

Zeolite-Modified Electrodes and Electrode-Modified Zeolites

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I. Introduction

A. The Urge To Modify

Not satisfied with electrode surfaces that passively accept or provide electrons or content with electrode surfaces that actively accelerate or hinder certain electron-transfer reactions, chemists in the last 15 years have turned to designing chemical structures on electrode surfaces that redefine the chemical and physical

microenvironment in which heterogeneous electron-transfer reactions occur.¹

The primary precept driving the chemical modification of electrode surfaces requires that the molecular



Debra R. Rolison was born in Sioux City, IA, in 1954. She obtained a B.S. in chemistry in 1975 from Florida Atlantic University in Boca Raton, FL, where she was a Faculty Scholar. She performed undergraduate research with Professor Franklin A. Schultz (FAU) on liquid-membrane anion-selective electrodes as detectors for ion-exchange chromatography and on nonaqueous electrochemical characterization of bioinorganic model compounds based on μ -oxo- and μ -sulfido-bridged molybdenum dimers and with Professor William Dolbier (University of Florida) on the synthesis and physical organic characterization of Diels-Alder adducts. She received her Ph.D. in Analytical Chemistry from the University of North Carolina at Chapel Hill in 1980. Her doctoral thesis, under the direction of Professor Royce W. Murray, involved the preparation and characterization of RuO₂-polycrystalline electrodes in nonaqueous electrolytes and the modification of metals and TiO₂ electrodes with plasma-polymerized vinylferrocene or photodeposited polyvinylferrocene and their X-ray photoelectron spectroscopic and electrochemical characterization. She joined the Naval Research Laboratory (Washington, DC) as a research chemist in 1980. Her research at the NRL focuses on electrode processes occurring in microstructured environments, with special emphasis on the influence of zeolite molecular sieves on electrochemical reactions. She initiated the use of zeolite overlayers on planar electrodes as a modified-electrode approach to harnessing the molecular-sieving character of zeolites to the electrochemical interphase. She recently pioneered the application of metal microstructures in zeolites as supported ultramicroelectrodes for dispersion electrolyses. She continues to apply her interest in X-ray photoelectron spectroscopy to characterize uncommon chemical environments, recently using XPS to study reactions between refractory metals and carbonates in molten fluorides. Her most recent direction is the use of extended X-ray absorption fine structure to follow, in situ, the reactions leading to the formation of Pt microstructures supported on zeolite Y and to explore the in situ characterization of dispersed ultramicroelectrodes and colloids in solution and under reactive conditions. She is a member of the American Chemical Society, the Association for the Advancement of Science, and the Society for Electroanalytical Chemistry. She coauthored and edited *Ultramicroelectrodes*, the first text on this very active research area in electrochemistry, with Professors Martin Fleischmann, Stanley Pons, and Peter Schmidt. She has been appointed to the Advisory Board for *Analytical Chemistry* for the 1990-1992 term.

layer retain its innate nature once immobilized on the electrode surface. Without this transference of the chemical and physical properties of the modifier from its bulk to its immobilized state, rational design of the microscopic environment is hopeless. That this transference predominantly occurs has been amply characterized by the plethora of articles reporting the retention of the chemical, electrochemical, optical, and physical character of molecular layers immobilized on electrode surfaces, as summarized by a number of reviews on modified electrodes.¹⁻⁴

Much of the work on modified electrodes relies on organic or organometallic monomolecular or polymeric layers adsorbed at, covalently bonded to, deposited on, or self-assembled at electrode surfaces.¹⁻⁴ Akin to the research on supported reagents,⁵ this approach heterogenizes homogeneous chemistry. In the mid-1980s, research arose focusing on the use of inorganic or mineral structures formed or placed at electrode surfaces. Early examples of these inorganic modifiers include metal oxide particles,⁶ clays,^{7,8} zeolites,^{9,10} porous aluminum oxide films,¹¹ and the metallocyano-derived lattices.¹²⁻¹⁴

Wedding these more structurally regular modifiers to the electrode surface helped to push chemical modification of electrodes toward what Murray et al.⁴ refer to as *integrated systems*. This concept denotes the design of a microscopic reaction zone involving multiple chemical/physical components with specific tasks, only one of which includes heterogeneous electron transfer.

B. Advantageous Features of Inorganic Modifiers

Heterogenizing heterogeneous chemistry, i.e., the combination of an inorganic lattice and an electrode surface, offers new perspectives on electrode processes occurring in an environment dominated by the inorganic lattice.

1. Durability

Beyond the fundamental and fascinating study of the nature of the electrode once modified, modified electrodes promise practical dividends as applied to corrosion protection (or the general preservation of the integrity of the inherent electrode material), electro-synthesis, electrocatalysis, electroanalysis and solid-state sensors, electrochromic devices, electromediated schemes, and photoelectrochemical reactions.

Many of these applications demand long-term stability of the modifying layer, especially under reactive conditions, both in terms of the endurance of its immobilization to the electrode and in terms of the chemical stability of the molecular species comprising the modifying layer. Polymeric modifying layers are typically more durable for repetitive turnovers than are monomolecular layers;⁴ inorganic lattices or particles present even stiffer resistance to dissolution, decomposition under temperature extremes, or chemical degradation.

2. Three-Dimensional Template

The structural integrity that can arise with a crystalline lattice also provides a framework for the design of integrated systems of complex molecularity. Rather

than be confined to a two-dimensional or quasi-two-dimensional overlayer on the electrode surface, the three-dimensional architecture of an inorganic lattice can be exploited.

3. Molecular Discrimination/Molecular Recognition

Inherent in many inorganic materials are pores, channels, or layered spacings of molecular dimensions. These molecular gateways impart a selective screen, so that differentiation results on the basis of molecular size or shape of solutes. Further discrimination arises if fixed charged sites are part of the inorganic lattice, producing an ionic filter as well. In these senses, the inorganic layer can "act" as a passive discriminator, allowing, e.g., preconcentration of an analyte or reactant.

4. Confluence of Heterogeneous Catalysis and Electrocatalysis

Electrocatalysis is a special case of heterogeneous catalysis. By studying classical heterogeneous catalysts in an electrochemical interphase, their catalytic influence can be brought to bear on recalcitrant electrode processes. Alternatively, an electrode-immobilized heterogeneous catalyst can interact and react with a high flux of electrogenerated product and be submitted to the additional driving force of potential or current. That is, reaction schemes involving both chemical reaction (C) and electron-transfer reaction (E)—in electrochemical terminology, CE, EC, ECE, ECEC, etc.—should be candidates for susceptibility to the one-two punch of an electro/heterogeneous catalyst. It is also feasible that new reaction pathways and classes of reactions may be observed due to the synergism of a heterogeneous catalyst in an electrochemical interphase.

II. Zeolites and Electrochemical Interfaces

In particular, why is a zeolite an inorganic material of especial interest in an electrochemical environment? The answer is enmeshed in the characteristics, chemical and physical, of a zeolite. Zeolites offer a nearly ideal embodiment of each of the general advantages described above. As will be discussed in the following sections, the sum of the zeolite's parts presents a unique package for structuring an electrochemical/electron-transfer environment.

A. Chemical and Physical Properties of Zeolites

Zeolites are crystalline aluminosilicates with a great capacity for water and the ability to be completely hydrated and dehydrated without damage to the crystalline lattice. Table I lists some of the chemical and physical properties of the zeolite types used, to date, to modify electrode surfaces.

1. Structural Architecture

The intracrystalline architectural diversity of the natural zeolitic minerals and their synthetic analogues and extensions results from the three-dimensional network formed from conjoining SiO_4 and AlO_4 tetrahedral building blocks; the ensuing structure is an inorganic, cross-linked, and crystalline macromolecule. Figure 1 illustrates the oxygen-sharing, Al-O-Si

TABLE I. Physical and Chemical Properties of Zeolites^a Used at Electrochemical Interfaces

| Z type | unit-cell compn (typical, fully hydrated) | cation-exch capacity/mequiv/g | | Si/Al | unit-cell vol/nm ³ | void vol/cm ³ /cm ³ | kinetic diam ^b /nm | T ^c /°C |
|-----------|--|----------------------------------|---------------|---------|----------------------------------|--|----------------------------------|--------------------|
| | | anhydrous Z | hydrated Z | | | | | |
| A | Na ₁₂ [(AlO ₂) ₁₂ (SiO ₂) ₁₂]·27H ₂ O | 7.0 | 5.5 | 0.7-1.2 | 1.870 | 0.47 | 0.39 | 660 |
| X | Na ₉₆ [(AlO ₂) ₉₆ (SiO ₂) ₁₀₆]·264H ₂ O | 6.4 | 4.7 | 1-1.5 | 15.36-15.67 | 0.50 | 0.81 | 660 |
| Y | Na ₅₆ [(AlO ₂) ₅₆ (SiO ₂) ₁₃₆]·250H ₂ O | 5.0 | 3.7 | >1.5-3 | 14.90-15.35 | 0.48 | 0.81 | 700 |
| L | K ₉ [(AlO ₂) ₉ (SiO ₂) ₂₇]·22H ₂ O | | | 2.6-3.5 | 2.205 | 0.32 | 0.81 | 845 |
| mordenite | Na ₈ [(AlO ₂) ₈ (SiO ₂) ₄₀]·24H ₂ O | 2.6 | 2.3 | 4.17-5 | 2.794 | 0.28 | 0.39 | |

^a Data taken from ref 15. ^b The kinetic diameter represents an intermolecular distance of closest approach for two molecules colliding with zero initial kinetic energy and illustrates the dynamic size of species that can successfully enter through the zeolite pores.¹⁵ ^c Temperature at which structural changes are first noted by X-ray diffraction, for heating in air.

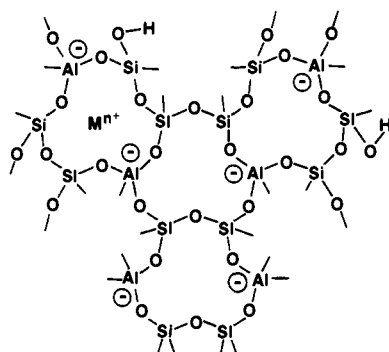


Figure 1. Two-dimensional representation of the Al-O-Si linkages that create the framework structure of aluminosilicate zeolites. Also illustrated are (i) the fixed anionic sites associated with Al atoms in the lattice requiring counterbalancing cations and (ii) the presence of terminating hydroxyl groups (adapted from ref 15).

framework that readily builds up.

The tetrahedral coordination of Si-O and Al-O (generically referred to as T-O) permits a variety of ringed structures to form, like the six T atom rings shown in Figure 1. These rings link to form the cage and channel structures that give rise to the molecular discriminatory nature of zeolites. Figure 2 exhibits the framework representations of the zeolites used at electrochemical interfaces: types A, X, Y, and L and mordenite. T atoms (Si or Al) lie at the intersection points of the lines, while the linking oxygen atom lies slightly displaced off of the center of the line. This particular representation of zeolite structure demonstrates the pore opening, void spaces, and cage aspects of these materials. Another common representation uses stereoplots of the T-T linkages.^{16,17}

2. Chemical Characteristics

In addition to showing the preliminary stages of the zeolitic framework, Figure 1 also displays two chemical features of the aluminosilicate zeolites that provide much of the chemical diversity of the system. For every Al atom in the lattice, with its AlO₂/SiO₂ stoichiometry, a fixed negative charge results. These anionic sites are counterbalanced by mobile cations, typically alkali-metal or alkaline-earth cations, that easily ion-exchange for other metal cations or cationic metal complexes of appropriately small dimensions.

The second feature is the termination of bonding at the crystal faces with hydroxyl groups. Hydroxyls are the form in which protons are held in the zeolite,¹⁸ and they are responsible for the strong-acid nature of the aluminosilicate zeolites and their extensive use in

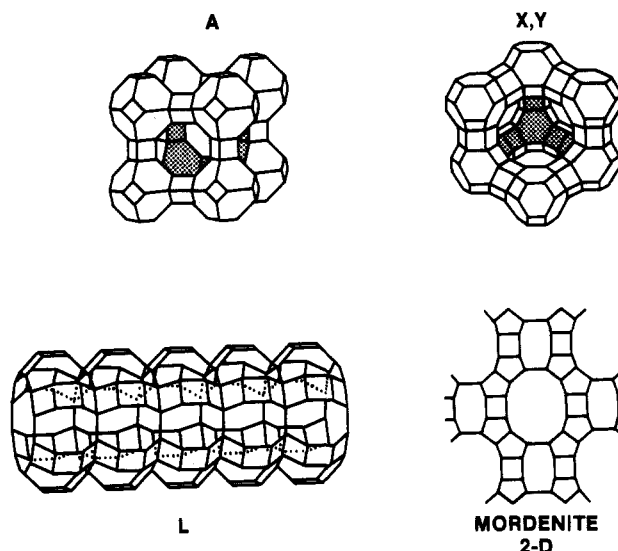


Figure 2. Three-dimensional representations of the framework structure of zeolite types A,⁸⁷ X and Y (faujasite),⁸⁸ and L⁸⁷ and a two-dimensional representation of the framework structure of mordenite.⁸⁹

acid-catalyzed reactions,¹⁹ not the least of which is the cracking of petroleum.

Much of the recent zeolite research is focused on the synthesis and characterization of substituted aluminosilicate structures, where Si or Al is replaced by an isomorphous atom. The new classes include aluminophosphates (AIPO), silicoaluminophosphates (SAPO), and metal-substituted analogues of AIPO and SAPO structures (MAPO and MAPSO, respectively), where the metal can be Li, Mg, Be, or a transition metal. This area was recently reviewed.²⁰ Because the cation-exchange capacity is diminished, sometimes nearly eradicated, by the loss through substitution of the aluminum atoms in the lattice, some of these molecular sieves may be less immediately versatile in electrochemical systems. The expanded structural and molecular recognition possibilities these aluminosilicate derivatives can offer have yet to be explored at electrochemical interfaces, but that will, no doubt, be remedied shortly.

B. Possible Zeolite and Electrochemical Intersections

The chemical and physical nature of zeolites, as described above, not only offers readily exploitable features when used to modify electrode surfaces but also offers advantages in the design of electrode materials and microscopic electrochemical reactors. This premise

has been demonstrated for systems incorporating electron-transfer species, but where the focus is on goals other than those electrochemically oriented.

1. Systems of Electrochemically Related Interest

Figure 2 shows that the molecular size control provided by the zeolite structure offers several sieving features. For example, the faujasitic topology, to which the synthetic types X and Y belong and to which type A is related, has small cages (truncated octahedra referred to as sodalite cages¹⁵) that, when linked with smaller T atom rings, form the supercage. For types X and Y, the opening into the supercage is approximately 0.74 nm and this value limits the size of species that can sorb into the zeolite and diffuse through the three-dimensional system.

The molecular dimensions of the supercage (approximately 1.3–1.4 nm in diameter for types X and Y) and the sodalite cage (with an approximately 0.2-nm aperture) permit another form of molecular discrimination, one in which molecular species can be assembled from ions or molecules small enough to penetrate into the supercage or the smaller sodalite cage, but after reaction/assembly form a species too large to exit.

The supercage has been used to support metal and metal oxide clusters for catalysis²¹ and for "ship-in-the-bottle" syntheses. Examples of the latter include forming supercage-encapsulated $\text{Ru}(\text{bpy})_3^{2+}$ from $\text{Ru}(\text{NH}_3)_6^{3+}$ ion-exchanged into faujasitic zeolite and thermally decomposed while exposed to 2,2'-bipyridine²² or assembling supercage-encapsulated iron phthalocyanine from $\text{Fe}^{\text{II}}\text{-X}$ (or Y) heated to 200 °C in the presence of phthalonitrile.²³

Entrapping species in the smaller sodalite cages of types A, X, and Y has been applied by Wang and Herron to create semiconductor clusters of CdS.²⁴ This approach is of particular interest for exploring nonlinear optical properties as a function of cluster size and the degree of communication throughout the zeolite.

The combination of the cation-exchange capacity of the aluminosilicate zeolites and the molecular sieving aspects of the zeolite structure adds a further degree of molecular discrimination. Mallouk and co-workers have especially taken advantage of zeolites as both a reactant support and a size and charge filter to compose electron-transport chains to study vectorial electron transfer, that is, electron transfer characterized by charge separation and current rectification.²⁵

In one series of experiments using zeolite type L (in which diffusion is one-dimensional, as type L has, as does mordenite, linear channels rather than the three-dimensional network found in types A, X, or Y), Mallouk et al. studied photoinitiated electron transfer between a covalently linked donor-acceptor molecule (where the donor moiety was a $\text{Ru}(\text{bpy})_3^{2+}$ derivative and the acceptor moiety was a viologen derivative (diquat²⁺)) and a zeolite-encapsulated secondary acceptor (benzylviologen, BV^{2+}).²⁶ The donor portion (the diquat moiety) could penetrate into the zeolite while the size-excluded $\text{Ru}(\text{bpy})_3^{2+}$ portion remained immobilized on the zeolite's external surface. The photo(electro)chemical reactions yielded an oxidized ruthenium/reduced BV^{2+} state with an unusually long lifetime (35 μs). With such systems, Mallouk's group is laying the foundation of artificial photosynthesis.

2. Ionic Possibilities

Aluminosilicate zeolites are microstructural templates that coincidentally provide a high ionic strength environment. Although electronic insulators, these zeolites, when hydrated, are solid solutions of high ionic molality and even when dehydrated exhibit fair ionic conductivity.¹⁵ As all electrode processes rely on the movement of charged species to maintain electrical neutrality, aluminosilicate zeolites provide another (and necessary) piece of the complete electrochemical interphase.

In 1965, Freeman demonstrated the versatility of zeolites in a practical solid-state electrochemical system, that of a battery.²⁷ Zeolite X was used as the ionic host for the catholyte (Cu^{2+} , Ag^+ , or Hg^{2+}) and as the ionic separator in its sodium-exchanged form (Na-X). Pressed pellets of, e.g., $\text{Cu}^{\text{II}}\text{-X}$ and Na-X were sandwiched between a gold current collector and a zinc anode. The half-cell reactions are the expected oxidation of $\text{Zn}(0)$ to $\text{Zn}(\text{II})$ and reduction of $\text{Cu}(\text{II})$ to $\text{Cu}(0)$, with type X providing a ready solid-state ionic path for cationic transport.

III. Zeolite-Modified Electrodes

Recent reviews on the materials science aspects of zeolites²⁸ and the use of clays and zeolites to coat electrodes²⁹ have included discussions on the use of and interest in zeolite layers on electrodes. Figure 3a represents the general view of a zeolite overlayer on a planar electrode surface. As zeolites are commercially obtained as crystalline powders, several methods have been used to hold the zeolite at the electrode surface. The means by which zeolites have been placed at electrode surfaces are summarized in Table II and include the chemical specifics of and references to the research thus far on zeolite-modified electrodes.

A. Methods of Preparation

As zeolites are electronic insulators, they must be coupled to an electrical source/sink to study their influence on electrode processes. With the exception of the direct use of compacted zeolite films or pressed pellets of zeolite sandwiched between planar electrodes, all of the zeolite-modified electrode approaches rely on composites to form a durable coating at or as part of an electrode surface.

1. Zeolite/Polymer Suspensions

The simplest course is to cast an electrode coating from a suspension of zeolite particles and dissolved polymer. After evaporation of the solvent, the polymer enfolds the zeolite and holds it to the surface, as long as the zeolite/polymer-modified electrode is used in electrolytes in which the polymer is sparingly soluble.

The polymer of universal choice to bind zeolites to an electrode surface, since its first use by deVismes et al.,¹⁰ is polystyrene. The problems with this "soft" composite approach include a lack of mechanical durability of the coating in stirred solutions and a general irreproducibility from coating to coating. Shaw and co-workers showed, using scanning electron microscopy, that part of the problem is morphological, arising from the good adherence of polystyrene to the electrode material (Pt) and its poor adherence to the zeolite

TABLE II. Preparation Methods for Zeolite-Modified Electrodes^a

| method | zeolite type | electron-transfer cofactor | ref |
|---|---|--|----------------|
| coelectrodeposition | | | |
| A. Z/organic salt (ratio dependent on organic) | Na-A, K-A | 1,4-DNB, TCNQ, 1,3-DNB, Ru(bpy) ₃ ²⁺ | 9, 30 |
| B. Z/conducting polymers | Na-A | pyrrole | 31 |
| evaporation of Z/polymer suspension | | | |
| 1. 10 mg of polystyrene/100 mg of Z/1 mL of THF | Na-Y | TMPyP ²⁺ | 10 |
| 2. 5 mg of polystyrene/80 mg of Z/10 mL of CH ₂ Cl ₂ | Na-A, Na-Y | MV ²⁺ | 32, 33 |
| 3. 10 mg of polystyrene/100 mg of (ML) Z/1 mL of THF | Na-Y | M(bpy) ₃ ²⁺ (M'(CpR) ₂ or M'(Cp)CpR) (M = Ru, Os; M' = Co, Fe) | 25, 34 |
| 4. 10 mg of polystyrene/100 mg of (V/P) Z/1 mL of THF | Na-Y | M(TMPyP ²⁺)/viologen (M = Zn(II), Co(II)) | 25, 35 |
| 5. 3 mg of polystyrene/12.7 mg of Fe ^{II} -Z/0.2 mL of THF | Na-X, NaCa-A, NaK-A, sodium mordenite | Fe ²⁺ /Fe ³⁺ | 36 |
| 6. 50 mg of polysulfone/100 mg of Z/1 mL of CHCl ₃ | Na-A | Cd ²⁺ , Al ³⁺ ^b | 31 |
| Z-composite | | | |
| A. Z/epoxy | | | |
| 1. Z pellet infused with low-viscosity epoxy resin (10 g of vinylchlorohexane dioxide + 6 g of propylene glycol diglycidyl ether + 26 g of nonenylsuccinic anhydride + 0.4 g of (dimethylamino)ethanol) | cesium mordenite | Cs ⁺ , Ag ⁺ , K ⁺ , Na ⁺ , Li ⁺ , Ba ²⁺ , Ca ²⁺ , Cu ²⁺ ^b | 37 |
| 2. Z pellet infused with low-viscosity epoxy resin (unspecified resin) | Na-A, NaCa-A, Na-Y | Cu ²⁺ , Fe ³⁺ ^b | 38 |
| B. Z/carbon paste | | | |
| 1. 1 Z/10 (1 g graphite/1 mL of vaseline) | natural Z from volcanic rock (Canary Islands) | Hg ²⁺ | 39 |
| 2. 40-50% Z/C paste (Type S, Bioanalytical Systems) | Na-A, Na-Y | (i) Ru(NH ₃) ₆ ³⁺ , MV ²⁺ , PV ²⁺ , HV ²⁺ , Cu ²⁺ (ii) MV ²⁺ | 33 40 41 |
| 3. 1.1 g of hydrated Z/2.1 g of graphite (Acheson 38)/1.9 g of mineral oil | Na-A | Ag ⁺ | 41 |
| 4. 9 mg of Cu ^{II} -Z/67 mg of C powder/24 mg of paraffin oil | sodium mordenite | Cu ²⁺ | 42 |
| C. Z/carbon/polymer composite: 4.4 wt % (7.2 wt %) Z/4.8 wt % (7.6 wt %) Ketjenblack C (Akzo-Chemie)/1 wt % (2.2 wt %) AIBN/89.7 wt % (83.1 wt %) 60:40 styrene-divinylbenzene | Na-A [Na-Y] | [Ru(NH ₃) ₆ ³⁺ , MV ²⁺] | 43 |
| D. Z/conductive powder mixture | | | |
| 1. 0.05% Z/100 g of Pb powder (30 μm)/10 mL of H ₂ O/10 mL of H ₂ SO ₄ | general | Pb/PbSO ₄ | 44 |
| 2. 15 mg of Ag ^I -Z/50 wt % graphite | mordenite-type | Ag ⁺ /Ag ⁰ | 45 |
| 3. (100 g of Na ₂ SiO ₃ ·9H ₂ O/100 mL of triethanolamine/700 mL of H ₂ O)/graphite (Aquadag) (or MoS ₂ or TiS ₂) + 40 g of NaAlO ₂ ·3H ₂ O/1.25 g of Z/(100 mL of triethanolamine/700 mL of H ₂ O) | 13X | general | 46 |
| 4. 30 mg of Z/30 mg of graphite | Na-Y | M(TMPyP ²⁺) (M = Mn(III), Co(III), Fe(III)) | 10 |
| silane-linked Z overlayer: | | | |
| $\text{SnO}_2 \text{-(O)}_2 \text{-Si-}\overset{\text{+}}{\text{N}} \text{-}\overset{\text{+}}{\text{N}} \text{-Si(O)}_2 \text{Z}$ | LZ-Y-72 | Fe(CN) ₆ ⁴⁻ /Os(bpy) ₃ ²⁺ /Fc ⁺ | 25, 47 |
| Z only | | | |
| A. pressed pellets—mechanical contact to electrodes | | | |
| 1. two electrodes: current collector and Zn anode | Na-X | (Cu ²⁺ , Ag ⁺ , Hg ²⁺)/Zn | 27 |
| 2. two or three Pt electrodes (T = 210-430 °C) | Na-A, Na-A-NaNO ₃ ^c | Na ⁺ (O ₂ ?) | 48, 51 |
| 3. WE, Ag; CE, PtSn; RE, Pt (T = 355 °C) | Na-A | Ag ⁺ /Ag ⁰ , Na ⁺ (O ₂ ?) | 48 |
| 4. two or three Pt electrodes (T = 250-425 °C) | [Cd(NO ₃) ₂] _n Na _{12-n} -A-xNaNO ₃ ^c | Cd ²⁺ /Cd ⁰ , Na ⁺ (O ₂ ?) | 49, 50 |
| 5. WE, Pt or Ag; CE, Pt or Ag; RE, Pt (T = 23, 255-425 °C) | Na-A, [Pb(NO ₃) ₂] _n Na _{12-n} -A-xNaNO ₃ ^c | Pb ²⁺ /Pb ⁰ , Na ⁺ (O ₂ ?), Ag ⁺ /Ag ⁰ | 51 |
| 6. WE, Pt; CE, Ag; RE, Ag (T = 315-400 °C) | Ag ^I -A ^d | Ag ⁺ /Ag ⁰ (O ₂ ?) | 52 |
| 7. WE/RE, Pt/Ag or Ag/Pt; CE, Ag (RT, 325 °C) | Li-A, Na-A | H ⁺ /OH ⁻ /H ₂ O/H ₂ /O ₂ , Li(hydr) | 53 |
| B. floated or compacted film—mechanical contact to electrodes | | | |
| 1. Cu, stainless steel, or graphite electrodes | Na-X | H ₂ O, EtOH, acetone | 54 |
| 2. Two Pt electrodes (RT, 350-500 °C) | Na-A, Na-Y | O ₂ , UO ₂ ²⁺ , Co ²⁺ , Ni ²⁺ , Cu ²⁺ | 55 |

^a Abbreviations: DNB, dinitrobenzene; TCNQ, tetracyanoquinodimethane; bpy, 2,2'-bipyridine; TMPyP²⁺, tetrakis(N-methyl-4-pyridyl)porphyrin; MV²⁺, methylviologen; Cp, cyclopentadienyl; PV²⁺, propylviologen; HV²⁺, hexylviologen; Fc⁺, ferrocenium; WE, working electrode; CE, counter electrode; RE, reference electrode. ^b Z layer used as an ion-exchange membrane for the potentiometric determination of the metal cations listed. ^c Z modified by the inclusion complex listed via exposure to the appropriate molten nitrate salt(s). ^d Z heated to 1273 K before electrochemistry, a temperature high enough to cause structural damage to the crystalline lattice of the zeolite.

particulates.³³ A SnO₂ surface, however, leads to a segregated layer where the zeolite particles are next to the oxide and overlain by polystyrene, presumably due to poor wetting of SnO₂ by the polymer.³⁴ The trend

seems to be to employ one of the other modification approaches after losing patience with polymer encapsulation. Certainly, issues of diffusion and transport, as affected by the presence of zeolite, are complex

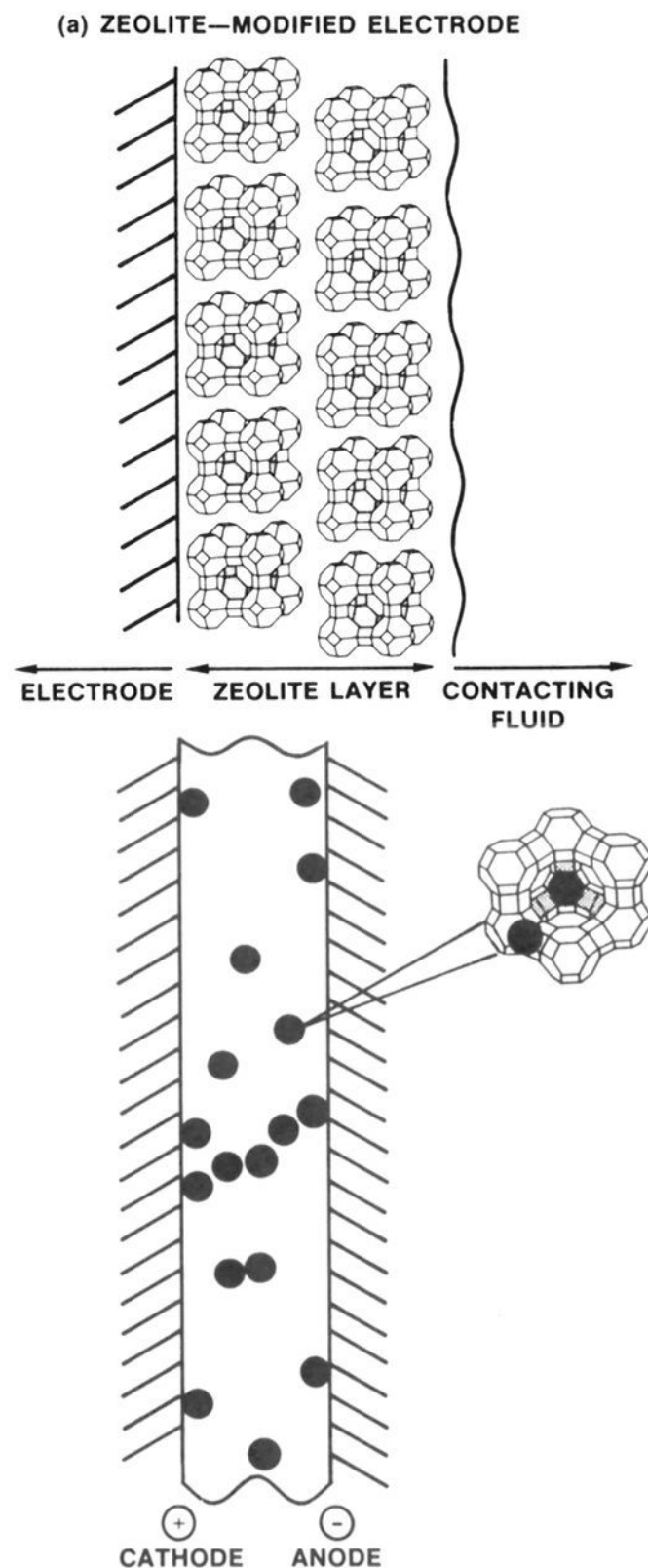


Figure 3. Schematic representations: (a) an overlayer of zeolite A on a planar electrode surface in contact with a fluid (liquid or gas); (b) general dispersion electrolysis cell showing the dispersed-particle electrode as contained between feeder electrodes with an exploded view of intra/extracrystalline Pt supported on zeolite Y.

enough without further contribution from a polymer binder.

2. Zeolite/Conductive Powder Mixtures

This method is also quite simple and relies on pressing the powder mixture into electrode grids, as commonly done in the battery industry, or, as can be done when using carbon powder, adding an organic oil or grease and using the mixture as a modified carbon paste electrode. The use of carbon paste as a binder and an electronically conducting matrix has an additional advantage in that the surface, if fouled during electrochemical action, can be readily renewed by removing the surface layer of the paste.

3. Zeolite/Carbon/Polymer Composites

Shaw and Creasy have recently shown the advantage of using a "hard" composite in which zeolite particles

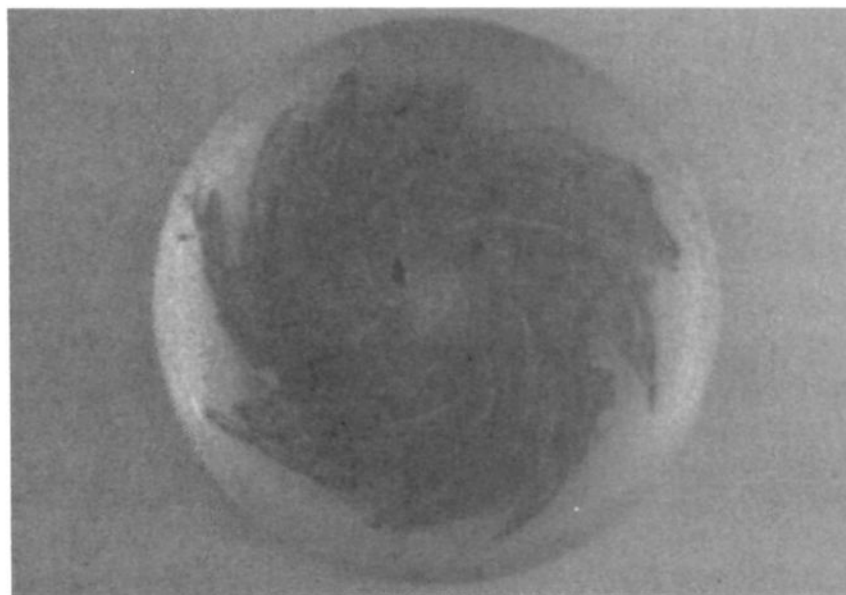


Figure 4. Photograph of a coelectrodeposited coating containing Na-A and 1,4-dinitrobenzene on a Teflon-shrouded Pt rotating-disk electrode.

and carbon powder are bound by a radical-initiated copolymerization of styrene and a cross-linking agent (divinylbenzene).⁴³ The resulting hard surface can be polished and exhibits better reproducibility and response times to electroactive solutes than zeolite-modified carbon paste electrodes.

4. Coelectrodeposition

Rolison and co-workers discovered that the strong cationic nature of zeolite could be used to affect the reductions of organic oxidants through ion-association reactions promoted by Na^+ . A coating can be formed at rotating Pt or glassy carbon disk electrodes consisting of the disodium salt of the organic dianion and type A zeolite particles.^{9,30} The quality and extent of the coating can be controlled by titrating Na^+ into the aprotic nonaqueous electrolyte,³⁰ although with time Na-A provides a solution concentration of Na^+ via ion-exchange reactions with the electrolyte cation.⁹

Figure 4 shows a Na-A/1,4-dinitrobenzene coating on a Teflon-shrouded Pt disk electrode. The coating conditions were such that the galactic swirl pattern characteristic of the hydrodynamic flow is emphasized. The coating is orange in tint, which is a color characteristic of the doubly reduced 1,4-dinitrobenzene. The primary problem with this composite is that water disrupts the ion associations between Na^+ and the organic dianion and between Na^+ in the zeolite and the organic dianion, so that these zeolite-modified electrodes can only be studied and used in nonaqueous media.

Our group has also achieved coelectrodeposition of type A zeolite and the conducting polymer polypyrrole.³¹ This was achieved in an "upside-down" configuration where a drop of the zeolite-pyrrole slurry (in 0.1 M $\text{Et}_4\text{NClO}_4/\text{CH}_3\text{CN}$) was placed on the disk electrode as it was held face up. Two Pt wires placed at the edges of the drop were used as the auxiliary and quasireference electrodes. The zeolite particles were gravity-encapsulated during the formation of polypyrrole as pyrrole was oxidized. Surprisingly uniform particle-polymer coatings formed.

The ideal is to have immediate access, even in a three-dimensional reaction zone, to an electrical conductor to supply and retrieve electrons on demand without blocking reagent access to and from the zeolite

and without the "silence" of electronically isolated zeolite layers. One hope is the synthesis of conducting molecular wires within the zeolite for ready communication to the outer environment. A logical approach is polymerizing conducting polymer precursors sorbed in zeolite. This has been demonstrated by Chao and Erf for pyrrole in type Y zeolite,⁵⁶ where Fe(III) impurities in the zeolites initiated the oxidation; FTIR characterization indicated that pyrrole oligomers had formed.

Recently Bein and Enzel have also pursued this line for pyrrole⁵⁷ and anilinium⁵⁸ sorbed in faujasite and mordenite zeolites. In addition, polyacetylene has been chemically formed at zeolite surfaces, but without following studies on the nature of such composites when used as zeolite-modified electrodes.^{59,60} Direct electropolymerization of monomers sorbed in zeolite has yet to be attempted.

5. Silane-Linked Zeolites

Li, Lai, and Mallouk have shown that a bifunctional silane can be used to covalently link a single dense layer of zeolite Y to a SnO₂ electrode, through Sn-O-Si linkages at the electrode and presumably by Si-O-Si linkages between the silane layer and the zeolite;⁴⁷ see Table II for a structural schematic. Fixed cationic sites in the silane permit assembly of electrostatically bound anionic electroactive species (associated with quaternary ammonium sites in the silane) and cationic electroactive species (associated with the zeolite) in a thin layer at the electrode surface. This approach avoids electrochemically silent layers of zeolite, but at the expense of ease of preparation.

6. Dry Film/Pressed Pellet

Finally, some work has been done with dry films or pressed pellets of zeolite compressed between planar electrodes. Voltammetric characterization of such modified electrodes is typically done at elevated temperatures. A variation of this is to perfuse a pressed pellet of zeolite with epoxy; such systems have only been studied under potentiometric (zero current) conditions.^{37,38}

B. Uses of Zeolite-Modified Electrodes

1. Molecular Recognition

The molecular sieving ability of zeolites can be used to discriminate between analytes of different size during reactive use. The zeolite can be used as a host matrix to preconcentrate and store suitably sized molecular reactants for subsequent use before, during, or after electron-transfer processes. Due to the cation-exchange capacity of aluminosilicate zeolites, these solutes can be cationic atoms and molecules in addition to charge-neutral species.

a. Reactant Host. The technological application of molecular discrimination/preconcentration by zeolites has actually led the fundamental studies of their effect on electrode processes. The effectiveness of zeolites as catholyte hosts has been demonstrated by Freeman²⁷ for solid-state batteries, as described above. Similarly, Coetzer and Thackeray⁶¹ used Na-A zeolite as a host for I₂ (up to 38.9 wt % in I₂) to act as a catholyte ma-

terial in a silver/iodine solid-state cell. Unless a thin Na-A(I₂) layer was used, the AgI discharge product eventually led to internal resistance problems.

Adding zeolite to the Pb paste anode in lead acid batteries leads to longer life cycle;^{44,62} this was attributed to the adsorption of oxygen by the zeolite. The affinity of zeolites for oxygen has also been exploited by adding zeolite layers to the oxygen cathode in fuel cells with⁶³ and without^{64,65} electroactive metal ions exchanged into the zeolite.

b. Self-Assembly/Vectorial Electron Transport. Mallouk's group capitalizes on the size/shape/charge-discriminating ability of zeolites to construct spatially defined (but restricted) electron-transport chains as inorganic analogues of the electron-carrier chains functioning in biological systems. The light-driven example was described above; electrochemically driven systems have also been explored by the use of zeolite-modified electrodes.^{25,34,35,47}

In one example of zeolite-assembled unidirectional electron transfer,³⁵ methylviologen (or BV²⁺ or diquat²⁺) was ion-exchanged into Na-Y to a loading of one viologen for two supercages. The zeolite was then partially capped by a subsequent ion-exchange reaction with cobalt (or zinc) tetrakis(*N*-methyl-4-pyridyl)porphyrin chloride (Co^{II}TMPyP⁴⁺): the degree of porphyrin ion exchange was estimated to be at monolayer coverage on the zeolite exterior. This cation-modified zeolite was cast, with polystyrene, onto the surface of SnO₂.

On the basis of, e.g., the voltammetry of BV²⁺ and Co^{II}TMPyP⁴⁺ in solution at SnO₂, and the voltammetry of the analogous porphyrin(viologen)-modified Y coating on SnO₂, Li et al. determined that (1) the porphyrin blocked direct electrode reduction of the entrained viologen, (2) direct electrode reduction of the porphyrin ring permitted mediation of the reduction of the viologen dication in the zeolite to the radical cation (charge trapping), and (3) Co^{II/I} mediation permitted the one-electron reoxidation of radical cation or viologen neutral (charge-"untrapping" reaction). This result is an electrode-confined microstructurally designed demonstration of charge rectification as first reported by Abruña et al.⁶⁶ for polymer bilayers on modified electrodes.

2. Analytical Uses

a. Amperometry. Selectivity in analysis is highly desirable, and combining a zeolite (as a size/charge filter or analyte/reactant preconcentrator) with an electrode (to provide direct control of the potential of the reaction) offers inviting analytical prospects. Our group observed this directly as a consequence of characterizing zeolite A/organic salt codeposited coatings. In addition to voltammetry attributable to the organic oxidant present in the coating, a major peak due to oxygen reduction was obtained at the appropriate potential in deoxygenated CH₃CN electrolyte.⁹ Oxygen, sorbed into the zeolite upon exposure of the modified electrode to air (or oxygen-saturated solution), would diffuse from the zeolite in the oxygen-free environment of the electrolyte and be detected amperometrically at -1.0 vs SSCE (sodium-saturated calomel electrode).

The size restrictions a zeolite can impose were readily seen by the inability to nitrogen-purge the smaller

aperture potassium ion compensated zeolite A coatings of entrained oxygen, while coatings prepared with sodium ion compensated zeolite A could be readily purged. Switching to argon (with a smaller kinetic diameter than nitrogen) allowed both K-A and Na-A coatings to be purged of oxygen.⁹ A more efficient purge of the oxygen stored by zeolite in the coating is to degas the electrolyte solution while the electrode is poised at the potential for oxygen reduction.

Creasy and Shaw used simplex optimization to adjust the parameters of methylviologen-modified zeolites A and Y in carbon paste for the optimal voltammetric signal for the methylviologen-catalyzed reduction of oxygen.⁴⁰ This method allowed them to optimize the ratio of zeolite to carbon paste as well as the viologen loading of the zeolite. They point out that the design of complex, multicomponent systems can be improved by the use of optimization strategies.

Zeolite-modified carbon pastes have been used to sequester Hg^{2+} ³⁹ and Ag^{+} ⁴¹ from aqueous solutions at open circuit and then, when queried under potential control, reveal the amount. For Hg^{2+} , Hernández et al. would first reduce the sorbed $\text{Hg}(\text{II})$ at negative potentials and then scan to positive potentials and use the resulting anodic stripping peak to quantify the amount of $\text{Hg}(\text{II})$ present in solution;³⁹ a linear response for current was obtained from 0.11 to 2.2 $\mu\text{g}/\text{mL}$.

Wang and Martinez determined the amount of zeolite-preconcentrated Ag^{+} ion from the reduction current of the differential-pulse voltammogram.⁴¹ They also determined that the analysis of $\text{Ag}(\text{I})$ at a level of 1 $\mu\text{g}/\text{mL}$ was not compromised by the presence of 10 $\mu\text{g}/\text{mL}$ concentrations of $\text{Co}(\text{II})$, $\text{Mn}(\text{II})$, $\text{Ca}(\text{II})$, $\text{Pb}(\text{II})$, $\text{Cu}(\text{II})$, and $\text{Ti}(\text{IV})$, while $\text{Fe}(\text{III})$ completely depressed the $\text{Ag}(\text{I})$ response and $\text{Bi}(\text{III})$, $\text{U}(\text{IV})$, $\text{Ni}(\text{II})$, $\text{Zn}(\text{II})$, and $\text{Ti}(\text{I})$ enhanced the currents obtained.

Other groups have characterized zeolite-modified electrodes for their response to $\text{Cu}(\text{II})$ ^{33,42} and $\text{Fe}(\text{III})/\text{Fe}(\text{II})$.³⁶ pH effects have been noticed^{36,39,41} for the analysis of metal ions in aqueous solutions with use of zeolite-modified electrodes. In the case of $\text{Ag}(\text{I})$,⁴¹ precipitation of AgOH at high pHs diminished the current expected, based on the initial solution concentration of $\text{Ag}(\text{I})$. For the $\text{Fe}(\text{III})/\text{Fe}(\text{II})$ system, peak current was strongly dependent on the acid concentration and essentially nulled at $\text{pH} > 2$.³⁶ The authors proposed that proton-uptake equilibria by the zeolite controlled the electroactivity of the electrostatically bound $\text{Fe}(\text{II})$. As zeolites, especially the aluminum-rich zeolites, can decompose in the presence of strong acid via dealumination,¹⁵ the pH of the analyte becomes a critical factor to consider in any zeolite-based analysis.

b. Potentiometry. Because of the cation-exchange capacity of the aluminosilicate zeolites, a natural electroanalytical application is the use of zeolite membranes for the equilibrium determination of cation concentration. As pointed out by Bard and Mallouk in their clay- and zeolite-modified electrode review,²⁹ the use of zeolitic membranes in ion-sensitive electrodes dates to 1939.⁶⁷ Marshall explored naturally occurring zeolite crystals as analogues of the glass membrane electrode, so that an inner solution of the cation to be determined was used during measurements;⁶⁷ the effect of anions and colloids on the equilibrium potentials was also studied.

Barrer and James studied synthetic and natural zeolites as ion-sensitive membranes by pressing the zeolite microcrystals with polymer powders (such as polystyrene) or casting them in thermosetting resins;^{68,69} selective membranes were obtained with the latter rather than the former. Using Na-A, in which Et_4N^{+} is size excluded, they observed complete selectivity for Na^{+} over Et_4N^{+} .⁶⁹

More recently, Johansson et al. embedded pressed mordenite-type zeolite pellets with low-viscosity resin and studied the membrane as a Cs^{+} ion selective electrode.³⁷ The membrane gave a near-Nernstian response for Cs^{+} and was selective for Cs^{+} over Ag^{+} , K^{+} $>$ Na^{+} $>$ Li^{+} and even more selective for Cs^{+} over the dications Ba^{2+} $>$ Ca^{2+} $>$ Cu^{2+} . The nature of the zeolite and the molecular sizes that can penetrate the lattice provide a variety of design possibilities; e.g., Cs^{+} cannot penetrate the naturally occurring zeolite analcite, so an analcite membrane is completely selective for Na^{+} over Cs^{+} .⁶⁹

Demertzis and Evmiridis studied $\text{Fe}(\text{III})$ - and $\text{Cu}(\text{II})$ -exchanged synthetic zeolite types A and X in pelletized, epoxy-embedded membranes with special attention to the effect of zeolite/epoxy adhesion on the deviation of the response from ideal Nernstian behavior.³⁸ Only the membranes with good adhesion properties gave Nernstian response, in agreement with Barrer and James' observation that cracks in the membrane provide solution paths for transport that diminishes the ability of the zeolite to control the potential-determining ion-exchange reactions.^{68,69} $\text{Fe}^{\text{III}}\text{-X}$ was especially poor as an ion-selective membrane.³⁸ As a means of minimizing solution penetration, Barrer and James' reported that type A or X membranes impregnated with silicone oil gave excellent selectivities.⁶⁹

Ion-exchange processes in nonaqueous solvents, especially alcohols, have been investigated with zeolites,¹⁵ but the use of zeolitic membranes as nonaqueous ion-selective electrodes has not. Townsend has recently discussed the relative lack of research on the ion-exchange character of zeolites,⁷⁰ occasioned primarily by the limited (commercial) application of zeolites as ion exchangers. Their characterization as nonaqueous ion exchangers is even more limited. The examination of zeolites in electrochemical interphases has included nonaqueous electrolytes; eventually, an understanding of the thermodynamic and especially the kinetic nature of ion-exchange processes in zeolites during electrochemical reaction will be required. Further, the effect of electric fields on ion-exchange processes in zeolites is unclear.

3. Reactivity

Rather than focus on the influence of zeolites on electrochemical reactions, some research has centered on the use of potential or current to propel desired reactions with(in) the zeolite. In an attempt to prepare dispersed, zeolite-supported clusters of $\text{Ag}(0)$, Pereira-Ramos et al. pressed a mixture of graphite and silver-exchanged mordenite zeolite powder on a stainless-steel grid and, using chronopotentiometry, studied the reduction of $\text{Ag}(\text{I})$ in the zeolite with time in aqueous electrolytes.⁴⁵

Zeolite-supported metallic silver could be formed, but apparently only after exchange of an electrolyte cation

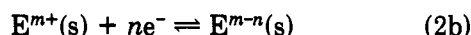
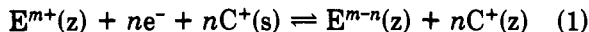
for Ag^+ in the zeolite permitted zeolite-free $\text{Ag}(\text{I})$ reduction at the steel current collector and graphite particles to $\text{Ag}(0)$ dendrites and crystallites. The authors then proposed that migration of small $\text{Ag}(0)$ particles back into the zeolite occurred. Electroreduction conditions that generated smaller crystallites at the electrical conductors were preferable for the quality of the ultimate dispersed Ag^0 -mordenite product.

Another manner in which electrode potential can be used to control a desired reaction in zeolites, although not as zeolite-modified electrodes, is by the bulk electrolysis of zeolite suspensions.^{71,72} This approach has been used to metalate large amounts of fully exchanged silver(I) mordenite⁷¹ or to prepare large amounts of product from the catalyzed oxidation of a hindered phenol by $\text{Mn}^{\text{II}}\text{TMPyP}^{4+}$ -modified faujasite;⁷² in the latter case, the feeder electrode recycled the catalytic $\text{Mn}(\text{II})$ center.

4. Diffusion and Transport Issues

One of the most important characterizations of any modified electrode is the nature of molecular and charge transport through the modifying layer. When the modifying layer contains micrometer-sized cation-exchangeable particulates that are microporous and impose additional diffusional character, the description of transport becomes slightly intricate.

Shaw et al. have started to address the description of transport in zeolite-modified electrodes using the following terminology to posit two charge-transport mechanisms



where E^{m+} is the electroactive probe, C^+ is the electrolyte cation (univalent for bookkeeping simplicity), and z and s refer to zeolite and solution phases, respectively.³³

In mechanism 1, the electroactive solute already sorbed/exchanged into the zeolite undergoes electron transfer within the zeolite (by means unspecified), and to maintain charge neutrality, an equal, but opposite, charge moves into the zeolite from the sea of cations in the surrounding electrolyte. Should a sorbed neutral be oxidized, cations would have to be expelled from the zeolite lattice.

In mechanism 2, the electroactive solute undergoes ion exchange with cations in the surrounding electrolyte (step a). Once in solution, the zeolite-free electroactive solute is reduced normally (step b), i.e., at the electrode or by electron-transfer mediators in solution. Experimental evidence exists for mechanism 2 in the results for electroreduction of Ag^{I} mordenite,^{45,71} $\text{Cu}^{\text{II}}\text{-Y}$ (or $\text{Cu}^{\text{II}}\text{-A}$)/polystyrene on Pt,³³ Cu^{II} mordenite/C paste,⁴² and Fe^{II} zeolite/polystyrene on Pt³⁶ and is implicit in the analytical determinations of Ag^+ with Na-A/C paste⁴¹ and Hg^{2+} with zeolite/C paste.³⁹

Once the electroactive probe is in solution, the voltammetric current obtained for it will depend on its concentration (and the concentration of $\text{E}^{m+}(\text{s})$ will be related to its mobility into/out of the zeolite, as well

as the mobility of the electrolyte cation displacing it) and the mass transport of $\text{E}^{m+}(\text{s})$ to the electrode. Since the zeolite provides a high (>1 M) concentration of solute, mass transport to the electrode will not be strictly described by linear diffusion as concentration gradients, migration, and thin-layer/edge effects can all be anticipated to play a role; Shaw and co-workers invoked these factors to explain the voltammetry obtained for methylviologen-exchanged Y.³³

Diffusion within zeolites is a much studied phenomenon (see ref 73 for some recent perspectives), with molecular mobility intimately related to the match between intracrystalline pore sizes, the dimensionality of the intracrystalline channel structure, and the size/shape of the solute. Shaw and co-workers explored this aspect for electrochemical situations by using electrolytes of varying cation size and the electroactive probes $\text{Ru}(\text{NH}_3)_6^{3+}$, methylviologen (MV^{2+}), and Cu^{2+} sorbed into zeolite Y.³³ In competitive adsorption of $\text{Ru}(\text{NH}_3)_6^{3+}$ and MV^{2+} , Y was shown to preferentially concentrate $\text{Ru}(\text{NH}_3)_6^{3+}$; however, the magnitude of current for MV^{2+} was relatively greater, indicating greater mobility of MV^{2+} into/out of the zeolite.

By varying the cation of the electrolyte, and thus the size of the hydrated cation available for ion exchange with $\text{Cu}^{\text{II}}\text{-Y}$, Shaw et al. showed that the current due to reduction of $\text{Cu}^{2+}(\text{s})$ was increased by the use of cations with small hydrated radii.³³ The smaller cations, as expected, were more effective at displacing $\text{Cu}(\text{II})$ in the zeolite by ion exchange. This result also corroborates mechanism 2.

This dependence of the analytical response on the nature of the supporting electrolyte cation (its charge, size, and concentration) complicates the use of zeolite-modified electrodes as analytical sensors. Zeolite-modified electrodes offer analysis of cations and molecules on a basis of ionic or size competition (and concentration), not as uniquely selective filters. As with many analytical schemes, the character of the analysis needs to be understood before an analysis is attempted.

Mechanism 1 is of interest in designing electrochemical reactors around zeolites where the electron transfer occurs within the zeolite so as to take full advantage of the size/shape selectivity of the zeolite. The key is intra/intercrystalline electron-transfer communication. As discussed above, synthesizing molecular conducting wires in the zeolite is one promising prospect to achieve this ambition. Another is using the zeolite as the template to structure intracrystalline nanometer-sized electrodes. This approach has been christened "electrode-modified zeolites" and is described below.

IV. Electrode-Modified Zeolites

Structuring nanometer-sized metal and metal oxide particles in the interior of zeolites is an active area of research²¹ as a means of redirecting the catalytic properties of the zeolite. As a result, ample synthetic procedures can be found in the literature to prepare zeolite-supported conducting or semiconducting particles. With appropriate control of the synthesis, these particles can be predominantly confined to the supercages, which allows the intracrystalline architecture of the zeolite to define particle sizes on the order of 1 nm. Further, low weight loadings can be prepared to minimize the number of zeolite pore openings that are

blocked by the microstructured particles so that unhindered reagent access to the zeolite interior still occurs.

Rather than try to address these intracrystalline particles as electrodes via molecular wires, the use of feeder electrodes and dispersions of the metalated zeolites offers a mechanism whereby supported metal microstructures may function as electrode materials without a direct electrical contact. Dispersions and fluidized bed electroreactors are typically used with high ionic strength electrolyte and metal particles on the order of 10^2 – 10^3 - μm size,^{74–76} dispersed electrodes may function either as monopolar electrodes or as bipolar electrodes (where both cathodic and anodic reactions can occur on a single particle) and without direct contact to the feeder electrodes.

Recently, Pons and co-workers demonstrated that 0.1–10- μm Au, C, or Pt microspheres could function as dispersed ultramicroelectrodes.^{77,78} In keeping with the ability to use ultramicroelectrodes in low-dielectric media,^{79,80} electrolyses could be performed in solvents without dissolved electrolyte salt.

Rolison et al. have demonstrated that dispersion electrolysis can also be achieved when the dispersed electrodes are Pt microstructures supported on type Y zeolite (designated as Pt–Y).^{81,82} Because the procedure used to prepare the supported Pt (based on oxygen activation and hydrogen reduction of $\text{Pt}^{\text{II}}(\text{NH}_3)_4$ -exchanged Na–Y^{83,84} leaves approximately 10% of the Pt weight loading on the external zeolite surface (extracrystalline) and 90% of the Pt weight loading in the zeolite interior (intracrystalline), two types of potential Pt electrodes exist. This new use of zeolite-supported metal microstructures as electrode-modified zeolites is depicted in Figure 3b, showing dispersion conditions between feeder electrodes.

A. Intracrystalline Electrodes vs Extracrystalline Electrodes

Because the zeolite is an electronic insulator, although an ionic conductor, which may partially screen electric fields, it should be possible to develop a potential on intracrystalline-sited metals with sufficiently high electric fields. Low-field electrolyses (<300 V/cm) involving electroactive solutes capable of entering zeolite Y (pure H_2O , H_2 in pure H_2O , ferrocene in neat CH_3CN) and an electroactive solute too bulky to enter zeolite Y (bis(1,2-dibenzylcyclopentadienyl)iron(0)) established that electrolysis occurred only at the externally sited Pt particles⁸²—these are the particles that can physically contact the feeder electrodes and other charged, supported Pt particles.

The enormous intracrystalline Pt surface area (for 1 wt % Pt–Y, estimated at 2.5×10^4 cm^2/g for supercage-encapsulated Pt, 1 nm in diameter⁸²) did not contribute to the electrode processes, partly because the electric field is dropped across so many Pt particles that each is left with insufficient potential for electron transfer to receptive intracrystalline solutes. The combination of dispersion electrolysis and strategies that silence the externally sited metal particles or syntheses that exclusively site the metal in the zeolite interior, such as recently reported for zeolite L,⁸⁵ should permit the use of higher electric fields for the direct exploration

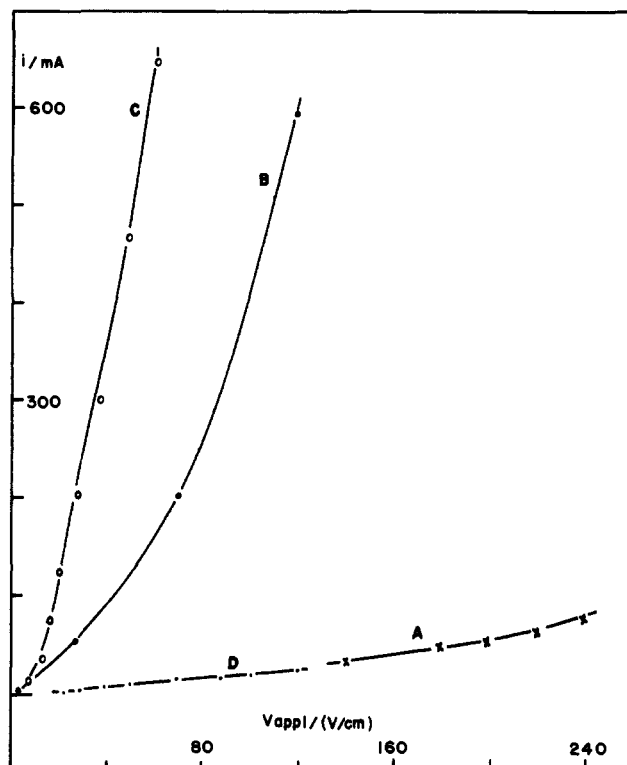


Figure 5. Current–applied voltage curves for supported Pt ultramicroelectrodes used in the dispersion electrolysis: (A, B) 20 mL of benzene–8 mL of water (averaged values for two experiments) with 0.1 g of 1% Pt/ γ -alumina used in A and 0.1 g of 1% Pt–Y used in B; (C) pure water, 0.1 g of 1% Pt–Y; (D) electrolysis using feeder electrodes only (no dispersed particles) with 30 mL of filtrate obtained after stirring 166 mg of 1% Pt–Y in 50 mL of H_2O for 30 min.

of electrode processes and electron transfer in the zeolite interior.

B. Ionic Contribution of the Zeolite Support

The strong ionic nature of Y zeolite played an important role in the effectiveness of dispersion electrolyses in these salt-free electrolytes, as seen by comparing dispersed 1% Pt–Y electrodes and 1% Pt supported on γ -alumina.^{81,82} (For comparison between different dispersed electrodes, effectiveness of electrolysis was defined as the magnitude of current at a given applied voltage.)

Figure 5 summarizes the pronounced enhancement in electrolytic effectiveness in aqueous media for Pt supported on Y zeolite over that at Pt supported on alumina: contrast curve A (1% Pt/alumina) and curve B (1% Pt–Y) for dispersion electrolysis of a two-phase medium of benzene and water. Electrolysis of pure water with dispersed 1% Pt–Y produced the even greater response seen in Figure 5, curve C. The low level of solution ionic conductivity resulting from exposure of 1% Pt–Y to water (from the generation of ions in solution due to zeolite-promoted autoprotolysis of water) is shown in Figure 5, curve D.

Control experiments demonstrated that the ionic conductivity of a dispersion containing water and zeolite Y was greater than that derived just from ions generated by zeolite-promoted autoprotolysis of water. An additional contribution to the ionic conductivity of the medium (i.e., the suspension and not just the solution) arose from the dispersion-driven mobility of the zeolite acting as a solid-state electrolyte.⁸²

C. Electrochemical Example of a Strong Metal-Support Interaction

Confinement of all electrochemical action to the externally sited Pt particles permitted a direct assessment of particle size on the effectiveness of the electrolysis of pure water by Pt-Y as the weight loading of Pt was increased.⁸² X-ray photoelectron spectroscopic analysis of 1, 5, and 10 wt % Pt-Y indicated that the size of externally sited Pt particles was in the order 1% Pt-Y < 5% Pt-Y < 10% Pt-Y, with the size of the particles sited on the exterior of 1% Pt-Y on the order of the escape depth of a Pt photoelectron (2.5 nm). The order was reversed for the effectiveness of water electrolysis with dispersed Pt-Y: 1% Pt-Y \gg 5% Pt-Y > 10% Pt-Y. On the basis of an estimated surface area of the externally sited Pt particles, 5% Pt-Y should have yielded slightly more current at a given voltage relative to 1% Pt-Y.

The increase in solution conductivity upon exposure to Pt-Y was shown to be identical for all three weight loadings,⁸² and as all three systems are on the same zeolite support, the first-order contribution of the zeolite to the solid-state ionic environment should be identical. The only variation is in the size of the supported Pt particle on the zeolite exterior. The implication is that as the size of the electrode particle decreases, more of the electrode particle experiences the solid-electrolyte nature of the zeolite support. Consequently, electrode processes at 1% Pt-Y occur in a relatively more uniform, high ionic strength environment. The enhanced electrolytic effectiveness of nanometer-sized Pt particles on zeolite Y illustrates the impact of strong metal-support interactions on electrode processes.

D. Electrode-Modified Zeolites: A Contained, Microscopic Integrated System

The effectiveness of zeolite-supported conductors as dispersed ultramicroelectrodes advances the investigation and practical application of zeolitic influence on electrode processes by permitting electrolyses on a preparative scale, with an enormous range of conducting metal and metal oxides and semiconducting compounds to explore, and in low-dielectric, composite-free environments. As demonstrated for Pt-Y, siting nanometer-sized electrodes in and on a solid electrolyte with molecular size and shape selectivity provides a package to explore fundamental issues concerning (1) electrochemical reactivity of metals at sizes where bulk metallic properties may not apply, (2) electrochemical analogues of strong metal-support interactions, and (3) intrusion of zeolitic character on electrode reactions, both by providing a high ionic strength environment and by molecular discrimination. The prospects for new chemistry/electrochemistry seem bright.

V. Conclusion

In 1986 in Tokyo, Professor R. M. Barrer provided a perspective on porous crystals, such as zeolites, during his opening address to the 7th International Zeolite Conference.⁸⁶ Toward the end of his lecture, Barrer reminded his audience that, while not the least of the zeolitic properties, the strong electrolyte nature of zeolites was underexplored. The exploration of the

potential consequences of zeolites when used as materials in electrochemical environments has intensified since 1986, and the direction of this body of research promises insight into both electrochemical processes and zeolite materials science.

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