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Ceramic-Based Materials for Electrochemical Applications

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SUMMARY: Novel catalytic ceramic-based materials that simultaneously possess high surface area and adsorptive capacity, with proton and/or electron conducting properties, were developed for electrocatalytic and waste-stream treatment processes. These novel inorganic proton conducting membranes were produced by incorporating inorganic low-temperature proton conductors such as polymeric phosphates of polyvalent metals into the porous structure of different active or inert substrates such as ceramics (in the form of tubes, discs and paper), zeolites or carbon cloth. Electrocatalytic activity was obtained by coating electroconductive surface layers that acted both as electrode and catalyst. Bench scale and pilot scale test reactors were built and commissioned. Comparison with existing technologies was undertaken for several applications. Such high surface-area inorganic materials that support nanoscale metal clusters are being tested as electrode materials in anodic oxidation, inorganic fuel cells and hydrogen generation.

Introduction

There is a strong interest world wide in developing efficient, low cost, proton conducting membranes. Novel, fully inorganic membranes, comprising porous ceramic membrane supports in tubular and flat sheet form, impregnated with inorganic proton conductive materials, for instance, zirconium phosphates, have been developed by our group. This technology, patented in EU, USA and South Africa [1] has been shown to be successful for the preparation of proton-conductive membranes that offer high hydrogen permeability and permselectivity. Fabrication techniques developed for the production of inorganic membranes, such as extrusion casting as well as suspension type casting, sol-gel and CVD techniques, can readily be employed. These membranes possess important characteristics required of inorganic supports for the preparation of proton conducting membranes, such as low thickness and high mechanical flexibility.

The typical solid-state protonic conductors developed a couple of decades ago were mainly acidic or hydrous inorganic compounds, Later, entirely different classes of materials, such as polymers, oxide ceramics, and intercalation compounds, gained

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increasing interest as proton conductors [2,3]. Polymeric proton conducting membranes that are currently available on the market are restricted by several shortcomings of polymeric materials, such as low thermal stability, chemical inertness, high swelling in aqueous and organic media and the difficulty of applying various catalysts on polymeric surfaces. Such shortcomings are largely attributed to the fact that these membranes are made with various organic polymers, which are generally not suitable for application in electrochemical processes due to their environment-dependent structure and low specific surface area. On the other hand, there are inorganic polymeric materials that posses significant proton-conductive properties, accompanied by good chemical and thermal stability and high specific surface areas [4]. Moreover, nano-particulate metal oxide catalysts and conductive layers may be deposited on such materials to render them electrochemically active. These electrocatalytic structures may find application as catalytic electrodes in the electrochemical decomposition of organic pollutants, as proton conducting materials in fuel cells or in electrosynthesis.

The objectives of this study were to develop cost-efficient methods for the fabrication of such inorganic composite materials and to test their suitability for the applications described above. Inorganic proton-conducting membranes were produced by incorporating low-temperature proton conductors, such as phosphates of polyvalent metals and polyantimonic acid, into the porous structure of various supports. Electrocatalytic activity was obtained by the coating of electroconductive surface layers that act both as electrode and catalyst. High proton conductivity, in combination with low water permeability, makes these membranes ideal candidates for electrosynthesis applications and fuel cells. The optimization of process parameters such as reactor efficiency, current density, time and energy consumption was necessary. This was followed by upscaling electrocatalytic prototypes, the use of nanostructures in electrocatalysis and fuel cell applications and a comparison with existing technologies.

Cost efficient methods of manufacturing inorganic composite materials is necessary. The methods used for catalyst immobilisation in the membrane matrices ranged from chemical synthesis to chemical vapour deposition and sputtering to electroplating [5]. Incorporation of active metal species on zeolite composites, or various carbon and ceramic supports, may be followed by impregnation with proton conductors and deposition of conductive layers. Controlled precipitation may be performed by organometallic compounds for both reduction and stabilization, surfactant shell removal by reactive annealing, bimetallic alloys and variation of alloy composition. A few specific examples of process conditions used and results obtained using these materials are presented in the following three sections.

A. Electrochemical Oxidation of Organic Pollutants

A promising application of proton conducting membranes is their use as solid electrolytes for the electrochemical oxidation of organic pollutants present in aqueous solutions.

Phenol, which is listed as a priority pollutant by the US Environmental Protection Agency, is considered to be one of the major water pollutants that need to be recovered, removed or destroyed [6]. It reacts with chlorine during water treatment and produces chlorophenols, which are carcinogenic [7]. Oil refineries, coke plants, plastic plants and chemical industries are sources of phenolic waste. Present Swiss guidelines limit phenol concentration to 0.05 mg/dm^3 and even lower concentration limits are under discussion [8]. The electrolysis of phenol is a possible route for synthesis of quinones [8]. Further reactions of quinones and the ether and quinone-type polymer structures are slow, with the main products being organic acids (i.e. aliphatic acids) such as maleic and oxalic acid. Phenol oxidation can also be used as a model reaction to assess methods for treating aqueous organic wastes. It represents a large family of compounds and is a good test compound because of its well-known electrode fouling properties. The tarry deposit formed on electrodes during phenol oxidation is attributed to polymerization products. Formation of the yellow brown polymeric material at the anode surface is strongly dependent on experimental conditions such as alkaline medium (pH>9), low current density (<30 mA.cm^{-2}), high temperature (>50°C) and high phenol concentration (50mM) [9].

The production of quinones is of great concern from a toxicity point of view due to the fact that these reaction intermediates are even more toxic than phenol. Among these quinines, 1,4-benzoquinone represents one of the most toxic xenobiotics [10]. Accordingly, complete oxidation of phenol to CO_2 should be achieved to ensure environmentally safe discharges.

The main principle use of hydroquinone are in the manufacture of black and white film developers; the manufacture of antioxidants and polymerization inhibitors; as a chemical intermediate in the manufacture of pharmaceutical, agrochemicals and dyes; in the production of cosmetics and topical creams; and as a laboratory reagent [11].

The mechanism for the electrochemical oxidation of phenol is presented in Figure 1.

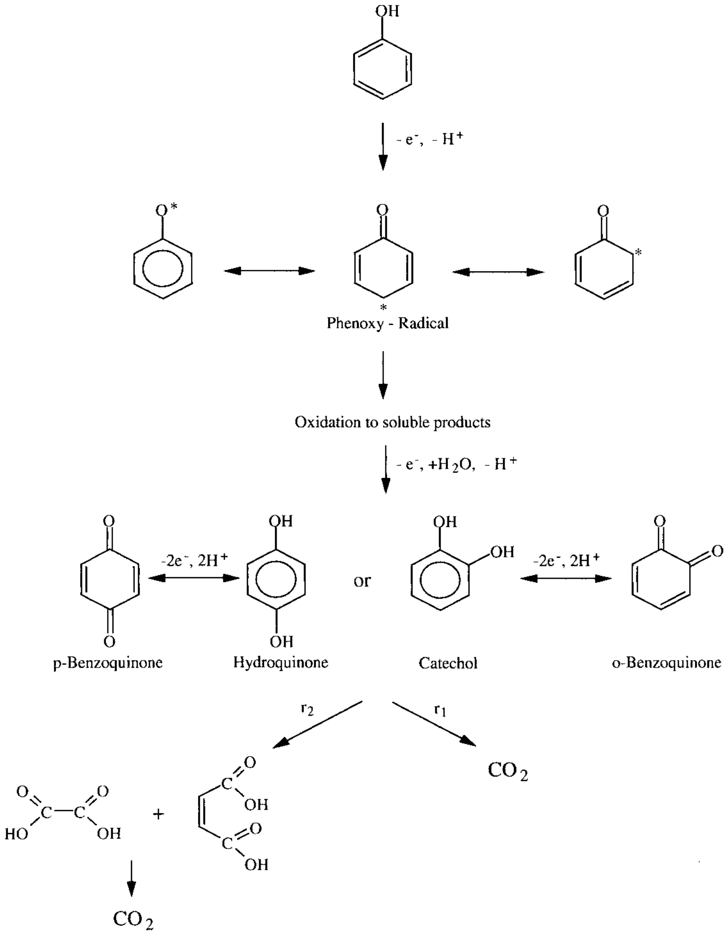

Fig. 1: Mechanism for the electrochemical oxidation of phenol.

Selection of Catalysts

The removal of undesirable impurities from liquid (usually aqueous) phases by electrochemical processes requires suitable catalytic electrodes and potential/current conditions suitable to destroy these impurities [12]. The mechanisms and products of some anodic reactions are largely dependent upon the anode material [13]. The dependency of anodic reactions on the anode material can be illustrated by, for example, formation of hydroquinone and benzoquinone at a Ti/IrO_2 anode and carbon dioxide at a Ti/SnO_2-Sb_2O_5 anode by the anodic oxidation of phenol [14].

The oxidation of organic materials is governed by two distinct mechanisms. That is, direct oxidation on electrocatalytic electrodes such as platinum, or indirect electrochemical oxidation, which can occur via surface mediators that remain fixed on the anode surface, where they are continuously generated [15]. Even though organic waste can, in general, be oxidized at numerous electrode materials [16], phenols cause inactivation of the anode through by deposition of oligomers that form when the phenoxy radicals attack the unreacted substrate.

Oxide-based anodes such as PtO_2 are generally not affected by metals fouling. It has been reported that phenol is oxidized faster at PtO_2 than Pt, graphite or nickel, with less adsorption of products onto the electrode surface [9]. Electrochemically active oxides such as RuO_2 and IrO_2, represent, in general, the most expensive element of the coating. When used under in severe conditions, loss of active material caused by chemical or electrochemical corrosion can make the process too expensive for technological application. Platinum is a favoured anodic materials because of minimum degradation or corrosion in acid, or when used as an anodic or cathodic electrocatalyst [17].

Electrochemical oxidation has also been studied at dimensionally stable anodes (DSA). DSA electrodes are characterized by a thin active coating (usually a few microns) deposited on a base metal, usually a valve metal: Ti, Zr, Ta, Nb [18]. Comninellis et.al. have studied the electrochemical oxidation of phenol at various anodic materials and the reaction intermediates. Measurements of the current efficiency have shown that traditional anodes (Pt, Ti/IrO_2, Ti/RuO_2, Ti/PbO_2) give relatively low current efficiencies [19]. This is in contrast to the Ti/SnO_2 anode, which not only gives high current efficiencies, but allows quasi-complete total organic carbon (TOC) determination.

Properties of the Support Material

The ceramic or ceramic-based membranes selected as support materials for the anodic oxidation of phenol in this study are composed of Al_2O_3 or a mixture of Al_2O_3 (70%) and yttrium-stabilized ZrO_2 (30%). They include: rigid ceramics produced by, for example, slip-casting or a moulding method, or ceramic felts, or ceramic papers of metal mesh coated with ceramic layers, or a similar material. The membranes are made either in tubular or flat form and possess high mechanical and chemical stability, relatively high surface area, and pore sizes suitable for high through flow of water (0.2 to 0.9μm).

Conferring Electroconductivity

Inorganic ceramic membranes do not possess any conducting properties for electricity. Thus, to be used as porous electrodes for the electrochemical oxidation of phenol, their surfaces need to be modified by deposition of electroconductive layers. Several methods can be employed for the deposition of various electroconductive materials on the surfaces of ceramic membrane supports. Moreover, the desired electroconductive coating should have certain properties for it to be useful as a current collector or anode in the electrochemical oxidation of phenol. These properties include sufficient electroconductivity (preferably > 1 $Ohm.cm^{-1}$) to minimize potential drop over the surface of the membrane; a hydrophilic nature and porosity in order to permit the passage of water through the membrane and high electrochemical stability under anodic conditions.

The property of high catalytic activity for water electrolysis is an important parameter in the electrochemical oxidation of phenol. The proposed mechanism presented in Figure 1 depicts that the first stage of the electrochemical oxidation of phenol is the production of hydroxyl radicals by water electrolysis [20].

$$2H_2O \longrightarrow 2OH^{\bullet} + 2H^+ + 2e^-$$

The hydroxyl radicals are adsorbed at the electrode surface and react with the organic molecule (phenol or its oxidation product) or can subsequently react to form O_2.

$$Org + OH^{\bullet}_{ads} \xrightarrow{r_1} product \qquad (1)$$

$$2\,OH^{\bullet}_{ads} \xrightarrow{r_2} H_2O + 1/2O_2 \qquad (2)$$

At the same time organic molecules are adsorbed at the electrode surface and oxidized directly to carbon dioxide.

$$(Org)_{ads} \xrightarrow{r_3} CO_2 + H_2O. \qquad (3)$$

Suitable electrically conductive materials can be selected from a group consisting of pyrolytic carbon or metals such as gold, platinum, platinum group metals, metal oxides or mixtures thereof. In this particular study, carbon and gold were tested. Carbon was deposited by pyrolysis of LPG gas in a tube furnace at a predetermined temperature and gas flow rate. Membranes with a surface resistance of 1 Ω/cm, sufficient for their application in electrochemical reactors, were obtained. Gold was deposited on the ceramic support by electron beam deposition and sputtering. The electrically conductive materials also exhibited some catalytic properties in the anodic decomposition of organic compounds.

Catalyst Preparation

The electrochemical oxidation of phenol was studied using ceramic-based electrodes impregnated with inorganic proton conductors and coated with catalytic layers. Pt, PtO_2 and SnO_2, being the most effective catalysts, were investigated. These catalysts were deposited onto the surfaces of previously described electroconductive ceramic membranes and onto adjacent carbon papers, which served as current leads, and backing layers.

Several catalyst-loading methods were employed depending on the type of electroconductive coating applied to the ceramic membrane supports. The Pt catalyst was loaded onto the respective conductive membranes by two different techniques. In the first case, the gold-coated electroconductive support was dip coated with a solution containing Pt ions, followed by drying and annealing. In the second case, Pt was loaded onto the carbon-coated electrode by electroplating. Introduction of the proton conducting material was carried out by impregnating the membrane with a ZrO_2 sol, treating with H_3PO_4, followed by calcination of deposited particles at moderate temperatures, as described in [1].

Organic Decomposition

The electrochemical oxidation of phenols was studied in electromembrane reactors comprising a catalytic electromembrane (either a tubular membrane or a flat or disk-like membrane), which served as the anode, and a suitable cathode. A phenol-containing solution of a suitable concentration (to be electrochemically oxidized) was pumped through the membrane pores, initially coming into contact with the catalytic layer and thereafter with the proton-conducting phase. The reactors were designed to work as flow-through apparatus, whereby the feed solution was recycled as retentate and the samples were collected periodically from the permeate. The reason for recycling the retentate was to prevent leakage, since a high-flow pump was used.

The following results were obtained from experiments employing tubular membrane reactors. All the experiments were conducted at room temperature, with 250-ml of feed solution ($0.1 g.L^{-1}$ phenol in 0.1M Na_2SO_4) and an applied potential difference of 2.50 V. The voltage was supplied by a BAS CV 27 external power source. The disappearance of phenol from the permeate samples was monitored by UV-VIS spectrophotometer and the formation of oxidation products was observed by GC-MS and HPLC. Table 1 summarizes the results that were obtained using various gold-coated and carbon-coated electromembranes.

Table 1: Electrochemical oxidation of phenol on tubular electromembranes

	Gold-Platinum	Gold-Platinum (Proton Conductive)*	Carbon
Phenol Removal	76 %	94 %	99 %
Current Density	$2.4 mA.cm^{-2}$	$1.4 mA.cm^{-2}$	$1.9 mA.cm^{-2}$
Flow Rate	$241 L.m^{-2}.h^{-1}$	$241\text{-}150 L.m^{-2}.h^{-1}$	$222 L.m^{-2}.h^{-1}$
Energy Consumption	$0.41 kWh.g^{-1}$	$0.06 kWh.g^{-1}$	$0.05 kWh.g^{-1}$
Identified Product	Benzoquinone- trace	No quinones	Benzoquinone- trace

*Impregnated with zirconium phosphate

The introduction of the proton conductor phase into the gold-platinum electrode enhanced process parameters such as the extent of phenol oxidation, removal efficiency and energy consumption. The formation of aromatic by-products was not evident in the HPLC analyses of the permeate samples collected from the proton-conductive gold-platinum electrodes.

Experiments performed with flat membrane reactors were conducted at room temperature, with 250-ml of feed solution (0.1g.L^{-1} phenol in 0.1M Na_2SO_4) and an applied potential difference of 2.65 V. Table 2 summarizes the results that were obtained at untreated Al_2O_3 membranes and Al_2O_3 membranes impregnated with zirconium phosphate. A carbon cloth was used as the backing layer and current collector.

Table 2: Results obtained at untreated Al_2O_3 membranes and Al_2O_3 membranes treated with proton-conducting zirconium phosphate

	Untreated Al_2O_3 membrane	Al_2O_3 treated with Zirconium phosphate
Phenol removal	56 %	90 %
Current density	4.6 mA.cm^{-2}	3.7 mA.cm^{-2}
Flow rate	127 L.m^{-2}.h^{-1}	135-69 L.m^{-2}.h^{-1}
Energy consumption	0.017 kWh.g^{-1}	0.009 kWh.g^{-1}

These results show that the introduction of zirconium phosphate as proton conductor significantly improves the removal efficiency. The chemistry of the functioning of proton conductors is complex: these materials may function by facilitating the transport of protons, that are generated during water electrolysis, towards the cathode.

B. Proton Conducting Membranes for Hydrogen Separation and Fuel Cell Applications

Hydrogenation and dehydrogenation membrane reactors for industry need to use proton conductors or proton electron mixed conductors as membrane materials. When pure proton conductors are used as electrolytes, the membrane reactors for the dehydrogenation reaction may be operated in fuel cell mode. This is thus a cogeneration system, where hydrocarbons are directly used as fuel to produce electricity as well as chemical products, by the process of the dehydrogenation reaction. In particular, methanol may be used in such fashion as a source of hydrogen for methanol fuel cells.

Moreover, inorganic hydrogen separation membranes are based upon the use of solid, non-porous, proton conductive materials. In order to realize the use of such materials with methanol in a process for hydrogen generation and separation for fuel cells, anode materials with the following properties are required: high proton and electronic conductivities, total conductivity higher than 10^{-1} S/cm, good catalytic function for hydrogen and good gas permeability. The electrode should provide a fast dynamic process for hydrogen generation.

Protonic conducting membranes can be employed in proton-exchange membrane fuel cells. At present Nafion is used almost exclusively for this purpose. From the application point of view, a membrane with the following properties would be useful: non-fluorine containing, able to be operated at high temperatures, higher mechanical strength at lower thickness and able to operate at lower resistance [21]. New organic materials have been synthesized, or improved, by impregnation or mixing with phosphoric acid, inorganic fillers and Nafion, by using different supported materials such as a microglass fiber [22]. However, leakage of the liquid electrolytes is a problem and additional sealing is necessary [22]. Moreover, the high-cost of the membranes is limiting for large scale applications. Nafion is rather expensive and additional treatment could increase the price. An alternative is to use an inorganic substrate and an inorganic filler. It could offer higher temperature and chemical stability, at a more moderate cost. Application of a fibrous substrate could increase the mechanical strength of the membrane. The material of choice as a filler could be zirconium phosphate. It is stable in a hydrogen/oxygen atmosphere, is a low cost material, and is non-toxic (which could be a very important factor for large-scale applications, because fuel cells aspire to be an environmentally friendly solution for energy production). This idea is not novel. In 1961 Dravnieks [23] used zirconium phosphate in a fuel cell and Alberti [24] prepared glass-fiber membranes impregnated with zirconium phosphate. However, the resistivity and the temperature stability of such membranes proved to be too low for fuel cell applications.

During the past few decades, knowledge concerning electrolytes, conductivity mechanisms and membrane technology has improved greatly. Recently it was demonstrated that inorganic membranes could be an alternative to polymer membranes. Vaivars et al. impregnated membranes with zirconium phosphate and increased the temperature stability by using a composite effect [25]. Belyakov and Linkov [26] developed a method to impregnate membranes with a crystallized sol of an oxide of a polyvalent metal and thereafter treated such membranes with phosphoric acid. Nafion membranes impregnated with zirconium phosphate were tested by Yang et al. [27] and microglass fibers impregnated with a Nafion by Haufe and Stimming [22].

Currently, mainly two types of inorganic proton conductive materials are known. The first type includes a wide range of oxide and sulphide-based materials, which display significant proton conductivity only at elevated temperatures. The second type includes solid inorganic polyacids, in which low-temperature proton transport occurs. Only polyantimonic acids and acidic phosphates of polyvalent metals exhibit substantial low temperature proton transport. Protons that are part of phosphate groups form layers between metal atoms in acidic polyphosphates of zirconium and titanium. Hence, a concentration of protons in specific directions and comparatively short distances between protons exist in these materials. Materials such as these are very attractive for application as proton conductive elements in fuel cells, since they combine the advantages of high- and low-temperature fuel cells such as fast electrode kinetics, fuel flexibility and low-cost electrolyte, electrode and interconnecting materials. Moreover, the electrode should provide a fast dynamic process for hydrogen. Preparation methods and characteristics of some compounds for gas separation, their proton conductivity and regenerability as a function of temperature and relative humidity, are presented here.

Membrane Preparation

In order to improve the mechanical properties of zirconium phosphates and maintain precise control over the pore properties of composite membranes, these materials were impregnated into the matrices of porous ceramic membranes. When impregnated into ceramic membranes, inorganic proton conductive phases possess surface areas that are orders of magnitude larger than conventional proton conducting polymers. They are also significantly cheaper than polymeric proton conductors and more suitable for coating with electrocatalytic or conductive phases.

The methods investigated for zirconium phosphate preparation included the reaction of zirconium salts with phosphoric acid or its salts. The compounds prepared by such reactions have an amorphous structure and a high water content. They densify upon drying, resulting in microcrack formation and loss of proton conductivity. Other methods, using crystallized sols of zirconia that retain their particle size after drying [28], included phosphorization of the zirconia particles to form zirconium phosphate, the transformation of which led to an increase in volume occupied by zirconium phosphate particles. This is attributed to the introduction of a large number of phosphate groups during the cleavage of oxide bonds. These groups fill the membrane matrix densely, ensuring good contact between phosphate particles. In order to enhance the electrochemical cell formation and to enable the application of a potential drop generated by an external power source, electroconductive metal coatings were deposited on the membrane surfaces. Electroless methods of plating metals such as Ni were used.

Alternate methods for the preparation of proton conducting membranes that possess good ion conductivity included the application of opposing ion motion in an imposed electrical field. At levels of phosphate depositions of 1.5 and 2.7%, conductivities of 6.84 and 16.63 (S.cm-1) were observed respectively. High ion-selective adsorption by use of such membranes with a zirconia / zirconium phosphate gradient, enabled the simultaneous electrosorption of cations and anions with enhanced ion sorption capacity and regenerability.

Gas Permeability

Gas permeability experiments, using feed gas mixtures of H_2 and He, over Ni surface-coated membranes containing varying amounts of impregnated zirconium phosphate showed optimum H_2 permeability with complete exclusion of He after six consecutive impregnation operations [28]. Hence, proton conductivity conferred onto ceramic membranes by impregnation of zirconium phosphate into the membrane matrices resulted in maximum hydrogen selectivity over He of 12.15, well above the theoretical Knudsen value of 1.41.

Thermal Stability

The thermal stability and regenerability of a zirconium phosphate-impregnated zirconium oxide membrane (1 mm thick), prepared according to the method described in [1], was studied. The ZrO_2 substrate was impregnated five times, in succession, with a ZrO_2 sol and phosphoric acid. The thermal stability was compared to a Nafion 117 membrane. Nafion 117 was boiled in sulphuric acid for 12 h and washed with distilled water. Both membranes were then dried at 80°C for 18 hours and then equilibrated at room temperature under atmospheric conditions. The conductivity of both membranes decreased by a few orders. However, the zirconium phosphate membrane's conductivity was readily restored within 20-30 minutes after exposure to air, whereas the conductivity of the Nafion membrane was reduced to 10^{-6} S/cm. Reversible water loss is important for practical application of the membrane in a fuel cell. Water is released during the fuel cell performance and could provide the self-humidifying effect. It is for this reason that the performance of a dried out inorganic membrane will be restored.

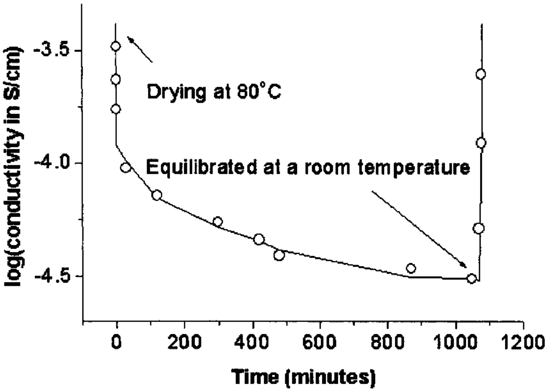

Fig. 2: Drying of the zirconium phosphate-impregnated zirconium oxide membrane.

C. Composite Zeolite Electrode Materials

High electrode surface area is of importance for processes described in the previous two parts of the current paper. Direct growth of microporous zeolitic phases upon supports will promote the preparation of high surface area electrodes [29]. Petrik et al. [30] developed techniques for zeolite preparation by reformulation of molar regimes that resulted in very rapid synthesis of nanoparticulate zeolite beta with enhanced external surface areas and mesoporosity. Such rapid synthesis techniques to prepare zeolites are being used for the production and optimization of bifunctionalized zeolitic phases containing nanophase metals as composite electrodes or as ultra micro electrodes.

Preparation of nanoelectrodes, by supporting a catalyst / metal (Pt or Ru) on zeolites for use as electrocatalysts, was shown to be applicable for water electrolysis [31]. Supported nanoscale electrodes for dispersion water electrolysis offer a solid state ionic environment, and the electrode is sized where bulk metallic properties do not apply. Nanoelectrodes can sustain current 100 to 1000 greater than large feeder electrodes with similar surface area, and also overcome slow reaction times, difficult electrolyte separation and high electrode cost. Optimization of deposition techniques for production of nanophase metals upon zeolites and their use as ultra micro electrodes for hydrogen production is being studied.

Furthermore, composite electrodes comprising an inert support with incorporation of a nanostructured bifunctional zeolitic phase that may be phosphated and include superacidity or nanoparticulate metals are being developed. Liao et al [32] developed a Zr-substituted zeolite, isostructural to MFI, namely catalyst SO_4^{2-}/ZrO_2-SiO_2. The most promising zeolite phase being applied in composite configuration as an electrode is a newly formulated Zr-MFI zeolite in which Al was isomorphously substituted with Zr. Shape, selectivity and activity for catalytic applications may thus be improved by the production of a Zr oxide surface with potential super acidity in a constrained environment. These active Zr sites may be phosphated, greatly increasing membrane adsorption capacity and possibly inducing proton conductivity. Previously it was shown that treatment with phosphoric acid, to give phosphated zirconia (P-ZrO_2), significantly altered the properties of ZrO_2 [28]. Moreover, the combination of zeolitic properties with phosphated Zr may offer a unique shape-selective, super acidic catalytic surface, particularly in composite form for electrocatalysis. Such novel membrane characteristics, including superacidity, enhanced adsorption capacity, proton conductivity and deposition of conductive layers are being explored.

Optimization of molar regimes, synthesis conditions, support type, and techniques for metals incorporation were investigated in order to determine the most suitable configuration for the successful and rapid preparation of layers of various zeolites such as BEA, FAU or Zr- MFI on porous supports. Composite fabrication may be achieved by physical admixtures as inks or by hydrothermal techniques. Molar regime optimization was performed for rapid hydrothermal synthesis. New reactor designs were developed for hydrothermal preparation of composites using viscous gels. Various support types were tested including ceramic papers, carbon cloths, alumina or zirconium supports containing metal grids, fiberglass, etc, in order to evaluate stability under highly alkaline hydrothermal zeolite synthesis conditions. Electroconductivity was promoted by the deposition of electroconductive phases and prepared materials are currently being tested for hydrogen production by water electrolysis.

Conclusion

Highly active electromembranes for the electrochemical oxidation of phenol were developed from inorganic ceramic membranes by the deposition of thin layers of electroconductive material, incorporation of suitable catalysts and the introduction of proton conductive materials. Suitable reactors that employ these electromembranes were developed. The direct oxidation of phenols, using ceramic-based electromembranes impregnated with proton conductors, was achieved; there was complete conversion of phenol and hence the removal of the total phenol index.

Novel ceramic membranes containing acidic phosphates of polyvalent metals useful for substantial proton transport have been developed. Proton conductivity was conferred by impregnation of zirconium phosphate into the porous structure of ceramic supports and resulted in high hydrogen selectivity. Proton conductivity could also be achieved by the deposition of conductive phases onto membranes using opposing ion motion in an imposed electric field. Moreover, new methods for the deposition of electroconductive phases upon these proton conductive composite membranes were developed, in order to enhance electrochemical cell formation and achieve a potential drop generated by an external power source. Optimized molar regimes, synthesis conditions, support types, and techniques for metals incorporation allowed for the successful and rapid preparation of layers of various bifunctional zeolites such as Zr-MFI on various porous supports. Phosphating of Zr-zeolite composites may lead to new proton-conducting materials. The novel inorganic proton conducting materials prepared were applicable to hydrogen separation, fuel cells, anodic oxidation, and as solid separators of protons or other cations in solutions.

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