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Corrosion inhibition alternatives and a novel chromate-like option: Review

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Hexavalent chromium has dominated the corrosion inhibitor's market as a benchmark alternative due to its unparalleled excellent corrosion inhibition properties. However, it was phased out because of its carcinogenic effects. Subsequently, many alternative inhibitors have been introduced into the inhibitor's market but failed to meet the performance of this benchmark inhibitor. Recently, intelli-ion (AX1) was reported as a new alternative to hexavalent chromium based on Scanning Kelvin Probe (SKP) carried out on hot-dip galvanized steel (HDG) substrates for chromate and intelli-ion inhibitors. The intelli-ion system showed impressive performance at generation 1, with increased protection offered by the generation 2 product, showing no visible failure after 4 days test procedure. To further validate this, the cut edge corrosion performance of intelli-ion (AX1) and benzotriazole (BTA) was studied on galvanized steel specimen in 5wt.% NaCl solution using Scanning Vibrating Electrode Technique (SVET). From the SVET current density maps of AX1 (specimen A and B) vs. BTA (specimen C) after 24 h in 5 wt.% NaCl solution. The AX1 inhibitor had a better overall cut edge corrosion inhibition performance than the BTA.

INTRODUCTION

Corrosion has a huge economic cost due to the degradation of materials and their properties which leads to loss of time during maintenance and through the severe failure of structures that often results in environmental impacts such as hazards and injury to living organisms [1-3].

Because of the huge cost associated with the corrosion of materials, it is imperative to protect these materials such as metals and their alloys from corrosion [4-6].

Strategies such as; isolating the structure from aggressive media – using coatings or thin film-forming substances and make up for the loss of electrons from the corroded structure either by cathodic protection through impressed current or by using active sacrificial anodes. The above strategies are known as corrosion inhibition, while the substances that bring about corrosion inhibition are known as corrosion inhibitors. They are substances applied to an environment that significantly reduce the corrosion rate of materials exposed to that environment. Corrosion inhibitors may include organic or inorganic substances that adsorb on the metallic structure to isolate it from its surrounding media to inhibit the reduction-oxidation (Redox) process.

Organic inhibitors create their inhibition through adsorption whereby their molecules are adsorbed on the metal or alloy surfaces to form a protective layer [7,8]. Alternatively, inorganic inhibitors act as anodic inhibitors, and their metallic atoms are enclosed in the film to improve their corrosion resistance. Basically, corrosion inhibitors may be categorized as cathodic, anodic, or mixed, depending on whether their effect is mainly in retarding the cathodic or anodic reaction of the corrosion process or both. The inhibition of anodic or cathodic corrosion reactions can be due to the reduction of the active surface area of metal and/or to a change in the activation energy of the oxidation or reduction process in corrosion [9]. The synergism of cathodic and anodic corrosion inhibitors often determines improved protection and allows for the reduction of the inhibition concentration [10]. Whichever reaction is impeded by the corrosion inhibitor, will interact at the metal/solution interface by forming a film, which may be of three different types: a) Passivating film; b) Precipitation film; and c) adsorption layer [11].

Recently, research studies in corrosion inhibition are geared towards the design, synthesis, development, and consumption of sustainable inhibitors to substitute traditional toxic ones. This is in line with global sustainable development goals (SDGs) anchored on the sustainability of materials and environment. Currently, various environment-friendly alternatives derived from natural resources such as biopolymers, plant extracts, chemical medicines (drugs), etc. are widely used to replace toxic corrosion inhibitors [8]. Moreover, various biopolymers in their pure and modified forms are copiously utilized as sustainable corrosion inhibitors [12-16]. Compounds derived through multicomponent reactions (MCRs), microwave (MW) and ultrasound (US) irradiations are also regarded as sustainable inhibitor alternatives [17-22]. Polyethylene glycol (PEG) [23-31] and ionic liquids (ILs) possess low vapor pressure and are considered as designer environment-friendly alternatives [32-35]. The chemicals blended using green solvents such as water, ILs and supercritical CO_2 can also be regarded as sustainable chemical species. An exhaustive literature review reveals that these compounds are copiously utilized as metallic corrosion inhibitors in various corrosive electrolytes [36-38].

Although, several methods of corrosion control have been formulated by corrosion researchers. One of the oldest (before 1960) methods of corrosion control was the application of inorganic compounds, mainly nitrites, chromates, borates, molybdates, silicates, and zinc salts [3]. These compounds become effective by forming a highly effective passive film over metal surfaces (passivation) through their adsorption. However, they were replaced by more economical alternatives such as phosphonic acid, gluconates, polyacrylates, surface active chelates, polyphosphates, poly phosphonates, phosphonates, and carboxylates during 1960–1980 [3]. Overall, these compounds are precipitated at the metal/environment interface and therefore they are called precipitating inhibitors (precipitators). Also, ecological considerations came to the fore and non-environmentally friendly chemicals were substituted by natural alternatives including natural and bio-polymers, biosur-factants, vitamins and tannins during 1980–1995. Recently (1995 to present), environment-friendly approaches such as the use of rare earth metals (REM), polyfunctional compounds, the synergism of organic/inorganic compounds using REM, and the encapsulation of inhibitors are the main areas of focus [39]. These alternatives have demonstrated very low or no toxicity and high protection effectiveness.

Currently, organic inhibitors are confirmed as one of the most effective and profitable methods of corrosion inhibition because of their association with E4 (efficiency, economy, ecology, and environmental friendliness) [6-8]. Organic corrosion inhibitors are used for various industrial applications. However, there are challenges in using these compounds. One of the biggest challenges of using organic corrosion inhibitors is their limited solubility, especially in polar electrolytes [40, 41]. Because of their hydrophobic nature, organic corrosion inhibitors, especially compounds containing aromatic rings and non-polar hydrocarbon chains, show limited solubility that adversely affects their protection efficiency. Therefore, current research studies in corrosion science and engineering are geared toward the development of corrosion inhibitors that contain hydrophilic polar functional substituents in their molecular structures.

However, this review article aims to highlight the performance of some corrosion inhibitors including hexavalent chromium's unique inhibition properties before it was phased out and the performance of some of its replacement alternatives. Furthermore, the paper will examine the validity of a new corrosion inhibitor with claims of chromate-like performance recently reported, known as "intelli-ion" (AX1) based on the investigation of scanning kelvin probe (SKP) and the results of scanning vibrating electrode technique (SVET) as reported. In addition, a detailed description of SVET technique will be done for readers to better appreciate the discussion of the SVET results.

Chromium and other alternative inhibitors

Chromium complexes have been excellent for corrosion control for decades. Key industries such as marine, automotive, and oil and gas have relied on hexavalent chromium [Cr (Vi)] for protection against corrosion. This chemical is highly effective in its role in corrosion inhibition. However, it is also known to cause cancer in humans and animals.

The carcinogenic nature of hexavalent chromium has been documented since the 1920s after multiple studies reported an increase in the prevalence of nasal and lung cancer amongst industrial workers in direct contact with chromium complexes [42-44]. Because of these health challenges, chromium compound use has now been restricted. Despite this setback, it is important to note that hexavalent chromium-based coatings remain a benchmark in the field defined by exceptional versatility, which also includes remarkable corrosion protection and cost-effectiveness [45]. The remarkable corrosion protection performance of chromates remains unrivaled over a very wide range of pH and electrolyte concentrations [46, 47] an excellent corrosion protection performance unable to be matched by alternative corrosion inhibitors to date since it was restricted.

Corrosion inhibitor alternatives to hexavalent chromium

Some of the alternatives that replaced hexavalent chromium since it was phased out include the following:

- Rare-earth-based coatings
- Vanadate-based coatings
- Lithium-containing coatings
- Organic coatings and nanocomposites
- Organic-based coatings
- Phosphate coatings
- Metal-rich primers
- Zinc Phosphate-an industry standard inhibitor
- Intelli-ion

Rare-earth-based coatings

These were first introduced in the late 1980s as promising alternatives for Cr(vi) replacement on aluminum alloys [48]. The rare-earth complexes tend to form cerium or lanthanum oxides and hydroxides at a pH greater than 10 and therefore could inhibit cathodic reactions on corroding surfaces [49-53]. Indeed, rare-earth complexes were able to inhibit the corrosion of several metals and alloys such as Zn, galvanized steel, Mg, or Al alloys and successfully integrated into primers or conversion coatings [54,55]. However, the rare-earth-based oxides could dissolve in an acidic environment and therefore make this inhibitor's surface layer less stable compared to the hexavalent chromium layer. Also, several other studies carried out on coated Al alloys AA2024-T3 showed minor improvement in pitting potential and corrosion current, thereby clearly recording limitations in its corrosion inhibition efficiency [56]. Another limitation of rare-earth-based inhibitors is the apparent cost-intensive nature of their extraction even though they seem to be abundant on the Earth's crust. The rare-earth market is monopolized by some countries of origin with export restrictions since they are mostly found within their geographical location.

Vanadate-based coatings

The next alternative is vanadate-based coatings. This kind of corrosion inhibitor was introduced in the 1960s [57]. Also, was the introduction of sodium metavanadate ($NaVO_3$) as a potential inhibitor for the corrosion of steel on hot carbonate systems. After a few decades, vanadate-based-conversion coatings on Al alloys 2024 were successfully developed and were reported to adsorb on the cathodic sites, as such significantly inhibiting the oxygen reduction rate [58-63]. There's also the issue of carcinogenicity of vanadium and its compounds [64] as found in the treatment of diabetes in humans, but also with significant evidence of lung tumors in rats and mice after V_2O_5 inhalation. The vanadium compounds showed promising properties, however, the carcinogenicity in the compounds has rendered this alternative no longer viable.

The Lithium- containing coatings

These are yet another alternative with unique properties, showing interesting inhibitive properties of Li when exposed to Al, on a pH > 7 [65-67]. It was reported that Li was readily intercalated into the Al hydroxide matrix as such stabilizing the passive film when exposed to an aggressive environment [68]. Again, Kosari et al reported the formation of A-Li layered double hydroxide (LDH) during the anodic dissolution of an Al—Cu—Li--containing alloy [69,70]. This compact polycrystalline layer was able to provide adequate corrosion inhibition to Al alloys and pass a salt spray test following (ASTM B-117) standard. Recently, the use of Li salts loaded in a replacement for $SrCrO_4$ primers became of interest, showing impressive corrosion inhibition properties after a neutral salt spray test exposure [71]. Although this inhibitor was only used on Al alloys, it is still not industrialized, even though it holds interesting promise.

Organic Coatings and nanocomposites

These are alternative corrosion inhibitors that are used to impart corrosion protection to metals, they include organic inhibitors, hybrid sol-gel, and polymer base coatings [72]. The organic-based coatings are used to protect Al alloys and are comprised of multiple layers such as primer and top coat [73]. However, such multi-layered polymeric coatings are yet prone to air and moisture, resulting in coating degradation and eventually enhancing corrosion [74]. The corrosion performance of the organic coating itself can be greatly improved if its barrier properties are enhanced. For example, graphene-based nanocomposite coatings are good inhibitors of carbon steel and pure iron [75-79]. Glover et al (2017) reported exceptional corrosion resistance performance at the cathodic site when graphene nanoplatelets were added into polyvinyl butyral coating. A major setback however, is that the cost of graphene is very high making this alternative inaccessible [78].

Phosphate Coatings

Phosphate coatings are also another alternative to hexavalent chromium. These coatings are usually such that a metal phosphate surface layer is precipitated onto the metal from a phosphoric acid solution bath to form the conversion coating. Despite its reported biocompatibility for Mg-implant applications, the phosphate compounds that form on the metal surface are often prone to chemical dissolution in an alkaline environment and depend on the nature of the phosphate cation [80]. This is because phosphates such as $Zn_3(PO_4)_2$ have limited pH stability in aqueous solutions ranging between pH 5 and 10, unlike Cr_2O_3 which has wider pH stability ranging from pH 2 to 12 [81,82]. Phosphates, therefore, cannot be a suitable alternative to replace hexavalent chromium.

Metal-Rich Primers

These are another alternative to hexavalent chromium. They have a thickness of between 25-30 mm and are loaded with active metals such as Zn and Mg which serve to protect steel and Al alloys [83]. The Zn or Mg particulates in spherical or flake form can induce cathodic inhibition when in electrical contact with the metal. The oxides or hydroxides of the active metal particles could also serve to provide long-term protection to the underlying metal substrate as stated in the literature [84]. However, the self-corrosion of these active metal particles within the primer itself has proven to be a setback for the metal-rich primer coatings.

Zinc Phosphate – an industry standard inhibitor

Amongst the various corrosion inhibitor alternatives that sought to replace hexavalent chromium, none of the alternatives offered excellent corrosion performance that exceeded that of hexavalent chromium. There are significant limitations to each methodology that has been trialed to achieve chromium-free corrosion inhibitors. Because of the excellent corrosion inhibition performance of hexavalent chromium which has been documented decades ago before it was phased out, researchers are currently making serious effort to have an alternative that will rival the excellent benchmark inhibitor. Since the phasing-out of hexavalent chromium, a popular alternative in the oil and gas industry has been Zinc phosphate. To some extent it is effective, but this inhibitor does not match the performance of chromate complexes and despite the various alternatives and extensive research since the 1980s, hexavalent chromium remains the benchmark corrosion preventive compound in most industries [85].

Currently, 45 % of the corrosion inhibitor market is dominated by phosphates. Research has shown that adding zinc phosphate in a coatings system can inhibit the anodic site of metal corrosion and prevent the horizontal diffusion of the corrosive medium into the coating/substrate interface and slows down the dis-bonding of the coating.

Again, it is reported that phosphates don't pose the same health and environmental risks as chromates, however, they do still present environmental issues through leaching when acting as inhibitors – Which is classified as a category 1 Environmental Hazard within the coatings system. At loadings of 2.5 % and above, the coating will be classified as a category 2 Environmental Hazard so will still require hazard labeling [86-90].

Zinc phosphate salts on their own are not immediately very effective mainly because of their low solubility. As such, in a corrosive environment, significant amounts of time must elapse before there are enough concentrations of phosphate anions to react with the substrate surface cations to form an inhibitive precipitate layer. This eventually leads to a time delay where corrosion can proceed unhindered.

Intelli-ion

Driven by the quest for an effective and environmentally hazard-free corrosion inhibitor in the inhibitors market, researchers recently unveiled a highly effective sustainable inhibitor known as "Intelli-ion" AX1 which showed highly improved corrosion inhibition. According to the report, the technology is a new breed of inhibitors that is driving innovation in the protective coatings market. The report claims that "Intelli-ion" AX1, incorporates an active ingredient that has never been used effectively within coatings – making it a unique innovation. Sheikholeslami (2021) stated "that the technology protects in a smart way via three modes of electrochemical protection. The active ingredient sits dormant in a micro-reservoir and is triggered on demand when corrosion is detected at the coating surface via ions

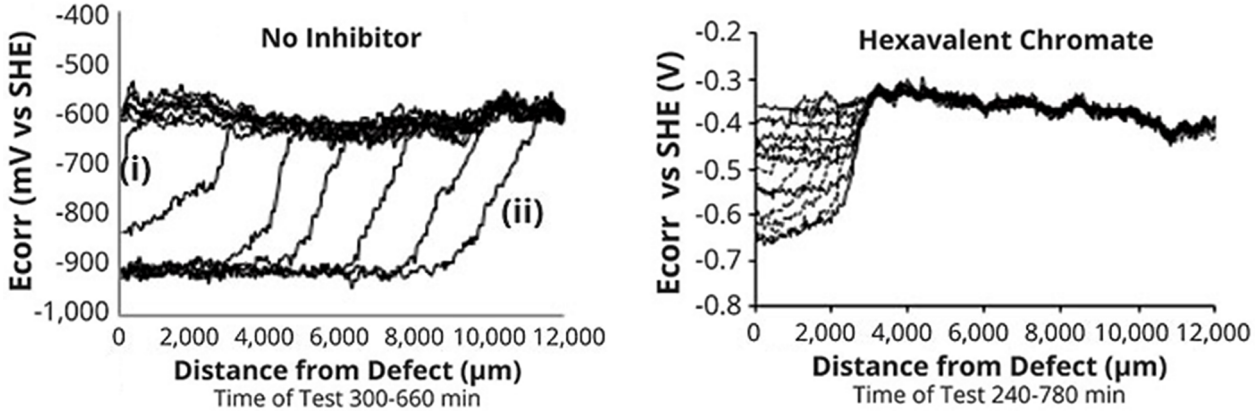


Fig. 1. Free corrosion potential maps versus time, clockwise unpigmented, strontium chromate, Intelli-ion Gen. 1 and Intelli-ion Gen. 2. (Adapted with permission from Cacace and Dodds., 2018)[93] *(Continue on next page)*

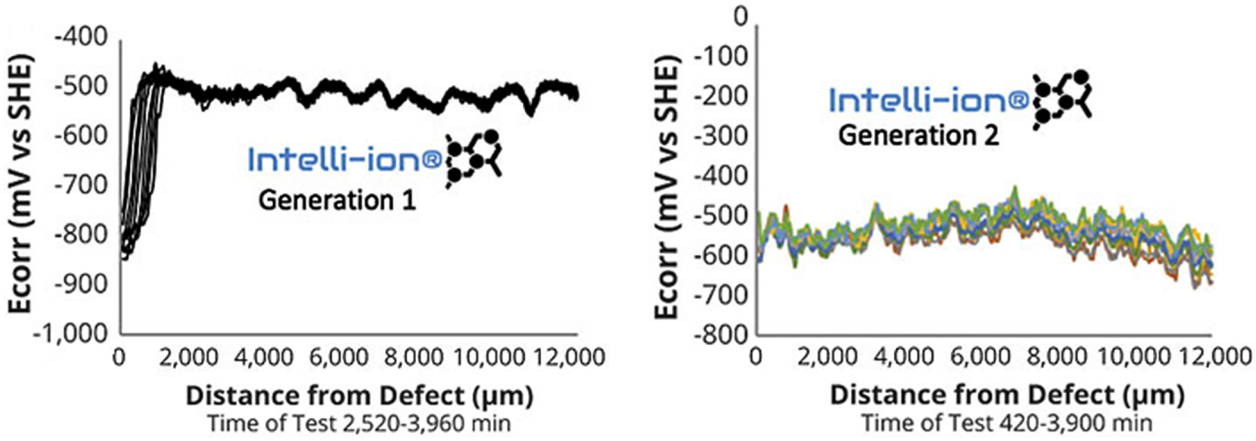


Fig. 1. Free corrosion potential maps versus time, clockwise unpigmented, strontium chromate, Intelli-ion Gen. 1 and Intelli-ion Gen. 2. (Adapted with permission from Cacace and Dodds., 2018)[93]

or pH changes. Ions that pass through the coating are sequestered – rendering them neutral and also triggering the release of the inhibitor to migrate to the substrate surface. It forms a protective nano layer over the substrate surface at the anode and cathode by forming insoluble salts with dissolved metal ions preventing mass transport of the corrosive ions, at the same time moderating the pH under the thin film". [91,92],

To state succinctly, Intelli-ion: AX1 (like highly effective chromates) has demonstrated highly effective corrosion inhibition performance. Figure 1 below has demonstrated intelli-ion's improved chromate-like corrosion inhibition performance.

Figure 1 shows examples of spatially resolved maps of cathodic delamination of scanning Kelvin probe investigation of hot-dip galvanized steel (HDG) substrates for chromate and intelli-ion inhibitors. As the corrosion progresses, there is a sharp drop in the free corrosion potential, giving a cathodic delamination front, from which distance against time can be taken. The Intelli-ion system showed impressive performance at generation 1 with the new pigment system, with increased protection offered by the generation 2 product, showing no visible failure after 4 days of commencing the test procedure [93].

Intelli-ion was designed to replicate the excellent corrosion inhibition performance of the banned hexavalent chromium-based inhibitors. The impressive results shown in generation 2 intelli-ion inhibitor presents an excellent corrosion inhibition alternative that can close the gap in the coatings market created by the need for a highly effective inhibitor that is non-toxic and non-carcinogenic. Intelli-ion (AX1), according to the literature, is a novel and unique alternative technology in terms of corrosion inhibition performance which exhibits improved chromate-like inhibition performance.

Validating the corrosion inhibition performance of intelli-ion via svet experiment

Preparation of steel samples

According to Sheikholeslami et al, in an experiment in which three samples; A, B and C of galvanized steel sheet of composition 55 wt.% Al, 44 wt.% Zn, 1 wt.% Si were cut into 1 ×1 cm each and then mounted in a non-conductive epoxy cold mount in a way that only the cut-edge would be exposed after proper grinding and polishing. Mounted samples were grinded with grid sizes of #600, #800, and #1200 Silicon Carbide Abrasive Paper and polished with 9 µm, 6 µm, and 1 µm water-based diamond suspension [91,92].

Corrosive Environment

The test solution was prepared using 5% W/V NaCl in distilled water at pH 7.0. [91]

Inhibitors/Primer system

The intelli-ion (AX1) was used in a primer system with optimum loading levels of between 2-7 wt.% resin type and film thickness inhibitor.

The primer system benzotriazole (BTA high) was used as shown in Table 1 below. Primer samples were supplied by Beckers Group branch in Malaysia [91].

Tab. 1 Primer systems specification

Primer	Base	Pre-treatment	Inhibition system	Volume conc. %
BTA high	Waterborne	Yes	Benzotriazole	7-11wt.%

Method

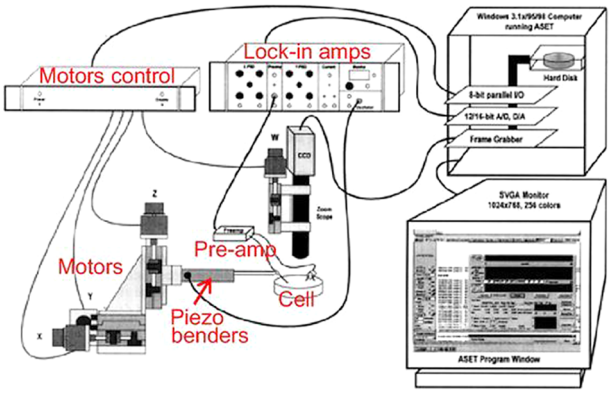
The galvanized steel composition was 55 wt.% Al, 44 wt.% Zn and 1 wt.% Si. The primer was then applied and cured on top of the galvanized layer on both sides with 10-15 µm thickness [91]. After then, the SVET was used to test the cut-edge of the specimens.

A detailed description of scanning vibrating electrode technique (svet)

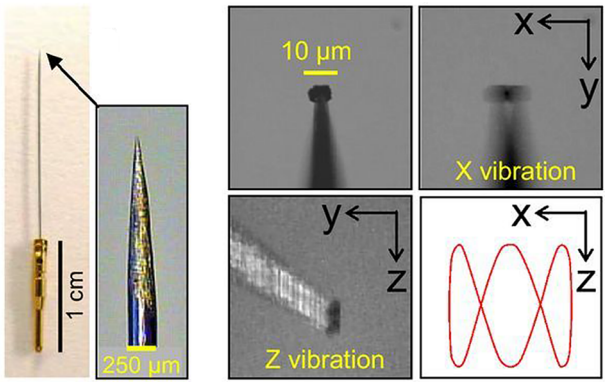
Before discussing the results of the SVET experiment it is very important to give a detailed description of how the SVET experiment works. Therefore, SVET has been described by Bestos et al. [94] as a technique to image corrosion. This means that it can be applied in an electrochemical cell which consists of an anode, cathode, an electrolyte and an electrical connection. Figure 2a, is a typical SVET system. It consists of a video camera that allows one to control the probe position and obtain images of the sample, a three-motor system to move the probe with 1 µm precision, a pre-amplifier and two lock-in amplifiers, one for each vibration. A second camera located laterally is optional. It is also possible to modify the system to move the sample instead of the probe. The vibrating electrode is connected to the end of a plastic arm which is fixed to a linkage with two piezoelectric vibrators responsible for the X and Z vibrations (with frequencies ranging from 40 Hz to 1000 Hz). An anti-vibration table, a Faraday Cage and an uninterrupted power source are recommended for optimal performance. Figure 2b, shows the tip of the vibrating electrode, usually an 80/20 % platinum-iridium needle 1.5 cm long and 225 µm in diameter, thinned at its end and coated by a 3 µm layer of Parylene-C polymer applied by CVD (Chemical Vapor Deposition). The electrode tip is a hemisphere of 1.5-2.5 µm radius and is the only point where the insulating film was removed by a voltaic arc. To be used as SVET probes, the electroactive area of the tip is increased by electrodepositing a small platinum black sphere of about 10-20 µm in diameter. Figure 2c shows the direction and nature of the vibrations along the (X, Y, Z) directions. Figure 2d shows a typical electrochemical cell. The sample is placed in an epoxy holder of 3 cm in diameter and insulated, except for the area to be mapped. The potential is measured between the vibrating electrode and a platinized platinum wire that works as a reference electrode [94,95].

Simplified SVET probe

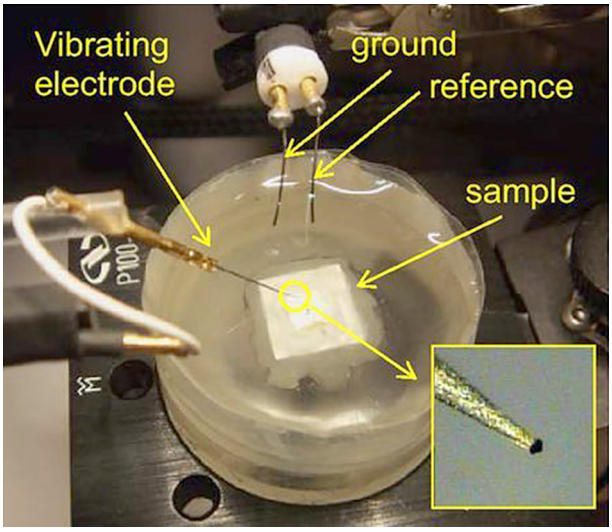
The main feature in SVET instrumentation is the probe, consisting of a micro-disc platinum electrode encased in glass that is positioned a short distance above the immersed surface of interest. The probe is vibrated at a particular frequency and measures the magnitude of potential gradients above the surface of the specimen By careful calibration using the procedure in the next section, SVET signals can be converted into current density values which can be mapped in the form of



a)



b) c)



d)

Fig. 2. a) shows the interaction between the different parts of the SVET system; b) SVET microelectrode; c) vibrating electrode depicting the two vibrations and a sketch of a Bandwidth curve with same amplitude in X and Z and frequencies of 1 Hz in X and 3 Hz in Z; d) shows interaction of the reference electrode, sample, vibrating electrode and ground state [96-98]

either 2D or 3D maps, which provide spatially resolved representations of the anodic and cathodic current j values measured over the scanned surface.

Quantification of localized corrosion rate can be obtained by numerical integration of SVET-derived current density distributions, which provides a value of integrated anodic and cathodic currents (i_a and i_c, respectively) emerging from the exposed surface for each individual scan. By summing the area-averaged anodic current density values throughout the experiment to obtain a total anodic current (I_a), a total equivalent mass loss can be calculated by applying Faraday's as indicated below:

$$\text{Mass loss} = \frac{I_a \times t \times M_{\text{substrate}}}{n \times F} \quad (1)$$

where I_a is the sum of total anodic current emerging over the entirety of the experiment, t is the time-lapse interval duration, $M_{\text{substrate}}$ is the molar mass of the corroding element, n is the number of the exchanged electrons in the anodic reaction of the element, and F is the Faraday constant that is 96,500 C/mol [99]

Calibration

In practice, the potential measured by SVET and the current density related to it is obtained by calibration [94-99]. The SVET probe is placed at a distance (usually 150 µm) from a point current source that drives a known current I (normally 60 nA). The point source can be an insulated metallic wire with an electroactive tip of 3 µm diameter or, a glass micropipette with a 2 µm diameter tip, filled with the testing solution and a platinized platinum wire inside as the current source. The current density i at a distance r from the point source is given by Hussain as stated below [96]

$$i = \frac{I}{4\pi r^2} \quad (2)$$

where $(4\pi r^2)$ is the area of the sphere with radius r. Figure 3a shows a representation of the current lines flowing away from the point source and spherical equipotential surfaces centered on the point source. For each sphere or radius r, the total current, I is always the same and the current density is obtained by dividing the total current by the area of the sphere. Figure 3b plots the variation of the current density, i, with the distance to the source, r, for I = 60 nA. The relationship between i and r is linear in a log-log plot, as shown in Figure 3c. For the typical calibration, the current density measured at the calibration point is $i = (60.0 \times 10^{-9}\ \text{A}) / [4\pi (150 \times 10^{-6}\ \text{m})^2] = 0.212\ \text{A m}^{-2} = 21.2\ \mu\text{A cm}^{-2}$. The SVET from AE measures the current density in two orthogonal directions (X and Z) therefore the calibration is performed in two points, one for each vibration. [98,99].

The potential measured by SVET in any point is related to the local current density i by:

$$\Delta V = -i\rho\Delta r \quad (3)$$

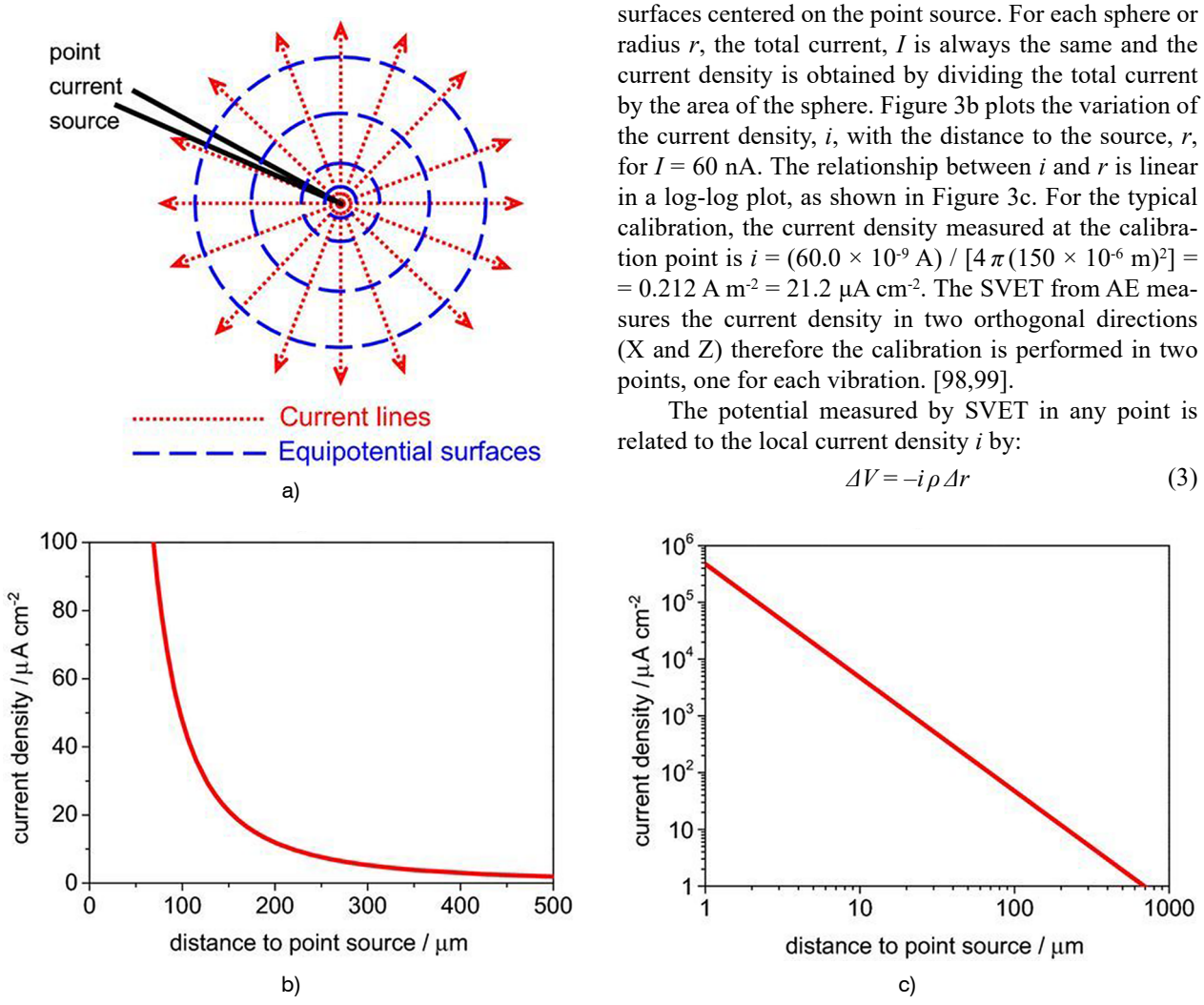


Fig. 3. a) Current lines originating from a point source; b) variation of the current density with distance from the point source (for I = 60 nA) calculated using Equation 2 and plotted in linear scale; c) the same plot in log-log scale.

where ΔV is the potential difference, i is the local current, ρ is the solution resistivity and Δr is difference in distance which is similar to Equation 1, but written for the potential difference and ρ is the solution resistivity [94-99]. During the calibration, the system measures the local potential difference and, knowing the theoretical current density at the calibration point, the proportionality factor between ΔV and i is determined. Then, during the measurements the proportionality factor allows one to relate the potential difference measured between the ends of the vibration with the current density that is flowing at the point of measurement. The calibration remains valid in different media provided the correct conductivity is updated when changing the solution or temperature. If the conductivity changes in the course of a measurement, deviations from the true current density will appear. Other factors that influence the proportionality factor, like system gain, frequency and amplitude of vibration are usually selected when the system is installed and not altered thereafter. Changing them requires re-calibration. It is important to note that the 'point source' calibration cell involves precise knowledge of the SVET probe tip relative to the point source electrode [94-99].

Following the above detailed description, the three samples A, B (coated with AX1 inhibitor) and C (coated with BTA inhibitor) according to Bastos et al., Saeedikhani et al., Hussain, Charles - Granville et al., De Viveiros et al., De Oliveira et al., and Newington [94-100] were subjected to cut-edge test.

Discussion of SVET experiment results validating corrosion inhibition performance of AX1

Figure 4 shows the sum of anodic current density through the SVET from the specimens after 24 hrs. of submersion in 5 wt.% NaCl. The SVET maps of sample C(BTA) showed high-intensity red color meaning positive anodic current density. In other words, the positive current flux was due to the metal dissolution. This high-intensity colored region is directly proportional to current density, hence increasing corrosion rate. However, the SVET maps of samples A and B(AX1) showed diminished blue color at the cathode indicating a negative cathodic current density. In other words, this negative current flux is due to a reduction reaction. Consequently, this weak color demonstrates the resistance of current at the cathode. Hence, reduced corrosion rate. To sum up, the results showed faint blue colored region depicting negative cathodic current density for the AX1 while there was a high intensity of red colored region depicting a positive anodic current density for BTA, hence increased corrosion rate for BTA and decreased corrosion rate for AX1. Above all, this reduced corrosion rate was attributed to the high corrosion inhibition performance

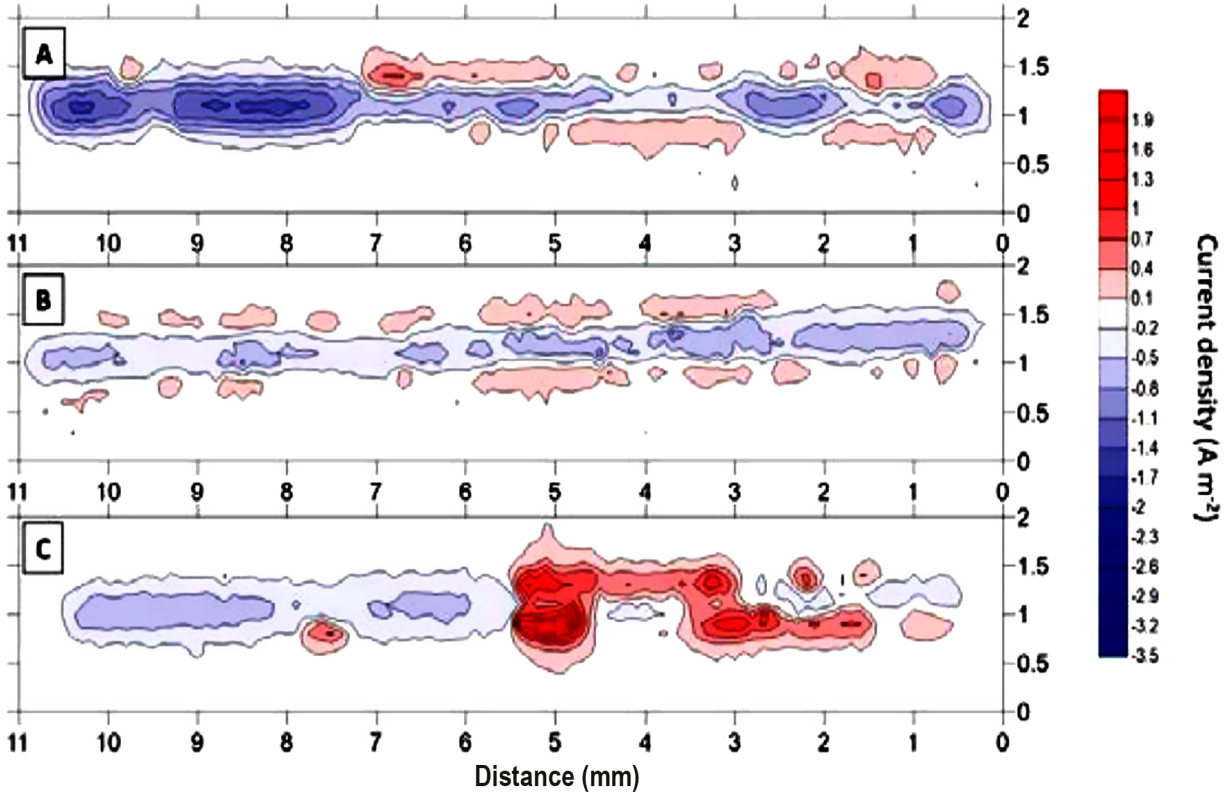


Fig. 4. SVET current density maps of AX1 (samples A and B) vs BTA (sample C) after 24 h in 5 wt. % NaCl solution (adapted with permission from Newington,2021) [100]

of the AX1 inhibitor against the BTA inhibitor. Therefore, intelli-ion (AX1) inhibitor had a better overall cut-edge corrosion inhibition performance on galvanized steel of 55 wt.% Al, 44 wt.% Zn, 1 wt.% Si in 5 wt.% NaCl after 24 hours submersion than benzotriazole (BTA) inhibitor at the same volume content.

CONCLUSION

The phasing out of hexavalent chromium has left researchers scrambling for the best alternative corrosion inhibitor that has the efficacy to replace its excellent inhibition performance. Meanwhile, over the last three decades, no alternative has been discovered. However, recently, intelli-ion was unveiled by researchers with promising prospects of becoming the needed alternative. Consequently, the performance of this new alternative has been validated. Firstly, through Scanning Kelvin probe. And secondly, through Scanning Vibrating Electrode Technique (SVET). Most importantly, the results have clearly demonstrated high corrosion inhibition effectiveness when intelli-ion was used in a primer system. Further research is encouraged to investigate new Co-blend options with intelli-ion, leveraging on synergism. As this will help to create more alternatives with higher corrosion inhibition performances.

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Conflict of interest

The authors declare that there are no competing interests whatsoever, be it commercial, financial or otherwise regarding the publication of this article. The review is a product of the available literature as expressed in the paper and serve as unbiased views in the opinion of the authors.

REFERENCES

1. Koch, G. "*Cost of corrosion, Trends in oil and gas corrosion research and technologies"*, Elsevier, Amsterdam, USA **2017**, 3–30.
2. Umoren S, A., Solomon M. M., Saji V, S. Corrosion Inhibitors for Sour Oilfield Environment (H_2S Corrosion), In *Corrosion Inhibitors in the Oil and Gas Industry*, Saji, V, S., Umoren, S, A., Eds.; Wiley **2020**, 229–254. https://doi.org/10.1002/9783527822140.ch8
3. Verma, C. et al. "Recent Developments in Sustainable Corrosion Inhibitors: Design, Performance and Industrial Scale Applications. *Mater. Adv.* **2021**, 2, 3806–3850. https://doi.org/10.1039/D0MA00681E.
4. Thompson N, G., Yunovich M., Dunmire D. cost of corro-sion and corrosion maintenance strategies. *Corrosion Reviews* **2007**, 25, 247–262. https://doi.org/10.1515/CORRREV.2007.25.3-4.247
5. Koch G, H. et al. *Corrosion cost and preventive strategies in the United States"*, Federal Highway Administration, United States **2002.**
6. Alhaffar, M, T. et al. Isoxazolidine Derivatives as Corrosion Inhibitors for Low Carbon Steel in HCl Solution: Experimental, Theoretical and Effect of KI Studies. *RSC Adv.* **2018**, 8, 1764–1777. https://doi.org/10.1039/C7RA11549K
7. Kaczerewska, O. et al. Effectiveness of O – Bridged Cationic Gemini Surfactants as Corrosion Inhibitors for Stainless Steel in 3 M HCl: Experimental and Theoretical Studies. *Journal of Molecular Liquids* **2018**, 249, 1113–1124. https://doi.org/10.1016/j.molliq.2017.11.142
8. Verma, C. et al. Choline Based Ionic Liquids as Sustainable Corrosion Inhibitors on Mild Steel Surface in Acidic Medium: Gravimetric, Electrochemical, Surface Morphology, DFT and Monte Carlo Simulation Studies. *Applied Surface Science* **2018a**, 457, 134–149. https://doi.org/10.1016/j.apsusc.2018.06.035
9. Gan, M. Corrosion Control (III): Corrosion Inhibitors. In *Corrosion in CO_2 Capture, Transportation, Geological Utilization and Storage*; Zhang, L., Ed, Engineering Materials. Springer Nature Singapore: Singapore **2023**, 111–130. https://doi.org/10.1007/978-981-99-2392-2_7
10. Montesinos-López, O, A. et al. Multi-Trait, Multi-Environment Deep Learning Modeling for Genomic-Enabled Prediction of Plant Traits. *G3 Genes|Genomes|Genetics* **2018**, 8, 3829–3840. https://doi.org/10.1534/g3.118.200728
11. Kolawole, F, O. et al. Mitigation of Corrosion Problems in API 5L Steel Pipeline-A Review. J. Mater. Environ. **2018**, 9
12. Imai, T. et al. Interaction of Indomethacin with Low Molecular Weight Chitosan, and Improvements of Some Pharmaceutical Properties of Indomethacin by Low Molecular Weight Chitosans. *International Journal of Pharmaceutics* **1991**, 67, 11–20. https://doi.org/10.1016/0378-5173(91)90260-U
13. Singla A, K., Chawla M. Chitosan: Some Pharmaceutical and Biological Aspects – an Update. *Journal of Pharmacy and Pharmacology* **2010**, 53, 1047–1067. https://doi.org/10.1211/0022357011776441
14. Guo, Z. et al. Antifungal Properties of Schiff Bases of Chitosan, N-Substituted Chitosan and Quaternized Chitosan. *Carbohydrate Research* **2007**, 342, 1329–1332. https://doi.org/10.1016/j.carres.2007.04.006
15. Portes, E. et al. Environmentally Friendly Films Based on Chitosan and Tetrahydrocurcuminoid Derivatives Exhibiting Antibacterial and Antioxidative Properties. *Carbohydrate Polymers* **2009**, 76, 578–584. https://doi.org/10.1016/j.carbpol.2008.11.031
16. Goosen M, F. *Applications of Chitan and Chitosan*. CRC Press, Florida, USA **1996**
17. Cioc R, C., Ruijter. E., Orru, R, V, A. Multicomponent Reactions: Advanced Tools for Sustainable Organic Synthesis, *Green Chem.* **2014**, 16, 2958–2975. https://doi.org/10.1039/C4GC00013G
18. Lima C, G, S. et al. Heterogenous Green Catalysis: Application of Zeolites on Multicomponent Reactions. *Current Opinion in Green and Sustainable Chemistry* **2019**, 15, 7–12. https://doi.org/10.1016/j.cogsc.2018.07.006

19. Gu Y. Multicomponent Reactions in Unconventional Solvents: State of the Art. *Green Chem.* **2012**, 14, 2091. https://doi.org/10.1039/c2gc35635j
20. Bariwal J, B., Trivedi J, C., Van Der Eycken E, V. Microwave Irradiation and Multicomponent Reactions, In *Synthesis of Heterocycles via Multicomponent Reactions II*, Orru, R. V. A., Ruijter, E., Eds.; Topics in Heterocyclic Chemistry; Springer Berlin Heidelberg: Berlin, Heidelberg **2010**, 25, 169–230. https://doi.org/10.1007/7081_2010_45
21. Verma R, S. "Greener" Chemical Syntheses Using Mechanochemical Mixing or Microwave and Ultrasound Irradiation. *Green Chemistry Letters and Reviews* **2007**, 1, 37–45. https://doi.org/10.1080/17518250701756991
22. Liu Y. β-Cyclodextrin Modified Natural Chitosan as a Green Inhibitor for Carbon Steel in Acid Solutions. *Industrial & Engineering Chemistry Research* **2015** *54* (21), 5664-5672 DOI: 10.1021/acs.iecr.5b00930
23. Chen, J. et al. Polyethylene glycol and solutions of polyethylene glycol as green reaction media. *Green Chemistry* **2005**, *7*, 64-82
24. Candy D., Macrogol B, J. (Polyethylene Glycol) Laxatives in Children with Functional Constipation and Faecal Impaction: A Systematic Review. *Archives of Disease in Childhood* **2008**, 94, 156–160. https://doi.org/10.1136/adc.2007.128769
25. D'souza, A, A., Shegokar, R. Polyethylene Glycol (PEG): A Versatile Polymer for Pharmaceutical Applications. *Expert Opinion on Drug Delivery* **2016**, 13, 1257–1275. https://doi.org/10.1080/17425247.2016.1182485
26. Roberts M, J., Bentley M, D., Harris J, M. Chemistry for Peptide and Protein PEGylation. *Advanced Drug Delivery Reviews* **2012**, 64, 116–127. https://doi.org/10.1016/j.addr.2012.09.025
27. Kocheva, K. et al. Parameters of cell membrane stability and levels of oxidative stress in leaves of wheat seedlings treated with PEG 6000. *Gen. Appl. Plant Physiol.* **2009**, 35, 127–133.
28. Li, Y. et al. Promoted Off-on Recognition of H_2O_2 Based on the Fluorescence of Silicon Quantum Dots Assembled Two-Dimensional PEG-MnO2 Nanosheets Hybrid Nanoprobe. *Microchim Acta* **2020**, 187, 347. https://doi.org/10.1007/s00604-020-04276-w
29. Kiasat, A, R. et al. *Simple Practical and Eco-friendly Reduction of Nitroarenes with Zinc in the Presence of Polyethylene Glycol Immobilized on Silica Gel as a New Solid – liquid Phase Transfer Catalyst in Water **2011***
30. Rytting, E. et al. A Quantitative Structure-Property Relationship for Predicting Drug Solubility in PEG 400/Water Cosolvent Systems. *Pharm Res*. **2004**, 21, 237–244. https://doi.org/10.1023/B:PHAM.0000016237.06815.7a
31. Yang H., Morris J. J., Lopina S. T. Polyethylene Glycol – Polyamidoamine Dendritic Micelle as Solubility Enhancer and the Effect of the Length of Polyethylene Glycol Arms on the Solubility of Pyrene in Water. *Journal of Colloid and Interface Science* **2004**, 273, 148–154. https://doi.org/10.1016/j.jcis.2003.12.023
32. Deyab M, A. Understanding the Anti-Corrosion Mechanism and Performance of Ionic Liquids in Desalination, Petroleum, Pickling, de-Scaling, and Acid Cleaning Applications. *Journal of Molecular Liquids* **2020,** 309, 113107. https://doi.org/10.1016/j.molliq.2020.113107
33. Ardakani E. K., Kowsari E., Ehsani, A. Imidazolium-Derived Polymeric Ionic Liquid as a Green Inhibitor for Corrosion Inhibition of Mild Steel in 1.0 M HCl: Experimental and Computational Study. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2020**, 586, 124195. https://doi.org/10.1016/j.colsurfa.2019.124195
34. Masri N. A., Mutalib M. A., Leveque J. M. A Review on Dicationic Ionic Liquids: Classification and Application. *Ind Eng Manage* **2016**, 5. https://doi.org/10.4172/2169-0316.1000197
35. Angell C. A. Ionic Liquids, Superionic Glasses, Quasi-Ionic Liquids, Quasi-Liquid Ionics, All with High Conductivities but Some with Little Fluidity. Where Does the Paradigm End? *Meet. Abstr.* **2014**, 2 1416–1416. https://doi.org/10.1149/MA2014-02/25/1416
36. Banger, A. et al. Application of Green Solvent in Green Chemistry: An Overview. *gctl* **2023**, 9, 01–14. https://doi.org/10.18510/gctl.2023.911
37. DeSimone, J. M. Practical Approaches to Green Solvents. *Science* **2002**, 297, 799–803. https://doi.org/10.1126/science.1069622
38. Reslow M., Adlercreutz P., Mattiasson B. On the Importance of the Support Material for Bioorganic Synthesis. Influence of Water Partition between Solvent, Enzyme and Solid Support in Water-Poor Reaction Media", *Eur J Biochem* **1988**, 172, 573–578. https://doi.org/10.1111/j.1432-1033.1988.tb13927.x
39. De Damborenea J., Conde A., Arenas M. A. Corrosion Inhibition with Rare Earth Metal Compounds in Aqueous Solutions. In *Rare Earth-Based Corrosion Inhibitors*. Elsevier **2014**, 84–116. https://doi.org/10.1533/9780857093585.84
40. Khramov A. N. et al. Hybrid Organo-Ceramic Corrosion Protection Coatings with Encapsulated Organic Corrosion Inhibitors. *Thin Solid Films* **2004**, *447–448*, 549–557. https://doi.org/10.1016/j.tsf.2003.07.016
41. Omidvar M. et al. Development of Highly Efficient Dual-Purpose Gas Hydrate and Corrosion Inhibitors for Flow Assurance Application: An Experimental and Computational Study. *Energy Fuels* **2023**, 37, 1006–1021. https://doi.org/10.1021/acs.energyfuels.2c03454
42. Shah B A. Arsenic Contamination in Groundwater in the Middle Gangetic Plain, India: Its Relations to Fluvial Geomorphology and Quaternary Stratigraphy, In *Safe and Sustainable Use of Arsenic-Contaminated Aquifers in the Gangetic Plain*; Ramanathan, A., Johnston, S., Mukherjee, A., Nath, B., Eds, Springer International Publishing: Cham **2015**, 33–53. https://doi.org/10.1007/978-3-319-16124-2_3
43. Leopold I. H. Pharmacology and toxicology: Review of the Literature. *Arch Ophthalmol* **1950**, 44, 300. https://doi.org/10.1001/archopht.1950.00910020307011
44. Bidstrup P. L., Case R. A. M. Carcinoma of the Lung in Workmen in the Chromates-Producing Industry in Great Britain, *Occupational and Environmental Medicine* **1956**, 13, 260–264. https://doi.org/10.1136/oem.13.4.260
45. Kendig M. W., Buchheit R. G. Corrosion Inhibition of Aluminum and Aluminum Alloys by Soluble Chromates, Chromate Coatings, and Chromate-Free Coatings. *CORROSION* **2003**, 59, 379–400. https://doi.org/10.5006/1.3277570
46. Zhao, J. et al. Effects of Chromate and Chromate Conversion Coatings on Corrosion of Aluminum Alloy 2024-T3. *Surface and Coatings Technology* **2001**, 140, 51–57. https://doi.org/10.1016/S0257-8972(01)01003-9

47. Zehra S., Mobin M., Aslam J. Chromates as Corrosion Inhibitors, In *Inorganic Anticorrosive Materials.* Elsevier **2022**, 251–268. https://doi.org/10.1016/B978-0-323-90410-0.00014-3
48. Forsyth, M. et al. Effectiveness of Rare-Earth Metal Compounds as Corrosion Inhibitors for Steel. *CORROSION* **2002**, 58, 953–960. https://doi.org/10.5006/1.3280785
49. Li L., Gao J., Wang Y. Evaluation of Cyto-Toxicity and Corrosion Behavior of Alkali-Heat-Treated Magnesium in Simulated Body Fluid. *Surface and Coatings Technology* **2004**, 185, 92–98. https://doi.org/10.1016/j.surfcoat.2004.01.004
50. Birbilis N., Buchheit R. G. Electrochemical Characteristics of Intermetallic Phases in Aluminum Alloys. *J. Electrochem. Soc.* **2005**, 152, 140. https://doi.org/10.1149/1.1869984
51. Campestrini P., Terryn H., Hovestad A., De Wit J. H. W. Formation of a Cerium-Based Conversion Coating on AA2024: Relationship with the Microstructure. *Surface and Coatings Technology* **2004**, 176, 365–381. https://doi.org/10.1016/S0257-8972(03)00743-6
52. Wu L, K., Zhang X. F., Hu J. M. Corrosion Protection of Mild Steel by One-Step Electrodeposition of Superhydrophobic Silica Film. *Corrosion Science* **2014**, 85, 482–487. https://doi.org/10.1016/j.corsci.2014.04.026
53. Zheludkevich M, L. et al. Nanostructured Sol–Gel Coatings Doped with Cerium Nitrate as Pre-Treatments for AA2024-T3. *Electrochimica Acta* **2005**, 51, 208–217. https://doi.org/10.1016/j.electacta.2005.04.021
54. Montemor M. F. et al. Evaluation of Self-Healing Ability in Protective Coatings Modified with Combinations of Layered Double Hydroxides and Cerium Molibdate Nanocontainers Filled with Corrosion Inhibitors. *Electrochimica Acta* **2012**, 60, 31–40. https://doi.org/10.1016/j.electacta.2011.10.078
55. Pebere N., Lebon E. Local Electrochemical Impedance Spectroscopy: A Powerful Tool for Studying Corrosion Inhibition Mechanisms on 2024 Aluminum Alloy. *Meet. Abstr*. **2016,** 2, 1701–1701. https://doi.org/10.1149/MA2016-02/23/1701
56. Behrsing T., Deacon G. B., Junk P. C. The Chemistry of Rare Earth Metals, Compounds, and Corrosion Inhibitors. In *Rare Earth-Based Corrosion Inhibitors.* Elsevier **2014**, 1–37. https://doi.org/10.1533/9780857093585.1
57. Kolics A. et al. Cerium Deposition on Aluminum Alloy 2024-T3 in Acidic NaCl Solutions. *J. Electrochem. Soc.* **2003**, 150, 512. https://doi.org/10.1149/1.1615995
58. Irving E., Stoker A. W. Vanadium Compounds as PTP Inhibitor. *Molecules* **2017**, 22, 2269. https://doi.org/10.3390/molecules22122269
59. Kwolek P., Kościelniak B., Wytrwal-Sarna M. Pentavalent Vanadium Species as Potential Corrosion Inhibitors of Al_2Cu Intermetallic Phase in the Sulfuric (VI) Acid Solutions. *Materials* **2020**, 13, 1946. https://doi.org/10.3390/ma13081946
60. Ralston K. D. et al. Corrosion Inhibition of Aluminum Alloy 2024-T3 by Aqueous Vanadium Species. *J. Electrochem. Soc.* **2008**, 155, 350. https://doi.org/10.1149/1.2907772
61. McLauchlan C. C. et al. Inhibition of acid, alkaline, and tyrosine (PTP1B) phosphatases by novel vanadium complexes. *Journal of Inorganic Biochemistry* **2010**, 104, 274-281 10.1016/j.jinorgbio.2009.12.001
62. Iannuzzi M., Frankel G. S. Mechanisms of Corrosion Inhibition of AA2024-T3 by Vanadates. *Corrosion Science* **2007**, 49, 2371–2391. https://doi.org/10.1016/j.corsci.2006.10.027
63. Li X. et al. Materials science: Share corrosion data. Nature **2015**, 527, 441-442
64. Guan H., Buchheit R. G. Corrosion Protection of Aluminum Alloy 2024-T3 by Vanadate Conversion Coatings. *Corrosion* **2004**, 60, 284–296. https://doi.org/10.5006/1.3287733
65. Qu M. et al. Dynamically Monitoring Cellular γ-H_2AX Reveals the Potential of Carcinogenicity Evaluation for Genotoxic Compounds. *Arch Toxicol* **2021**, 95, 3559–3573. https://doi.org/10.1007/s00204-021-03156-3
66. Rangel C., Travassos M. A. The Passivation of Aluminium in Lithium Carbonate/Bicarbonate Solutions. *Corrosion Science* **1992**, 33, 327–343. https://doi.org/10.1016/0010-938X(92)90064-A
67. Yan J., Yu J., Ding B. Mixed Ionic and Electronic Conductor for Li-Metal Anode Protection. *Adv. Mater.* **2018**, 30, 1705105. https://doi.org/10.1002/adma.201705105
68. Lee Y., Cha J. A., Jung D. Y. Lithium Separation by Growth of Lithium Aluminum Layered Double Hydroxides on Aluminum Metal Substrates. *Solid State Sciences* **2020**, 110, 106488. https://doi.org/10.1016/j.solidstatesciences.2020.106488
69. Kosari A. et al. Cross-sectional characterization of the conversion layer formed on AA2024-T3 by a lithium-leaching coating. Applied Surface Science **2020**, 512, [145665]. https://doi.org/10.1016/j.apsusc.2020.145665
70. Sun, Y. et al. Highly Efficient Lithium Recovery from Pre-Synthesized Chlorine-Ion-Intercalated LiAl-Layered Double Hydroxides via a Mild Solution Chemistry Process. *Materials* **2019**, 12, 1968. https://doi.org/10.3390/ma12121968
71. Rangel C. M., Travassos M. A. Li-Based Conversion Coatings on Aluminium: An Electrochemical Study of Coating Formation and Growth. *Surface and Coatings Technology* **2006**, 200, 5823–5828. https://doi.org/10.1016/j.surfcoat.2005.08.145
72. Visser P. et al. Lithium Salts as Leachable Corrosion Inhibitors and Potential Replacement for Hexavalent Chromium in Organic Coatings for the Protection of Aluminum Alloys. *J Coat Technol Res* **2016**, 13, 557–566. https://doi.org/10.1007/s11998-016-9784-6
73. Visser P. et al. The Corrosion Protection of AA2024-T3 Aluminium Alloy by Leaching of Lithium – Containing Salts from Organic Coatings. *Faraday Discuss* **2015**, 180, 511–526. https://doi.org/10.1039/C4FD00237G
74. Parvizi R. et al. Probing Localised Corrosion Inhibition of AA2024-T3 by Integrating Electrode Array, SVET, SECM, and SEM-EDS Techniques. *Metals* **2023**, 13, 1703
75. Kartsonakis I. A. et al. Multifunctional Epoxy Coatings Combining a Mixture of Traps and Inhibitor Loaded Nanocontainers for Corrosion Protection of AA2024-T3. *Corrosion Science* **2014**, 85, 147–159. https://doi.org/10.1016/j.corsci.2014.04.009
76. Mohamed N, S. et al. Development of Smart Self-Healing Coating for the Corrosion Protection of Magnesium Alloys: A Brief Review. *Journal of Adhesion Science and Technology* **2022**, 1–19. https://doi.org/10.1080/01694243.2022.2158774
77. Bierwagen G. P., Tallman D. E. Choice and Measurement of Crucial Aircraft Coatings System Properties. *Progress in Organic Coatings* **2001**, 41, 201–216. https://doi.org/10.1016/S0300-9440(01)00131-X

78. Glover C. F. et al. In-Coating Graphene Nano-Platelets for Environmentally-Friendly Corrosion Protection of Iron. *Corrosion Science* **2017**, 114, 169–172. https://doi.org/10.1016/j.corsci.2016.11.009
79. Pourhashem S. et al. Exploring Corrosion Protection Properties of Solvent Based Epoxy-Graphene Oxide Nanocomposite Coatings on Mild Steel. *Corrosion Science* **2017**, 115, 78–92. https://doi.org/10.1016/j.corsci.2016.11.008
80. Ogle k. et al. The Alkaline Stability of Phosphate Coatings I: ICP Atomic Emission Spectroelectrochemistry. *Corrosion Science* **2004**, 46, 979–995. https://doi.org/10.1016/S0010-938X(03)00182-3
81. Yang Y. et al. Effect of a Brief Post-Weld Heat Treatment on the Microstructure Evolution and Pitting Corrosion of Laser Beam Welded UNS S31803 Duplex Stainless Steel. *Corrosion Science* **2012**, 65, 472–480. https://doi.org/10.1016/j.corsci.2012.08.054
82. Thomas, S. et al. Self-Repairing Oxides to Protect Zinc: Review, Discussion and Prospects. *Corrosion Science* **2013**, 69,11-22.https://doi.org/10.1016/j.corsci.2013.01.011
83. Nanna M. E., Bierwagen G. P. Mg-Rich Coatings: A New Paradigm for Cr-Free Corrosion Protection of Al Aerospace Alloys. *J Coat. Technol. Res.* **2004**, 1, 69–80. https://doi.org/10.1007/s11998-004-0001-7
84. Maier B., Frankel G. S. Behavior of Magnesium-Rich Primers on AA2024-T3", *CORROSION* **2011**, 67, 055001-1-055001–055015. https://doi.org/10.5006/1.3586018
85. Akpanyung K. V., Loto R. T. Pitting Corrosion Evaluation: A Review. *J. Phys.: Conf. Ser.* **2019**, 1378, 022088. https://doi.org/10.1088/1742-6596/1378/2/022088
86. Bierwagen G. et. Active Metal-Based Corrosion Protective Coating Systems for Aircraft Requiring No-Chromate Pretreatment. *Progress in Organic Coatings* **2010**, 67, 195–208. https://doi.org/10.1016/j.porgcoat.2009.10.009
87. Gharbi O. et al. Chromate Replacement: What Does the Future Hold"? *npj Materials Degradation* **2018**, 2, 12. https://doi.org/10.1038/s41529-018-0034-5
88. Wan H. et al. Effect of Zinc Phosphate on the Corrosion Behavior of Waterborne Acrylic Coating/Metal Interface. *Materials* **2017**, 10, 654. https://doi.org/10.3390/ma10060654
89. United Nations Environment Program **2021**, https://www.unep.org/news-and-stories/story/meeting-global-phosphorus-challenge-will-deliver-food-security-and-reduce
90. Sharfalddin A. A. et al. Therapeutic Properties of Vanadium Complexes. *Inorganics* **2022,** 10, 244. https://doi.org/10.3390/inorganics10120244
91. Sheikholeslami S. et al. Cut-edge corrosion behavior assessment of newly developed environmental-friendly coating systems using the Scanning Vibrating Electrode Technique (SVET). Corrosion Science **2021**, 192, 813. https://doi.org/https://doi.org/10.1016/j.corsci.2021.109813
92. Sheikholeslami S. Evaluation of cut-edge corrosion in environmentally friendly waterborne coil-coatings using the Scanning Vibrating Electrode Technique (SVET). Surface Coatings International **2020**, 5
93. Cacace. G; Dodds. P. *Innovation in Intelligent, Highly Effective Corrosion Inhibitors. PCI Magazine **2018.*** https://www.pcimag.com/articles/105381-innovation-in-intelligent-highly-effective-corrosion-inhibitors (accessed 2023-11-21)
94. Bastos A. C. et al. Review – On the Application of the Scanning Vibrating Electrode Technique (SVET) to Corrosion Research. *Journal of Electrochemical Society* **2017**, 164, 973. https://doi.org/10.1149/2.0431714jes
95. Saeedikhani M. et al. Electrochemical Modeling of Scanning Vibrating Electrode Technique on Scratched and Inclined Surfaces. *Journal of Electrochemical Society* **2021**, 168, 081505. https://doi.org/10.1149/1945-7111/ac1b50
96. Hussain A. Corrosion Studies Using the Scanning Vibrating Electrode Technique (SVET) – A Brief Review. *Current Smart Materials* **2021**, 14, 125–130. https://doi.org/10.2174/2666145414666210203114259
97. Charles-Granville R. S. et al. Application of Finite Element Modeling to Macro-Galvanic Coupling of AA7050 and SS316: Validation Using the Scanning Vibrating Electrode Technique. *Journal of Electrochemical Society* **2022**, 169, 031502. https://doi.org/10.1149/1945-7111/ac55ce
98. De Viveiros B. V. G. et al. Comparing the Corrosion Behaviour of AA2050 and AA7050 Aluminum Alloys by Scanning Vibrating Electrode and Scanning Ion-Selective Electrode Techniques. *Corrosion Engineering, Science and Technology* **2022**, 57, 85–96. https://doi.org/10.1080/1478422X.2021.1992132
99. De Oliveira M. C. L. et al. Investigating Local Corrosion Processes of Magnesium Alloys with Scanning Probe Electrochemical Techniques: A Review. *Journal of Magnesium and Alloys* **2022,** 10, 2997–3030. https://doi.org/10.1016/j.jma.2022.09.024
100. Newington E. *A 'New Breed of Corrosion Inhibitor for Steel*. Hexigone **2021**. https://www.hexigone.com/whats-new/a-new-breed-of-corrosion-inhibitor (accessed 2024-06-13)