Stannous – Literature Review

Jose Antonio Moreno, Vladimir Dozortsev, Richard Bacon

Aqua Metrology Systems, 1225 E. Arques Ave., Sunnyvale, CA 94085

ABSTRACT: Tin has served as an abundant source of useful chemistry throughout history and continues to do so today. From the dawning of the bronze age, to its affordable use in water treatment, the properties of tin have lent themselves toward being effectively utilized for modern applications. Tin, generally considered non-toxic, has been used in alloys in dental fillings; in food packaging materials; a food preservative; in lead-free solder; analytical chemistry; electroplating; and in the remediation of selenium, mercury, and chromium from contaminated water sources. While stannous chloride (SnCl2) has been used and studied as a water treatment reagent, more efficient and safer alternative has recently been developed. Electrolytic stannous ion generators have multiple advantages over stannous chloride and provide a safer, more cost-effective option for water treatment efforts.

INTRODUCTION

Very few elements are responsible for an entire age of human innovation — iron and the Iron Age, copper and the Copper Age, and the Bronze Age for which tin is largely responsible. At some time between 2000-1500 B.C., human ingenuity discovered the fact that tin makes an excellent alloy with copper to make bronze — one property of many that we would continue to discover which have made tin an oft-utilized element to this day.[1-7] Tin was an element discovered so early in antiquity that its initial origins are unknown; however, bronze objects dating back to the end of the 4th millennium B.C. have been found in Egyptian tombs. Due to the ancient relationship between man and tin, there is no historical evidence regarding the first extraction techniques. One of the earliest tin refineries belonged to Cornwall, England, where tin was smelted over wood fires in pits as early as 100 B.C.[8]

Today, two-thirds of tin is refined in its pure form through the baking of the mineral cassiterite, a tin oxide, in a furnace with carbon. The process relies on the following reactions between cassiterite, and a reducing carbon species:

$$SnO_2 + 2CO \leftrightharpoons Sn + 2CO_2$$

$$C + CO_2 \leftrightharpoons 2CO_2$$

The other one-third of tin produced comes from sulfidic minerals, which requires a more complex refinement process due to the propensity for these minerals to contain other metals. The procedure involves roasting the complex ores to volatilize away impurities while simultaneously converting tin-sulfides to tin-oxides to produce the pure metal.

Current world top-producers of tin are China, Brazil, Indonesia, and Malaysia with current world consumers being the United States, Japan, China, and Russia.[9-10] Owing to abundance, affordability, and the non-toxic nature of tin, its use spans a multitude of industries. Tin is quite the versatile reagent: from acting as an excellent alloy[11-13]; a biocide for marine vessels[14]; corrosion inhibitor in cooling systems[17-18]; an antioxidant in food[19]; in corrosion-resistant food packaging for steel cans[3]; as casts in the Pilkington process of glassmaking[20]; Lewis acid mediated catalysis in organic chemistry[21]; in solar cells[22]; lead-free solder[23]; analytical chemistry[2, 24-26]; and water remediation of contaminants such as selenium[27], mercury[28], and chrome (VI)[29]. More recently, researchers at Stanford University deposited tin as a one-layer thick sheet known as stanine, which was found to be the first-ever material to conduct electricity with 100 percent efficiency at room temperature.[30-31]

Another recent advancement in the use of tin involves the creation of water-soluble stannous ions utilizing electric current passed through tin metal in contact with an electrolyte solution, which provides a novel, cost-effective method to produce stannous ions in-situ. This new approach is effectively accessing the reactivity of tin without the need for dangerous tin formulations. The development of this novel method of delivering stannous ions as an alternative to the use of stannous reagents necessitates a review of the literature — essential to understanding the properties of this reagent and the range of its current and future applications.

PROPERTIES AND COMPOUNDS

The name tin comes from Old High German name, zin, which became tin in the Norse language. The elemental symbol for tin is Sn, owing from its Latin name, stannum. The element is number 50 on the periodic table, putting it among group 14 along with carbon, silicon, germanium and lead. The ground state electron configuration of tin is $[Kr]4d^{10}5s^25p^2$. One consequence of this configuration is that tin can lose both electrons in one, or both of those electron shells, offering the stable bivalent +2 stannous, or tetravalent +4 stannic ions. Tin held in an ionic state by two halogens (e.g., SnF2, SnCl2), disassociates into the +2 stannous ion in aqueous media and select organic solvents. Stannous in particular, has an exceptional ability as a reducing agent, making its reactivity especially useful in redox water chemistry, and will be the tin species of focus in this review.

In addition to its two stable ionic forms, tin can exist in two allotropes, gray and white tin. The gray tin, also known as alpha-tin, predominates when the temperature is below 13.2°C (55.76°F) and is characterized as a brittle, powdery material. As white tin transitions to gray tin, it increases in volume, which is why we observe a lower density. This form of tin has a limited scope of use but does find use as a semiconductor. The crystal structure of gray tin undergoes a conformational change to provide the common white tin version above 13.2°C. The change in allotrope is delayed or prevented by doping beta-tin with other metals, such as antimony or bismuth.[8] This beta allotrope is entirely malleable, ductile, corrosion-resistant, and readily conducts electricity.

A summary of common tin properties is given in the following table:

Relative atomic mass	118.69 amu
Transformation temperature alpha <-> beta	286.2 K
Enthalpy of transformation	1,966 J/mol
Density	
Alpha	5.765 g/cm^3
Beta @ 20°C	7.286 g/cm^3
Beta @ 100°C	7.32 g/cm^3
Beta @ 230°C	7.40 g/cm^3
Melting point	505.06 K
Boiling point	2,876 K
Specific electrical resistivity	
Alpha @ 0°C	5×10^{-6} Ωm
Beta @ 25°C	11.15×10^{-6} Ωm

Along with inorganic tin compounds, the metal can form up to four bonds with carbon to produce organo-tin species.

Notable uses of this classification of tin compounds are as wood preservatives, anti-fouling agents for marine crafts and as a reagent in the Stille metastasis.[14, 32-34] Organo-tin reagents are known to be toxic, with toxicity reaching its peak in the trisubstituted organo compounds.[35-36] Organotin compounds appear to affect the brain, liver, immune system and the skin.[37] These compounds require specific conditions and are not readily formed in nature even when inorganic tin is introduced into the environment.[28]

PREPARATION OF STANNOUS CHLORIDE SOLUTION

The most important commercially used inorganic tin reagent is stannous chloride ($SnCl_2$), an odorless, white, crystalline solid. A common method of synthesis is from the heating of tin metal in hydrochloric acid to produce the dihydrate form $SnCl_2 \cdot H_2O$, which can be further dehydrated by acetic anhydride to anhydrous $SnCl_2$.[38] Another common method is to react the tin metal with dry hydrogen chloride gas. This synthesis is labile at ambient temperature and pressure so stringent conditions are required when industrially produced.

HISTORIC USES

In addition to its use as a Bronze Age element, tin was responsible for the invention of the flat-glass mirror in Italy during the early 16th century. It was also used historically in the Netherlands during the 17th century as a mordant for the insect-derived cochineal scarlet dye.[8] Most notably, the metal was found to be of common usage in the packaging of foodstuffs. It is said that before canning, in 1795, Napoleon ordered a solution to food packaging be found to feed the men of his conquest. From this order, tin cans were born in 1810.[3] First occurring as pure tin cans, due to its non-toxic and corrosion-resistant properties, the process has evolved to the use of tin-plated steel cans instead.[3]

CURRENT USES

Electrolytic tin plating, first developed around 1915, is the process by which tin is deposited in a thin layer from an electrolyte solution containing tin salts and tin anode to a metal cathode upon application of electricity.[13] Currently, about 50% of all tin is used for plating.[3] While today's tin plate cans usually have a lacquered surface to minimize contact with the metal, tin, in the $SnCl_2$ form, has been used as an antioxidant in food.[19]

Tin's first use as solder can be traced back to the waterways of Rome. There lead pipes were found sealed at the joints with tin. Tin-lead (Sn-Pb) alloys still made up the bulk of modern electronic soldering material until only relatively recently as legislation in the U.S. during the 1990s proposed banning lead from most uses, including solder.[39] The ability of tin to resist oxidation has led to its use as an anti-corrosive agent in coatings.[15-16]

Tin and stannous are commonplace in many other industries, including dentistry. Because of its corrosive resistant behavior, tin has been used in an amalgam with mercury, silver, copper and zinc for dental fillings of tooth cavities.[40-41] Stannous ions in the form of SnF_2 was found to improve oral health when added to toothpaste by reducing plaque, halitosis and gingivitis occurrence.[6, 42] Stannous ions have other medical applications as well.

Stannous chloride is added as a reducing agent to an intravenous formulation of Technetium-99m for use in kidney and brain scintigraphy.[43] Therein it allows for the radionuclide, Tc, to chemically bond to its pharmaceutical counterpart to form a radiopharmaceutical.[44]

Tin has also been explored for its use in water treatment applications.

WATER TREATMENT

Given that stannous ions are great reducing agents, they have been used to remove selenite from acidic medium, as well as heavy metals, such as dissolved mercury and hexavalent chromium, from drinking water. The stannous ions are able to reduce carcinogenic heavy metals to less harmful forms, such as transforming hexavalent chromium to trivalent chromium, which is about one-hundred times less toxic to humans.[45]

What makes stannous ions such an attractive reagent for this application is not only the reductive power of stannous ions, but also the insoluble nature of the oxidized tin species, tin dioxide (SnO_2), in water. This insoluble precipitate can be filtered out after treatment. In several studies, it was found that SnO_2 also removes a harmful chemicals of interest, such as selenium and mercury, which only adds to stannous ion's ability to effectively remove toxic species from drinking water.[27-28]

The literature presents well-reviewed studies which all possess the following commonalities: stannous ions were used to reduce a chemical species to provide a safer or more manageable product, stannous forms an insoluble precipitate when reacted which aids in adsorption and capture the noxious chemicals of interest, there was no observed health effects from stannous ions on biological systems.

Despite unique stannous chloride reagent properties and potential applicability as a reagent to different water treatment systems, its practical implementation is very challenging. In fact, high corrosivity and toxicity of the stannous chloride solution require careful handling and supervision. The poor stability of stannous chloride makes this reagent impractical for industrial use as required dosage rates are unpredictable.[28, 46]

ELECTROLYTIC STANNOUS REAGENT GENERATION

Aqua Metrology Systems (AMS) has developed a unique means of producing a controlled amount of stannous ions in-situ. This is done through the process of electrolysis, wherein a current is passed through two electrodes in an electrolyte solution. In the case of the stannous ion generator, the electrodes happen to be tin metal anode and stainless-steel cathode in water. Water often possesses enough dissolved ions to conduct the electrical current between the electrodes. In rare cases, the water must be acidified slightly by addition of dilute acid to allow current to flow between the electrodes. Anodic dissolution of tin metal occurs, which generate tin ions. Because tin possesses multiple stable oxidation states, a specific charge density of the anode must be maintained to achieve stannous ions preferentially. AMS has invested heavily in researching the conditions necessary to produce stannous ions exclusively, which has produced a reliable and robust stannous ion generator.

The anodic dissolution of tin, and thus the quantification of stannous ions, can be understood through the well-studied laws of electrolysis, originally proposed by Michael Faraday in 1834.[47] Faraday's laws of electrolysis established the relationship between the current passed through the electrolyte and the mass of anodic dissolution that occurs. The relationship can be understood through the following equation:

$$m = \left(\frac{Q}{F}\right)\left(\frac{M}{z}\right)$$

Where m is the mass of anodic dissolution, Q is the total electric charge passed through the metal, F = 96.485°C mol^{-1}, known as Faraday's constant, M is the molar mass of the substance, and z is the electrons transferred per ion.

An important characteristic of electrolytic stannous ion generation is the precision of its control. In fact, the stannous ion generation process can be terminated immediately simply by switching the power off, and restored as soon as power is switched on, making it highly suitable for stop-and-run operation modes.

ADVANTAGES OF ELECTROLYTIC STANNOUS ION GENERATION

Three of the most significant benefits of this technology over traditional stannous chloride/sulfate reagents:

The first advantage of electro-generated stannous ions is in the high stability and reactivity of the ions. In contrast to conventional stannous chloride solutions which chemically degrade in the presence of oxygen in air and thus have a limited shelf-life once opened, electro-generated stannous ions are produced on an as-needed basis at the height of their reactivity.[48] The precursor to electro-generated stannous ions is highly stable tin metal, which eliminates the possibility of wasted reagent and lost capital. Additional costs are incurred owing to the disposal of expired stannous chloride reagent. The rapidly degrading stannous chloride reagent makes accurate dosing nearly impossible, resulting in less effective treatment if aged or expired reagent is used. In contrast, electro-generated stannous ion reagent can be dosed with high accuracy in broad range of concentrations.

The second advantage of electro-generated stannous ion related to its non-toxic nature. While stannous chloride solutions are highly acidic, toxic and corrosive, stannous ion reagent is produced in-situ using highly inert food grade tin metal. As opposed to dangerous and corrosive stannous chloride concentrates, electrolytic stannous ion generation process does not require special complex infrastructure or safety protocols.

Third, the electrolytic approach to stannous ion generation offers a safer, less expensive and simpler alternative to conventional stannous chloride solutions. In fact, this method utilizes inexpensive and readily available resources — tin metal and electricity. For the first time, smaller and often underserved municipalities now have an affordable treatment option available to remove heavy metals and other contaminants traditionally treated by prohibitively expensive stannous chloride. This translates into improved health outcomes of entire communities by providing cleaner, safer drinking water at a fraction of the cost of traditional treatment.

Furthermore, industrial safety is improved by eliminating the need for additional safety measures cost relating to chemical storage, and specialized personnel training for safe handling and dosing with caustic stannous chloride.

Stannous chloride solution is incompatible with other common reagents which can create additional hazards for water treatment professionals. For instance, SnCl2 and peroxides cause an exothermic reaction which can be explosive.[49] Stannous generators avoid these potentially dangerous situations by only generating the active reagent when and where it is required at the concentrations it is needed.

HEALTH AND SAFETY

A large part of the reason tin has persisted as a material throughout human innovation owes to its relative non-toxic properties. Significant studies on the effect of stannous chloride on microbial and animal models have demonstrated that the compound can induce biological effects.[50-55] Especially prolific was Yamaguchi, one of the first teams to begin establishing the toxicology profile of $SnCl_2$ in the late 1970s through experiments with mouse models. Their group found that doses of 30 and 60 mg Sn/kg body weight were enough to observe changes in the uptake of calcium in the kidneys and, insulin secretion in rats, respectively. However, the literature is lacking in analogous in-vivo human studies. Nevertheless, tin (II) chloride is considered non-toxic enough to be administered to humans intravenously as a reducing agent with radiopharmaceuticals.[43]

In May 2018, the European Food Safety Authority (EFSA) reevaluated the use of stannous chloride as a food additive. Under the EFSA, the Panel on Food Additives and Nutrient Sources found that the average exposure to tin as a result of its use as a food additive, 1.3 μg Sn/kg body weight, was well below their established regulatory maximum limit of 25 mg Sn/kg bw.[19] Therein they also cited tin's low potential for toxicity due to poor absorption by the digestive tract, a fact well established in the literature.[37]

FUTURE APPLICATIONS

As tin and stannous ions continue to find modern applications, the in-situ stannous generator technology will undoubtedly find use in those future applications. As previously detailed, the ability to produce minuscule amounts of stannous ion, on the nanogram scale necessary for precise medical devices, as well as on a kilogram scale, such as industrial water treatment operations and any amount in between, provides this technology with the versatility and ability to be used wherever tin is needed.

CONCLUSION

Tin has played a pivotal role in human innovation. Due to many of its amenable properties, tin has found a use in almost every industry. Though research suggests biological effects due to oral consumption of tin in animals, it is still largely considered safe. The non-toxic nature of the metal is largely why it has been used to keep our food and water safe for some time now.

Recently, a novel method to introduce tin as stannous ions for water treatment has provided a safer and more efficient option in a time when green practices are in desperate need and high demand. A thorough review of the literature has highlighted both past and contemporary uses, with a particular focus on water treatment, where the application of this new stannous ion generator technology can be realized. Future applications of this method can be envisioned in the medical field. The scalability of this method lends itself well to the trend of miniaturization and wearable devices in personalized medicine. The opportunity exists for the development of a continuous, on-demand supply of a range of ions with therapeutic uses. While the future of stannous remains to be capitalized upon, one thing for certain is that tin has and will remain a staple in human innovation.

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