6]^{3+} \) by MWCNT.

Some important conclusions that could be drawn from the study are presented in the Summary and Conclusion section.