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An Investigation into Quantum Chemical Study of Inhibitors and Experimental Evaluation of Smart Nanocontainers and Layers Against Corrosion

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A Dissertation Submitted as a Partial Fulfillment of the Requirements

for the Degree of Doctor of Philosophy in Chemistry (Ph.D.)

September 2009

Acknowledgments

Abstract

Quantum chemical methods are becoming ever more prevalent for assessing surface interactions of different molecules using cluster models, ab initio and semi-empirical methods considering the standard potential energy of surfaces. It is believed that the inhibition efficiency has lucid correlation with the total energy of inhibitor molecules and highest occupied molecular orbital energy levels evaluated by DFT study method. Results show that the pyridine molecules and highly active spots interact, therefore, inhibition mechanism is mainly associated with local properties i.e. pyridine molecules are drawn to defects such as corners and steps or kinks. The interaction takes place between the surface defect and the nitrogen group of the pyridine molecule. In addition, the possibility of ion pair formation between protonated pyridine and chloride ion and its influence on the general adsorption of pyridine on aluminum is also analyzed.

The efficacy of some lactones to counter iron corrosion in 1 M hydrochloric acid was also studied using ab initio quantum chemical deductions and its comparison with the available experimental data forms a part of this research. Thermo-chemical calculations for oxepan-2-one (L3) on iron cluster results of adsorption energies are close to the experimental values. The interaction energies of L3 and iron cluster with the natural bond orbital are also reported.

Zirconia based nano-structured hybrid sol-gel coating; impregnated with propargyl alcohol (PA) as corrosion inhibitor for mild steel was synthesized using 3-glycidoxypropyltrimethoxysilane (GPTMS) and subsequently optimized for internal cohesion as well as adhesion to the mild steel substrate. Electrochemical Impedance Spectroscopy (EIS) and Scanning Electron Microscopy (SEM) were used to assess the integrity of coatings. Results proved beneficial effect of PA inhibitor on sol-gel coat's barrier properties evident from low corrosion current and other electrochemical indicators as well as surface preparation.

Nanoecapsulation technology for slow release of a inhibitor reagent benzotriazole (BTA) within the polyelectrolyte matrix into the electrolyte was also studied. The

release properties of polyelectrolyte modified halloysite nanotubes, polyelectrolyte modified SiO_2 nanoparticles and polyelectrolyte capsules in conjunction with three polyelectrolytes of poly(allylamine hydrochloride), poly(styrene sulfonate) and poly(methacrylic acid) were investigated. The results indicate that the average diameter of the polyelectrolyte nanoreservoirs increase with increasing number of polyelectrolyte layers. Spontaneous release of the inhibitor observed, depended on the container type and polyelectrolyte shell components as well as pH, temperature and stirring in accordance with the aim of this research. The overall conclusion being that although severity of corrosion phenomena intensifies due to the above mentioned parameters, the compensatory effect of augmented inhibitor concentration exceeds such outcomes.

Contents

Chapter 1

Introduction

1.1. Historical Background of Corrosion

The word corrosion is as old as the earth, but it has been known by different names [1]. Corrosion is the deterioration of materials as a result of reaction with its environment [2]. A Roman philosopher, Pliny (AD 23-79) wrote about the destruction of iron in his essay 'Ferrum Corrumpitar'. Corrosion since ancient times has affected not only the quality of daily lives of people, but also their technical progress. There is a historical record of observation of corrosion by several writers, philosophers and scientists, but there was little curiosity regarding the causes and mechanism of corrosion until Robert Boyle wrote his 'Mechanical Origin of Corrosiveness'.

Philosophers, writers and scientists observed corrosion and mentioned it in their writings [1]:

Herodotus (5th Century BC) suggested the use of tin for protection of iron. Pliny the Elder (AD 23-79), an ancient Roman philosopher, wrote about spoiled iron. Lomonosov (1743-1756) studied the effects of acid and heat on metals. Austin (1788) noticed that neutral water becomes alkaline when it acts on iron. Michael Faraday (1791-1865) gave the two most important laws of electrolysis which can be used to predict the rate of corrosion. Louis Thenard (1819) was the first to suggest that corrosion is an electrochemical phenomenon. Sir Humphrey Davy (1824) proposed a method for sacrificial protection of iron by zinc. Hall (1829) established that iron does not rust in the absence of oxygen. De la Rive (1830) suggested the existence of micro-cells on the surface of zinc. Whitney (1903) provided a scientific basis for corrosion control based on electrochemical observation. As early as in eighteenth century it was observed that iron corrodes rapidly in dilute nitric acid but is not attacked in concentrated nitric acid.

Schonbein in 1836 showed that iron could be made passive [1]. It was left to U. R. Evans to provide a modern understanding of the causes and control of corrosion based on his classical electrochemical theory in 1923. Considerable progress towards the modern understanding of corrosion was made by the contributions of Evans [3], Uhlig [4], Fontana [2], Bockris [5], Schrier [6] and Gray [7].

In recent years, corrosion science and engineering has become an integral part of engineering education globally.

1.2. Consequences of Corrosion

Some important consequences of corrosion are summarized below [8]:

- ❖ Plant shutdowns
- ❖ Loss of products
- ❖ Loss of efficiency
- ❖ Contamination
- ❖ Nuclear hazards

1.3. Cost of Corrosion

In a study of corrosion cost to the U.S. economy conducted by National Association of Corrosion Engineers (NASE) [9], Half a century later, the direct corrosion cost was assessed in Koch et al. as around 276 billion US dollars, approximately 3.1% of the national gross domestic product. At least 35% of the above amount could have been saved by taking appropriate corrosion control measures [10]. In UK, the corrosion cost is estimated to be 4-5% of the GNP [4]. In Japan, the cost of corrosion has been estimated to be 5258 trillion Yen per year. For most industrialized nations, the average corrosion cost is 3.5-4.5% of the GNP. Below are some startling figures of corrosion losses [1]

Materials are precious natural resources and material reserves of iron, aluminum, copper, chromium, manganese and titanium are dwindling fast. Some day there will be an acute shortage of these materials [11].

There is bound to be a metal crisis and we are getting the signals. To preserve these valuable resources, we need to understand how they are destroyed and how they must be preserved by applying corrosion protection technologies [1]. It is generally accepted that engineering knowledge is incomplete without an understanding of corrosion. Airplanes, ships, automobiles and other transport

carriers cannot be designed without recourse to the corrosion behavior of materials used in these structures.

1.4. Corrosion Prevention

There are several methods for corrosion control which are considered below [2,12]:

- ❖ Corrosion Prevention by Design
- ❖ Materials Selection for Corrosive Environment
- ❖ Cathodic and Anodic Protection
- ❖ Corrosion Control by Inhibitors
- ❖ Coatings

Since in this project we have use corrosion inhibitors and coatings for corrosion protection, we consider them below.

1.5. Corrosion Inhibitors

Corrosion of metallic surfaces can be reduced or controlled by the addition of chemical compounds to the electrolyte, the compounds added are known as inhibitors which will reduce the rate of either anodic oxidation or cathodic reduction or both processes. The inhibitors themselves may form a protective film on the surface of the metal. It has been postulated that the inhibitors are absorbed into the metal surface either by physical (electrostatic) adsorption or chemisorption [13].

Physical adsorption is the result of electrostatic attractive forces between the organic ions and the electrically charged metal surface. Chemisorption is the transfer of, or sharing of, the inhibitor molecule's electrons to the metal surface, forming a coordinate bond. The adsorbed inhibitor reduces the corrosion rate of the metal surface either by retarding the anodic dissolution reaction of the metal or by cathodic evolution of hydrogen or both. Inhibitors can be used at pH values from acid to near neutral to alkaline [12].

The most common and widely known use of inhibitors is their application in automobile cooling systems and boiler feed waters [13].

1.5.1. Inhibitor Evaluation

Since there may be more than one inhibitor suitable for a specific application, it is necessary to have a means of comparing their performance. This can be done by determining the inhibitor efficiency as follows:

$$I_{eff} = \frac{R_0 - R_i}{R_0} \times 100 \tag{1-1}$$

where

I_{eff} = efficiency of inhibitor, %

R_0 = corrosion rate of metal without inhibitor present

R_i = corrosion rate of metal with added inhibitor

R_0 and R_i can be determined by any of the standard corrosion testing techniques and can be measured in any units, such as weight loss (mpy), as long as consistent units are used for all tests [2].

1.6. Paint Coatings

Coatings have been used for thousands of years as decorative and identification purposes. Industrial importance of coatings has been recognized after Second World War [14]. About one-third of the production of paint is used to protect and decorate metal surfaces. All forms of transporting vehicles such as trains, ships, automobiles, airplanes, buried structures, like tanks, oil and gas pipelines, offshore structures, steel structures and metallic equipment require the use of coatings. If the resistivity is increased and the electron flux is retarded, the rate of corrosion is decreased. By applying coatings of high resistivity, such as epoxies, vinyls, chlorinated rubbers, etc. the flow of electric current to the metal surface is impeded. Also, the higher the thickness of the coating, the higher would be the electrical resistance of the coating [15]. Another method to increase corrosion resistance is by the use of inhibitive pigments, like zinc chromate, red lead and zinc phosphate in coatings or even to use a pure metal more anodic than iron, such

as zinc-rich paints. The zinc metal prevents the corrosion of iron by releasing electrons into the iron surface. Thus, coating is an effective method to control corrosion [16].

Coatings must have a high degree of adhesion to the substrate and minimum porosity plus high electrical resistance which partly results from sufficient thickness and in turn enhances the impeding of (Cl^-) and (H_2O) diffusion into the substrate/paint interface [1].

1.7. Sol-Gel Coatings

The development of new coating systems with active corrosion protection instead of the carcinogenic chromates is an issue of prime importance for the wide range of industrial applications where effective corrosion protection is required [17]. Sol gel based coatings present a viable alternative to chromate surface treatment.

The term "sol-gel" an abbreviation for "solution-gelling", denotes a process by which largely inorganic materials are synthesized. Solution or sol is a dispersion of colloidal particles starts from precursors dissolved in a liquid and transformed to the solid state through a sequence of chemical reactions which involve polymerization at ambient temperature. A "gel" is an interconnected polymeric network formed by assembly of the sol.

This process is less expensive, easily adoptable and applicable to coat on materials having complex shaped geometry. In addition, sol gel technology offers other important advantage such as low life cycle environmental impact.

Two approaches can be utilized to reduce corrosion. Passive corrosion protection and active corrosion protection [18-20]. Passive protection is provided by a barrier film that prevents contact of corrosive environment with the metal surface; however, in the case when a defect is formed in the barrier layer the coating cannot stop corrosion. The second approach employs inhibitive species that can decrease corrosion activity. Sol-gel coating can only provide passive protection and defects or pores present in the sol gel coatings allow the corrosion species to penetrate toward the metal surface and initiate the corrosion processes [21].

According to Kakihana, there are three different kinds of sol-gel techniques [22]:

❖ Colloidal sol-gel method

❖ Inorganic sol-gel method

❖ Polymeric sol-gel method

The primary goal in all of these sol-gel processes is the preparation of a homogeneous precursor solution from which a homogeneous solid compound can be obtained.

The precursors for synthesizing these colloids consist of a metal or metalloid element surrounded by various reactive ligands. Metal alkoxides are most popular because they react readily with water.

Only two sol-gel processing techniques, in which a true gel is prepared, are recognized:

The formation of a network by destabilization of dispersed colloidal particles in a liquid, resulting in particulate gels.

Hydrolysis and polycondensation reactions of metal alkoxides, resulting in alkoxide gels.

Sol-gel materials encompass a wide range of inorganic and organic/inorganic composite materials which share a common preparation strategy which induced [23]:

Hydrolysis stage: The formation of hydroxide species

Condensation stage: The formation of oxide species

Gelation stage: The formation of a "spanning cluster", yielding a network which entraps the remaining solution, with high viscosity. The gelation step includes hydrolysis and condensation

Ageing stage: A range of processes, including the formation of further crosslinks, associated shrinkage of the gel as covalent links replace nonbonded contacts, structural evolution with changes in pore size.

Drying stage: Loss of water, alcohol and other solvents, first as synthesis cause expulsion of the liquid as the gel shrinks, then as evaporation of liquid within the pore structure with associated development of capillary stress. This may also

include supercritical drying, in which capillary stress is avoided by the use of supercritical fluids in conditions where there are no liquid/vapor interfaces

Densification stage: Thermal treatment leading to collapse of the open structure and formation of a dense material

The most widely used metal alkoxides are the alkoxysilnes [24]. Siloxane based sol gel derived coatings have been reported to possess good barrier properties because of formation of dense Si–O–Si network [25-27]. The adhesion between the alloy surface and sol gel pre-treatment is also high due to the formation of Me–O–Si bonds, whereas adhesion between the pre-treatment and top coating system can be increased by adding specific organic functional groups like epoxy in siloxane molecule [28,29].

1.7.1. Mechanism of Sol-Gel Network Formation

For sol-gel process hydrolysis and condensation of inorganic or metal-organic precursors is necessary. This precursor most commonly is metal alkoxides $(M(OR)_n)$, where R represents an organic (typically alkyl) group and (M) represents a metal. A variety of metal alkoxides can be used as precursors, alkoxides based on silane (M = Si, n = 4) and on zirconium (M = Zr, n = 4) are principally employed [25,30-32].

In the sol-gel process two distinct reactions take place hydrolysis of the alcohol groups and condensation of the resulting hydroxyl groups. The relative rates of these two reactions are governed by the concentration of the reagents and the presence of acidic or basic catalysts. Normally the alkoxide is dissolved in alcohol and hydrolyzed by the addition of water under acidic, neutral or basic conditions as shown in Eq. (1-2).

$$M(OR)_n + H_2O \rightarrow M(OR)_{n-1}(OH) + ROH \qquad (1-2)$$

The hydrolyzed species then condense to form network polymers. Mixtures of alkoxides with various metals will also form networks:

$$2\, M(OR)_{n-1}(OH) \rightarrow (RO)_{n-1}M–O–M(OR)_{n-1} + H_2O \qquad (1-3)$$

Organic sol-gel can be added into the network by replacing some of the precursor alkoxides with organic groups. The metal-carbon bond of the functional group is not readily cleaved in the polymer forming reactions [33].

Continued hydrolysis and condensation of the reactive M–OR groups will lead to a polymer that can be applied to a substrate by spin, dip, or spray methods. Primers are normally comprised of epoxy resins crosslinked with amine or polyamide curing agents. Other resin systems are also occasionally used. Epoxy, amine, urethane and other groups are present in the primer coatings. These groups can react readily with the same type of functional groups on the surface of sol-gel network. For example, epoxy groups contained in the sol-gel network can react with the amine groups present in the primer or topcoat formulation to become part of the organic film network. As a result of the chemical bonding, a smooth gradation without interfaces is formed between the metal substrate and the organic coating. This leads to superior adhesion characteristics and increased environmental durability. Polyurethanes and epoxies are most commonly used for topcoats [21].

To improve the passive corrosion protection mechanism of the coating when it is mechanically damaged, the incorporation of corrosion inhibitors into the coating is needed. Once trapped within the coating, the inhibitor becomes active when the coating is damaged and it slowly diffuses out of the host material. Despite its simplicity, it is difficult to control leaching of the entrapped inhibitors out of the coating. Solubility and possible interaction between the inhibitor and the coating solution is a concern as very often the inhibitors negatively influence the stability of the sol gel matrix [34-36]. Phosphates, vanadates, borates, cerium, and molybdenum compounds are known to have an inhibiting action on the corrosion processes of different metallic substrates and could be doped into a coating film [37].

Incorporation of inhibitive species into inorganic fillers used as ion exchangers allowed increasing corrosion protective properties of coatings [38,39]. Encapsulation of organic inhibitors by means of plasma polymerization [40] or

layer by layer assembly of polyelectrolyte [35,41] followed by incorporation in the coatings was found to improve release of inhibitor. Many kinds of inhibitors have been used to increase the corrosion protective properties of sol gel coatings on various metals like mild steel, aluminum and their alloys [20,32,36,42-45]. Cerium nitrate as inorganic inhibitor has positive influence on the corrosion protection of mild steel [46]. Voevodin et al. investigated the corrosion protection properties of epoxy/zirconia sol-gel coatings incorporating non chromate inhibitors such as $Ce(NO_3)_3$, $NaVO_3$, and Na_2MoO_4 [36]. Sol-gel films with $NaVO_3$ and Na_2MoO_4 did not provide corrosion protection due to decrease of the sol-gel network stability. However, the sol-gel doped with cerium performed at least as well as the undoped epoxy/zirconia films. The critical concentration of the cerium inhibitor is in the 0.2-0.6 wt% range. Higher concentrations could lead to the formation of defects in the network of the sol-gel film. An additional inhibition effect was revealed when phenylphosphonic acid was introduced into a hybrid sol-gel matrix containing phenyl groups. The entrapment of phenylphosphonate into the sol-gel matrix occurs due to phosphate-phosphate (P–P interactions).

To improve the corrosion protection properties of sol gel hybrid coatings on an aluminum AA2024 alloy, two organic corrosion inhibitors i.e. mercaptobenzothiazole and mercaptobenzimidazole have been encapsulated within the coating matrix together with or without cyclodextrin [47]. Superior corrosion protection has been reported for formulations that contain b-cyclodextrin explained by the act of slow release of the inhibitor from the cyclodextrin/inhibitor inclusion complexes and self healing of the corrosion defects. The complexes are more tightly trapped within the crosslinked coating material, making it difficult for the inhibitor to leach out easily. The slow release of organic corrosion inhibitor from the molecular cavity of cyclodextrin ensures the long term delivery of corrosion inhibitor and thus the healing of a damaged coating.

In other strategy inorganic nanoparticles can be a way of inserting corrosion inhibitors adsorbed on the surface of the inorganic nanoparticles for attaining controlled self healing properties. Zheludkevich et al. demonstrated the possibility of using zirconia nanoparticles as a reservoir for the storage and prolonged release of a Ce–based corrosion inhibitor [34]. The nanoparticles reinforce hybrid matrix and absorb Ce^{3+} ions, releasing them during contact with moisture inside the corrosion pit, as such the use of ZrO_2 nanoparticles provides better long term corrosion protection of the metallic substrate compared to the case where the Ce inhibitor is added to the sol-gel matrix. Several other attempts have been made to obtain "intelligent" active corrosion protection systems based on an ion exchange pigments being added to the coating system [48-50].

Silica and bentonite based Ce^{3+} cation exchangers in the polymer coatings enabled direct release of the inhibitor into the electrolyte in blisters and significantly retarded coating delaminating. The active corrosion protection effect was also revealed in the case of ion exchanged hydrocalcite pigments doped with Ce^{4+} ions or organic inhibitors.

Another approach for inhibitor entrapment was presented by Lamaka et al [51]. A TiO_x porous layer obtained by template synthesis was used as a nanostructured reservoir for the organic corrosion inhibitor benzotriazole which is formed of partly hydrolyzed titanium oxo-propoxide with the coordination number of Ti larger than its valence is a likely event [52]. This provides active corrosion protection and self healing ability of the coating system. The nanostructured porous TiO_x container layer was obtained by controllable hydrolysis of tetra isopropyl orthotitanate in the presence of the nonionic block copolymer Pluronic F127, forming a cellular network of 30 nm titania nanoparticles. The structured and benzotriazole loaded titania layer was coated with a sol gel based thin hybrid film (SiO_2/ZrO_2) to provide an additional barrier effect. The pretreatment formed by the nanostructured titania reservoir layer covered with the hybrid film demonstrates well defined self healing ability leading to effective long term active corrosion protection. After about 100 h of immersion of the nanocontainer

protected aluminum in 0.05M NaCl only a slight decrease of the Al_2O_3 underlayer film resistance was measured while first breakdown of the oxide film starts only after 330 h. However the resistance increases again, almost immediately achieving the values before breakdown and breakdown of the oxide layer followed by restoration of the film resistance occurs several times. The nanostructured porous character of the titania layer provides a very high effective surface area for the adsorption of the inhibitor. The developed surface formed by the titania layer also offers good adhesion between the oxide and the sol-gel film due to the high contact area between the two phases.

Shchukin et al. investigated the corrosion protection properties of sol-gel coatings with incorporated encapsulated organic inhibitors by means of layer by layer assembly of polyelectrolyte [35,41]. The release properties and reloading ability of polyelectrolyte modified halloysite nanotubes, polyelectrolyte modified SiO_2 nanoparticles, and polyelectrolyte capsules are studied. Polyelectrolyte shells, which modify the outer surface of the nanocontainers, are fabricated by using layer-by-layer assembly of polyelectrolyte bilayers. For coatings where the immediate release of the inhibitor is necessary, SiO_2-based or halloysite-based nanocontainers with consisting of weak polyelectrolytes are preferable, however, if continuous but gradual release is required, halloysite-based nanocontainers with one weak plus one or two strong polyelectrolyte shells are preferable.

1.8. Surface Preparation

Good corrosion protection rests on good adherence of coating to substrate and that depends on proper surface preparation. Polishing is the process of creating a smooth and shiny surface by rubbing it or using a chemical action, leaving a surface with significant specular reflection and minimal diffuse reflection. Polishing is usually multistage process starting with a rough abrasive and each subsequent stage uses a finer abrasive [53].

Electropolishing, or electrochemical polishing, is used to polish, passivate, and smooth metal parts.