

# Encapsulation of $\text{NaVO}_3$ as Corrosion Inhibitor into Microparticles and its Active Corrosion Protection for AA2024 Based Upon Inhibitor Control Release

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## ABSTRACT

The present work provides a one-step method of encapsulating a corrosion inhibitor,  $\text{NaVO}_3$ , relevant to protection of AA2024-T3, into hollow microparticles. By dispersing these microparticles into a PVB coating, the encapsulated  $\text{NaVO}_3$  may be continuously released into the electrolyte and heal the corroded sites spontaneously. The improvement of corrosion inhibition by  $\text{NaVO}_3$  microencapsulation described herein was validated by electrochemical methods and salt spray/immersion test.

**KEY WORDS:** coatings, corrosion inhibitor,  $\text{NaVO}_3$

## INTRODUCTION

Inhibitors are powerful functional agents that have been extensively applied in various industries to combat corrosion. They are usually combined with coating materials, like epoxy and polyurethane, which provide superior barrier properties. However, inhibitors only work when released in the right concentration range.<sup>1</sup> An inhibitor concentration that is too low not only leads to poor inhibition, it may also initiate and aggravate localized pitting corrosion.<sup>2</sup> On the other hand, when the concentration is too high, inhibitors may leach out too quickly. Such depletion of inhibitors may leave large defects in the coating matrix<sup>3</sup> and result in a higher

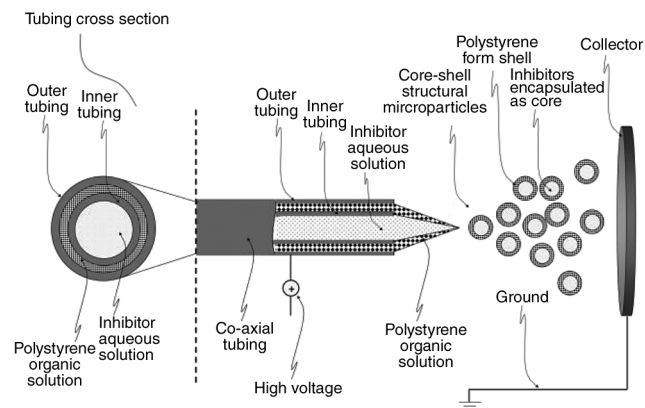
corrosion risk in the long term. Moreover, when the protective system is inclusive of a coating, high concentrations of inhibitors can result in high osmotic pressure, which stimulates water penetration into the coating and results in coating delamination.<sup>4</sup> For inhibitors such as vanadate, an excessively high concentration may lead to reduced corrosion inhibition resulting from concentration-dependent speciation and the change from an inhibiting form to a non-inhibiting form.<sup>5</sup> Encapsulating inhibitors into micro-reservoirs can be an effective strategy to address this issue. The microparticles can serve as a long-term reservoir for the inhibitors, thereby avoiding the quick leaching process. The shell can also prevent the direct interaction between inhibitors and coating matrix, which can lead to inactivation of inhibitors.<sup>6</sup> Additionally, these micro-containers enable a controlled/sustained release of inhibitors over a long term.

Extensive efforts have been made to create inhibitor impregnated microparticles. Popular current methods include a water/oil emulsion polymerization method,<sup>7</sup> self assembly,<sup>6,8</sup> and layer-by-layer deposition of oppositely charged polyelectrolytes.<sup>4,9-11</sup> Electrospin was also used to generate nanofiber containers<sup>12-14</sup> or solid microparticles<sup>15</sup> for corrosion inhibitor encapsulation. In this study, an adapted electrospray technique to prepare core-shell structural inhibitor encapsulated microparticles is reported. Sodium metavanadate ( $\text{NaVO}_3$ ) is utilized as the corrosion inhibitor and will be loaded into an inert polymer polystyrene (PS) shell model to form microparticles. The dissolved vanadate works as a good cathodic inhibitor by suppressing oxygen reduction reaction, which has been well

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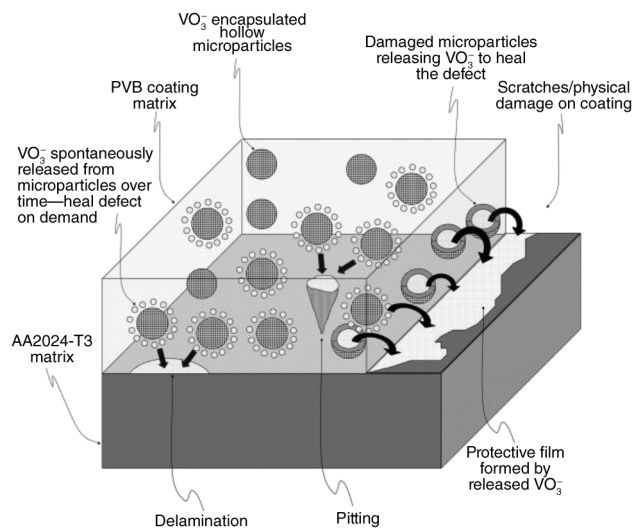
**FIGURE 1.** Fabrication process of PSV microparticles using the co-axial electro-spray technique.

documented in Ralston.<sup>16</sup> PS does not dissolve in water because of the lack of a degradable bond, but the dissolved  $\text{NaVO}_3$  can diffuse through the intrinsic free volume and pores generated by solvent evaporation during electro-spray. The shell material can be improved by using several functional polymers like pH-sensitive or degradable ones, depending on different applications.

## EXPERIMENTAL PROCEDURES

An adapted electro-spray technique<sup>17</sup> was used to fabricate  $\text{NaVO}_3$  encapsulated PS microparticles (denoted as PSV) (Figure 1). In brief, aqueous  $\text{NaVO}_3$  and PS dichloromethane solution were simultaneously ejected through a co-axial tubing. When a constant 15 kV voltage is applied, the mixed solutions are released from the tubing tip and form PSV microcapsules. Potentiodynamic polarization and electrochemical impedance spectroscopy were used to investigate the anti-corrosion properties of PSV microcapsules on an AA2024-T3 (Al-4.4Cu-1.5Mg-0.6Mn, UNS A92024)<sup>(1)</sup> substrate.

By dispersing PSV microparticles into a polyvinyl butyral (PVB) coating (denoted as AA2024+PVB+PSV), a coating with self-healing function may be achieved (Figure 2). Control group samples with vanadate-free PS microparticles dispersed in PVB coating are denoted as AA2024-PVB-PS. Samples prepared with direct electro-spray of  $\text{NaVO}_3$  into PVB coating but without the protection of PS microparticles are denoted as AA2024-PVB-V. The three groups of samples were scratched and exposed to B117 salt spray exposure<sup>18</sup> and an immersion test (0.5 M NaCl). An accelerated alternating current-direct current-alternating current (AC-DC-AC) method<sup>19</sup> was also used to quantify the anti-corrosion performance of the three coatings.



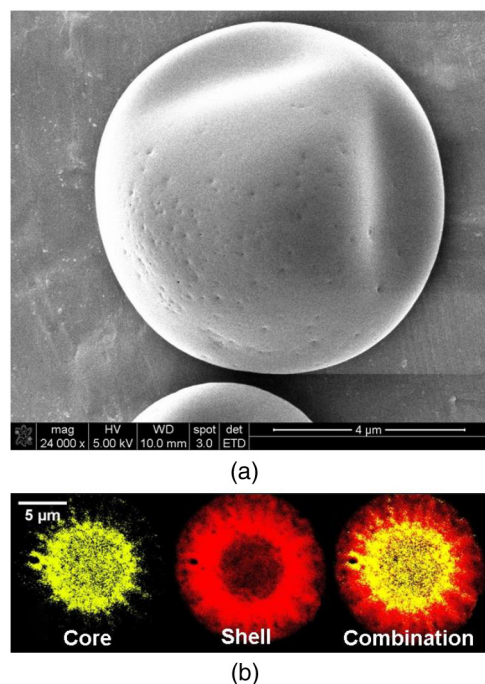
**FIGURE 2.** A self-healing smart coating achieved by embedding PSV microparticles into a PVB coating.

## RESULTS AND DISCUSSION

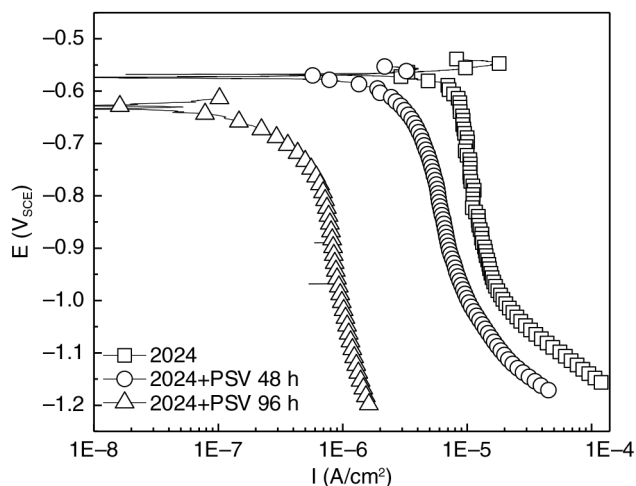
The successful fabrication of core-shell PSV microparticles was revealed by SEM and confocal microscopy (Figure 3). Figure 4 shows the cathodic polarization curves of AA2024-T3 sheets with and without the addition of PSV microparticles. The experiments were performed in 0.5 M NaCl. Four mg of PSV was added into the NaCl solutions for inhibitor release for 48 h and 96 h. In the potential range where diffusion controlled oxygen reduction occurs, there was a decrease in limiting current density for AA2024-T3 immersed in 48-h inhibitor release solution relative to bare AA2024-T3 substrate, which indicates fair inhibition. For AA2024-T3 coupons immersed in a 96-h inhibitor release bath, the limit current density was reduced as much as one order of magnitude, suggesting strong cathodic inhibition. This also indicates that inhibition was enhanced as  $\text{NaVO}_3$  was gradually released from the microparticles.

Both salt spray exposure and immersion test results showed that encapsulated  $\text{NaVO}_3$  microparticles significantly improved the resistance provided by the coating in regard to localized and uniform corrosion. The results of an accelerated AC-DC-AC method reveal that AA2024-PVB-PSV is the most corrosion resistant, while AA2024-PVB-V is the least, which further supports that the microencapsulation of  $\text{NaVO}_3$  improves the corrosion resistance of coatings. This also suggests that direct addition of  $\text{NaVO}_3$  into PVB coating may significantly reduce corrosion resistance. This is actually as expected because  $\text{NaVO}_3$  is hydrophilic, while PVB is hydrophobic and they are, therefore, not compatible phases.<sup>20</sup> When electrolytes penetrate the coating, water soluble inhibitors will quickly dissolve and leach out creating sizeable defects, pores, and/or channels. These defects may significantly accelerate the

<sup>(1)</sup> UNS numbers are listed in *Metals and Alloys in the Unified Numbering System*, published by the Society of Automotive Engineers (SAE International) and cosponsored by ASTM International.



**FIGURE 3.** (a) Surface morphology of PSV microparticles. (b) Core-shell structure of one individual PSV microparticle as observed by confocal microscopy. Rhodamine B base and FITC were added into core and shell, respectively, to provide fluorescence signal.



**FIGURE 4.** Cathodic polarization curve of AA2024-T3 coupon in 0.1 M NaCl solution with and without addition of PSV microparticles.

electrolyte uptake process and result in accelerated disbonding of the coating from its metal substrate. By encapsulating inhibitors into microparticles, the leaching process will be dramatically retarded because of the protection of the PS shell. When disbonding occurs, the released inhibitors may have sufficient time to block the reactive sites and heal the defects,

discouraging the oxygen reduction reaction, thereby resulting in the observed corrosion inhibition.

## SUMMARY

The present work provides a one-step method of encapsulating a corrosion inhibitor relevant to protection of AA2024-T3,  $\text{NaVO}_3$ , into core-shell PS microparticles. By dispersing these microcapsules into a PVB coating, encapsulated  $\text{NaVO}_3$  can be continuously released into the electrolyte and deposited onto reactive sites to form a corrosion resistant film that protects the surface when minor mechanical or chemical damage occurs within the coating. The self-healing function was demonstrated by salt spray exposure and immersion testing. Electrochemical tests also validate the anti-corrosion properties achieved by inhibitor microencapsulation described herein.

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