

# Chapter - 4

## Zeolitic Modified Materials as Electrode

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**Abstract**—*This chapter deals with the structure, properties, procedures, uses, and advances in the zeolitic-based electrocatalysts. A brief introduction on intra- vs extra-modified zeolite electrode has also been discussed in the last section of this chapter.*

### **Structural and Chemical Properties of Zeolites**

Zeolites are crystalline aluminosilicates microporous solids known as molecular sieves into which molecules may be adsorbed for environmental decontamination processes. Zeolites can be completely hydrated and dehydrated without destruction of their crystalline lattice. Zeolite also possesses a porous three-dimensional crystalline structure which is formed by the repeated units of Si, O, and Al. The framework structures are built from corner-sharing of  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedral building blocks linked through common oxygen atoms. The resultant structure is a cross-linked, inorganic, and crystalline macromolecule. The tetrahedra form a structural framework in zeolites with centrally located Si or Al atoms and corners

occupied by O-atoms being shared between  $\text{SiO}_4$  and  $\text{AlO}_4$  units. These are developed such that the structural framework generates voids or pores in the form of cages and channels.<sup>1,2</sup>

In an electrochemical environment, zeolite, an inorganic material, has special importance. It is due to the characteristics, physical, and chemical properties of zeolite. These are stable materials and can withstand up to longer periods in electrochemical conditions. The zeolite-supported conductors are also used as dispersed ultra-microelectrodes. These dispersed ultra-microelectrodes intrigued the investigation on zeolitic effect on electrode procedures by allowing electrolysis on a preparative scale. As a result, a huge range of conducting metals, metal oxides, and semiconducting compounds can be explored in low-dielectric and composite-free atmospheres. Commercially zeolites are available as crystalline powders and several chemical methods are available to hold the zeolite at the electrode surface. Recent studies on zeolites and their uses have a great interest in the coating of zeolites on electrodes.<sup>3,4</sup>

### **Designing of Zeolite-modified Electrode**

Zeolites are coupled to an electrical source/sink as they are electronic insulators, and this influences electrode processes. Several methods are available for zeolite-modified electrodes and a few of them are discussed below.

### **Polymeric-Zeolitic-Suspensions**

In this method, a suspension of zeolite particles and dissolved polymer are prepared for the coating purpose of the electrode. The dissolved polymer

then binds the zeolites and holds it to the surface after evaporation of the solvent from the above system when the zeolite/polymer-modified electrode is used as an electrolyte. Moreover, the electrolytes must be like that in which the polymer is sparingly soluble. Shaw *et al.*, after analyzing with the help of scanning electron microscopy (SEM), showed that the problem is associated with the morphology which is due to the good adherence of polystyrene polymer to the electrode material (Pt) and its poor adherence to the zeolite particles.<sup>5</sup> This problem is removed using a SnO<sub>2</sub> surface. As a result, this leads to a separated layer from where the zeolite particles are next to the oxide and covered by polystyrene<sup>6</sup>

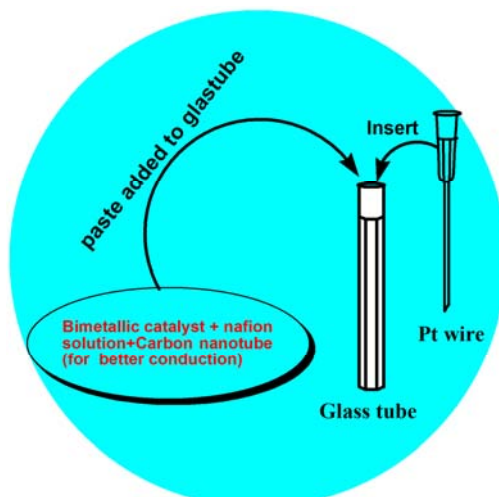
### **A Conductive Powder Mixture of Zeolite**

This method consists of zeolite and conductive powder mixture into the electrode grids, and is quite simple too. The approach is somewhat related to the process commonly done in the battery industry. It is also similar to a modified carbon paste electrode which is done using carbon powder and addition of an organic oil mixture. The modified carbon paste electrode is used as a binder, electronically conducting matrix which has an additional advantage in the surface. This method depends on pressing the powder mixture into electrode grids.<sup>3</sup>

### **Zeolitic-Carbon Polymerized Composites**

This process is a radical-initiated process using polymer. Recently, two scientists Shaw and Creasy have shown the advantages of using a “hard” composites. The “hard” composite contain zeolite particle sand carbon powder. A radical-initiated copolymerization of styrene and a cross-linking

agent (e.g., divinylbenzene) bounds the composition of zeolite particles and carbon powder. As a result, a hard surface is obtained, and then it is polished. This polished hard surface shows a better reproducibility and response times to electroactive solutes in comparison to the zeolite-modified carbon paste electrodes.



Modified bimetallic Direct Methanol Fuel Cell

### Designing of Electrode via Co-electrodeposition

Zeolites are also used to affect the reduction reactions of organic oxidants through ion-association reactions promoted by  $\text{Na}^+$ . It is due to the strong cationic nature of zeolitic materials which was discovered by Rolison *et al.*<sup>7</sup> Here, for the coating purpose, a rotating Pt or glassy carbon disk electrodes consisting of the disodium salt of the organic dianion and type A zeolite particles are used. In this method, a titration is done with  $\text{Na}^+$  into the aprotic non-aqueous electrolyte to control the quality and extent of the coating. During this process, Na-zeolite A provides a  $\text{Na}^+$  concentrate solution via ion-exchange reaction pathways with the electrolyte cation.

One of the major problems with this composite is that the water may break the ion associations between  $\text{Na}^+$  in the zeolite and the organic dianion, and  $\text{Na}^+$  and the organic dianion. As a result, these types of zeolite-modified electrodes can be used in non-aqueous media. Several research groups have also achieved co-electrodeposition of type A zeolite and the conducting polymer polypyrrole. In "upside-down" configuration, a drop of the zeolite-pyrrole slurry was placed on the disk electrode as it was held face up. Using this method, a uniform particle-polymer coating is formed. This is ideal to have immediate access even in a three-dimensional reaction zone, to an electrical conductor to supply and retrieve electrons on demand. Chao *et al.* demonstrated an approach for polymerizing conducting polymer precursors sorbed in type Y zeolite for pyrrole in which the Fe(III) impurities in the zeolites initiate the oxidation process. Recently, different research advances has also shown similar kind of results which sorbed in the zeolites.<sup>8,9</sup>

In the silane-associated zeolites approach, a bi-functional silane is covalently linked to a single dense layer of Y zeolite to a  $\text{SnO}_2$  electrode. This method was demonstrated by the Li and co-workers through Sn-O-Si linkages at the electrode, and there are Si-O-Si linkages between the silane layer and the zeolite Y. At the electrode surface, a thin layer is formed due to cationic and anionic electroactive species. Electrochemically silent layers of zeolite are avoided by this method.<sup>10</sup> Another approach called pressed pellet, or dry filmed approach involves dry films and pressed pellets of zeolite compressed between planar electrodes. For this kind of modified

electrodes, voltammetric characterization is typically done at high temperatures.<sup>11</sup>

### **Application of Zeolitic-Modified Electrodes**

#### **Host material**

Aluminosilicates such as zeolite can also be used to store the suitable sized reactants for subsequent usage before, during, or after electron-transfer processes and also have the cation-exchange capacity.<sup>3</sup> Freeman *et al.* discovered the effectiveness of zeolites for the solid-state battery.<sup>12</sup> Another example of a reactant host is Na-A zeolites for I<sub>2</sub> in a silver/iodine solid-state cell. In this case, it acts as a catholyte material. For longer life cycle for lead-acid batteries, zeolites are used to the lead paste, which leads to the adsorption of oxygen (*i.e.* affinity of zeolites for oxygen).

#### **As a promoter in Electron Transport**

The use of zeolite modified electrodes can also be explored in different electrochemically driven systems and light-driven processes. One example is methylviologen. Here, the ion-exchange reaction takes place and the degree of ion exchange was estimated at monolayer coverage on the external zeolite site. For polymer bilayers on modified electrodes, Abruna *et al.* demonstrated an electrode-confined microstructurally designed of charge modification.<sup>13</sup>

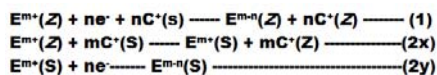
#### **Applications in Analytical Purpose**

In this section, the twofold uses of zeolite-modified electrodes are categorized as (a) potentiometry and (b) amperometry. One important use of zeolite is in the electro-analytical application due to its cation-exchange

capacity. Herein, equilibrium determination of cation concentration is determined by using zeolite membranes. Marshall *et al.* demonstrated that naturally occurring zeolite crystals are similar to the glass membrane electrode and demonstrates similar activity. From this, the electro-analytical measurements are also performed. Further study showed that synthetic zeolites also act as ion-sensitive membranes. This synthetic ion-sensitive membrane is prepared by pressing the zeolite microcrystals with polymer powders (such as polystyrene). Recently, Johansson *et al.* demonstrated the membrane as a Cs<sup>+</sup> ion-selective electrode.<sup>14,15</sup> The membrane is highly selective over the other cations (like Ag<sup>+</sup>, K<sup>+</sup> > Na<sup>+</sup> > Li<sup>+</sup>) and even more selective than the di-cations Ba<sup>2+</sup> > Ca<sup>2+</sup> > Cu<sup>2+</sup>. It depends upon the molecular size and also on the nature of the zeolite. For example, in analcite membrane, it is selective for Na<sup>+</sup> over Cs<sup>+</sup> ions. Zeolite can also control the potential-determining ion-exchange reactions. In the case of non-aqueous solvents, ion-exchange processes with zeolites have been studied, but the zeolitic membranes as non-aqueous ion-selective electrodes is not explored that much.<sup>15</sup>

Different types of zeolite modified electrode to air as oxygen sorbed materials are also discovered. Later on, for MV-modified zeolites A and Y, Creasy and Shaw simplify the optimization methods by adjusting the different parameters.<sup>16</sup> They optimize the ratio of zeolite to carbon paste and viologen loading of the zeolite. The zeolite-modified electrode is used for the detection of metal ions (Cu(II) or Fe(III)/Fe(II)) in aqueous solution and it affect the pH of the medium.<sup>17</sup>

For any modified electrode, one of the most important characterizations is the charge transport through the modifying layer. In zeolite-modified electrodes, Shaw and coworkers have demonstrated the description of transport of charge.



Here,  $E^{m+}$  = probe employed in the electroactive process,  $C^+$  = electrocatalytic cation, Z = zeolite phase and S = solution phase, respectively.

The aforementioned mechanism is explained as follows; in mechanism 1, electron transfer reaction occurs within the zeolite (indefinite) when the electroactive solute sorbed or exchanged into the zeolite. As a result, an equal but opposite charge transfers occurs into the zeolite from the cations in the surrounding electrolyte maintaining the charge neutrality. In the case of mechanism 2, an ion-exchange reaction with electroactive solute and cations in the surrounding electrolyte occurs in step 2x. In step 2y, the zeolite-free electroactive solute is decreased normally in solution. Voltammetric current is obtained when the electroactive probe is in solution, and it depends on its concentration and the mass transport of  $E^{m+}$  (s) to the electrode. The concentration of analytic solute is high due to the presence of zeolite (>1 M). As a result, the mass transport to the electrode is not strictly defined by thin-layer, migration, and linear diffusion as concentration gradients parameters and all these factors have important



role to play. Shaw *et al.* demonstrated the factors to explain the voltammetry obtained for MV-exchanged Y.<sup>3,18-20</sup>

Nowadays, diffusion within zeolites is an important phenomenon, and several works are going on in this area. Shaw *et al.* demonstrated this feature for electrochemical conditions by using electrolytes of various cationic size and the electroactive probes  $MV^{2+}$ ,  $Ru(NH_3)_6^{3+}$  and  $Cu^{2+}$  sorbed into zeolite Y. In this case, zeolite-Y is preferentially concentrated with  $Ru(NH_3)_6^{3+}$  in competitive adsorption of  $MV^{2+}$  and  $Ru(NH_3)_6^{3+}$ . However, for  $MV^{2+}$ , the magnitude of current is comparatively larger indicating the greater mobility of  $MV^{2+}$ . The analytical response dependent on the nature of the supporting electrolyte cation (*i.e.* its charge, size, and concentration) which creates problems regarding the utilizing of aluminosilicate-modified electrodes in the development of sensors. Zeolite modified electrodes deal with the analysis of cations and molecules which is basis of ionic or size competition and concentration. Zeolite can also be used as a template in order to structure intra-crystalline nanometer-sized electrodes.<sup>3,18-20</sup>

In the literature, there are various synthetic procedures to prepare zeolite-supported conducting or semiconducting particles. So different metal/metal oxides particles can be predominantly confined to the supercage by the appropriate control of the synthesis zeolite. Generally, in high ionic strength, electrolyte and metal particles in the order of  $10^2$ - $10^3$   $\mu m$  size dispersions and fluidized bed electro-reactors are used. The dispersed electrodes may perform either as mono-polar electrodes or as

bipolar electrodes. In recent times, several types of research are progressed on the use of dispersed ultra-microelectrodes. Pons *et al.* showed that Au, Pt, or C (0.1-10- $\mu\text{m}$ ) microspheres could function as dispersed ultra-microelectrodes. In low-dielectric media, the ultra-microelectrodes can be used.<sup>3,21,22</sup>

Rolison and co-workers have illustrated the dispersion electrolysis technique.<sup>3,23</sup> They have also shown that dispersion electrolysis can be obtained when the dispersed electrodes are Pt-microstructures supported on zeolite Y type aluminosilicate. These types of dispersed electrodes are designated as Pt-Y. The procedure used for the preparation of the supported Pt is based on oxygen activation and hydrogen reduction of  $\text{Pt}^{\text{II}}(\text{NH}_3)_4$ -exchanged Na-Y. This leaves approximately 90% of the Pt weight loading in the zeolite interior (i.e. intra-crystalline surface) 10% of the Pt weight loading on the external zeolite surface (i.e. extra-crystalline surface).<sup>3,24</sup>

Although zeolite is an ionic conductor, but at the same time, it also act as electronic insulator. Also, there is a high possibility to develop a potential on intra-crystalline-sited metals which results in sufficiently high electric fields.<sup>23</sup> The electroactive solutes which are capable of entering zeolite-Y results in low-field electrolysis (<300 V/cm) and electroactive solute that are too bulky to enter zeolite-Y results in the electrolysis only at the external site of Pt particles. These externally sited Pt particles can physically contact the feeder electrodes, and other charged supported Pt particles. The intra-crystalline Pt surface areas do not contribute to the

electrode processes and are left with insufficient potential for electron-transfer. In recent time, study reported that zeolite permits the use of high electric fields for the electrode processes and electron transfer in the interior of the zeolite.<sup>25,26</sup>

Zeolite-Y has a strong ionic character and due to this nature in the salt-free electrolytes, it plays an important role in the effectiveness of dispersion electrolysis. This can be explained by comparing 1% Pt supported and dispersed 1% Pt-Y electrodes on alumina surface. The effectiveness of electrolysis is defined as the magnitude of current at a given applied voltage for comparison between different dispersed electrodes. The dispersion-driven mobility of the zeolite acting as a solid-state electrolyte is also responsible for the ionic conductivity of the medium.<sup>3,23,27</sup>

### **Conclusion**

In conclusion, the role of zeolitic materials as electrodes has been described briefly in this chapter. Different types of designing methods and the applications of modified electrodes are also discussed. On the literature survey, it can be stated that zeolite-modified electrodes can be further tuned for better investigations in the field of electrocatalysis.

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