

Electrochemical Evaluation of Corrosion Control by Composite Hybrid Vanadate Conversion Coatings on 6061 Al

M. Oki^{1,2}, P. P. Ikubanni^{1*}, A. A. Adediran¹, O. S. Adesina³, A. A. Adeleke⁴,
P. K. Egba¹, H. I. Nwachukwu¹ and R. P. Ojediran¹

¹Department of Mechanical Engineering, Landmark University,
Omu-Aran, Kwara State, Nigeria

²Greenfield Creations (Nig) Ltd. (Corrosion consultants), Benue Close,
Agbara Estate, Agbara, Ogun State, Nigeria

³Department of Mechanical Engineering, Redeemer's University, Ede, Nigeria

⁴Department of Mechanical Engineering, Nile University of Nigeria, FCT, Abuja, Nigeria

*Corresponding author: ikubanni.peter@lmu.edu.ng

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Abstract

Environmental and health issues have created the urgent need to transition from CrO_4^{2-} legacy to more environment-friendly CC. The various international protocols on CrO_4^{2-} have restricted its usage, thus opening a floodgate of research activities on its urgent replacements. The current study which examines HSCE and V salt takes a cue from earlier outcomes in which a hybrid HSCE and M_2MoO_4 coating outperformed CrO_4^{2-} coating. The relatively faster diffusion rate of the chelated Mo (VI) complex of hybrid HSCE over Cr (VI) inhibited corrosion and provided a better barrier on the substrate. Thus, this study examined HC from HSCE in combination with V salt, a V salt-based CC and untreated Al 6061. From PDP measurements and EIS studies in a 3.5% NaCl solution, CC from VO_4 outperformed HC, and both outclassed untreated 6061 Al. R_{ct} values from EIS studies were 116 (lowest), 1825 and 3434 ohm/cm^2 (highest) for uncoated 6061 Al, HSCE/ VO_4 coating and VO_4 , respectively. From PDP studies, i_{corr} values were 24.934×10^{-6} (VO_4), 33.275×10^{-6} (HSCE/ VO_4) and 36.64×10^{-6} A/ cm^2 (6061 Al), respectively, compared to 1.6×10^{-6} A/ cm^2 , for CC from CrO_4^{2-} , in a similar study. These primary findings might support new opportunities for producing environment-friendly smart hybrid and mono CC based on V compounds for corrosion control on Al in the metal finishing industries.

Keywords: 6061 Al; CC; corrosion control; EIS; HC; HSCE from VO_4 ; R_p .

Introduction*

CC have come a long way. They are primarily employed for improving the CR and adhesion of coatings subsequently applied on treated surfaces. They are often termed smart coatings. When the surface is breached to expose the substrate, the smart

*The abbreviations list is on pages 318-319.

coatings release inhibitors to stifle corrosion reactions in such regions. CrO_4^{2-} has performed these duties diligently for several decades. Thus, any compound that will replace CrO_4^{2-} should, amid others, improve CR and paint adhesion [1]. In addition, its application process must be as simple as with CrO_4^{2-} applications [1, 2].

Al, its alloys and metal matrix composites derived therefrom are valuable, and are preferred in the metal fabrication industries, due to their low weight, recyclability, CR, strength, resilience, ductility, conductivity and formability. The applications range of these metals continues to expand, because of this unique mix of characteristics. Whenever freshly prepared Al is exposed to the environment, a thin oxide layer forms on its surface, providing effective protection against atmospheric corrosion [3]. However, in hostile environments, the passive film can be broken initially at imperfections in the oxide layer, causing corrosive attacks on the substrate. Al alloy matrices are usually riddled with Fe- and Mg-rich intermetallic phases, and some precipitates, which are mostly cathodic. These inclusions are the bane of Al alloys, in terms of disintegration due to corrosion activities [4]. Conversely, when some Mg precipitates, which may be anodic to the matrix, all are put together, they make Al alloys critically electrochemically unstable in aqueous environments. Several researchers have successfully employed organic and/or inorganic compounds as CI, for Al and its alloys, such as extracts of various plants parts, VO_4 , M_2MoO_4 , Ce salts [4-8] and a host of environmentally friendly rare earth ions. Ions of elements such as La, Pr and Nd [9] have shown to provide exceptional resistance to localized corrosion, through the formation of insoluble hydroxide/oxide layers.

Thus, this investigation seeks to develop and examine hybrid CC based on organic and inorganic CI as starting materials, with the addition of aqueous HSCE and V salts. VO_4 is known to be less toxic than CrO_4^{2-} , being generally more environmentally acceptable. On the other hand, *Hibiscus sabdariffa* is biodegradable and belongs to the class generally referred to as green CI. In an earlier work [10], aqueous HSCE was successfully employed as a starting material for eco-friendly CC on Al. With the use of FT-IR and SEM/EDS, the coating mapped the substrate grain and sub-grain boundaries. FT-IR analyses of the coating solution and the coating stripped from the substrate confirmed similar elemental compositions, with shifts in wavelength either up or downfield. Thus, the present study was a further attempt to reduce the carbon footprint in the metal finishing industries [10], which have thrived in the past decades with the use of CrO_4^{2-} . However, various governmental organs have legislated on the restricted use of this carcinogenic and environmentally hazard substance [11, 12]. In furtherance of CrO_4^{2-} replacement in coating baths and processes, various authors have established the partial acceptability of relatively less toxic substitutes compounds. These include VO_4 [13], M_2MoO_4 [14], zirconate [15] and permanganate [16], which have been shown to have lower CR than CrO_4^{2-} coatings. To improve on their CR, hybrid inorganic/inorganic coatings, such as zirconate/ CrO_3 [17], $\text{VO}_4/\text{M}_2\text{MoO}_4$ [18] and inorganic/organic hybrids, such as $\text{M}_2\text{MoO}_4/\text{HSCE}$ [19], have been reported to be superior to CrO_4^{2-} in a 3.5% NaCl solution. However, in a recent study, [20] revealed that the addition of some organic additives to CC solutions from Ti and Zr may have

some slight deficiencies in terms of paint adhesion, which may be initially good, but rapidly deteriorates with time. Zr/Cr(III) gained popularity from the 1990s until recently, when it fell into disuse in the canning industry, because it was found to contain Cr (VI) species. It has been shown that peroxides produced from cathodic reactions on second-phase inclusions in Al matrixes occur through electrons exchange with Cr (III), to form Cr (VI) [21]. Thus, the development of CC without Cr has become important and very urgent.

Oxyanions, such as VO_4 , have been described as effective CI for Al. However, due to V oxides high solubility in aqueous solutions, they have not been extensively researched. In epoxy-coated AA2014-T6 plates, the release kinetics and safety efficiency of VO_4 -based pigments have been investigated [22]. The authors concluded that VO_4 ions are effective in preserving Al alloy matrices. Subsequent research tested and compared multiple candidate inhibitors such as VO_4 and M_2MoO_4 , and rare earth elements ions, such as Ce, Y, and La. The authors concluded that the best performance was provided by VO_4 in aqueous solutions, from neutral to basic pH, approaching CrO_4^{2-} like levels, in some cases. Interestingly, no CI was much more efficient at lower Ph. However, VO_4 ions were among the better-performing species [22].

The discovery and production of non-toxic, natural, and environmentally friendly inhibitors have now been gaining attention in the art of green chemistry, to mitigate Al corrosion phenomenon in alkaline and/or acidic media [23, 24]. The effect of the two major constituents of aqueous HSCE, namely, organic acids and coloring substances, on Al and Zn dissolution in alkaline solutions, has been studied. The two constituents were effective in retarding the breakdown of both metals, but the coloring component performed substantially better than the organic acids. Anthocyanin, flavone and protocatechuic acid are among the various active components of this plant [25].

Thus, a major endeavor of this research was to form hybrid CC based on HSCE and VO_4 ions, which were further electrochemically assessed in terms of CR. The coupons received a CC in three different baths, before their surface characterization. The coupons were subjected to atmospheric and salt environments in an electrochemical experimental set-up. The exposed specimens and coatings development was monitored with naked eyes and photography.

Materials and methods

Materials

6061 Al electrode donated by First Al Plc, Nigeria, with a nominal composition (%) of 96.85 Al, 0.9 Mg, 0.7 Si, 0.6 Fe, 0.3 Cu, 0.25 Cr, 0.20 Zn, 0.10 Ti, 0.05 Mn and 0.05 other elements, was fabricated in the usual manner [2]. CC solutions were made up as follows: (a) VO_4 : 5g Na_3VO_4 were dissolved in 1 L water with some activators, and pH was adjusted with NaOH or HNO_3 , to achieve 3.5-4; (b) 50 g dried HSCE were soaked overnight in 1 L water with activators, and pH was adjusted as in (a); (c) VO_4 /HSCE was made up of 50:50 (a) and (b) solutions. Then, the electrodes were degreased and etched in a 10% NaOH solution, rinsed in water before desmutting in 50% HNO_3 ,

washed again in abundant water, and allowed to dry under the fan, for 30 min. Distilled water and laboratory-grade reagents (BDH chemicals, UK) were used throughout.

Methods

CC development

Cleaned and weighed electrodes were immersed in each coating solution for periods from 30 s to 10 min. After each IT, the electrodes were rinsed in water, dried under the fan for 30 min, and re-weighed before photographic examination. For each IT, triplicate samples were examined, and the weights mean was finally measured. CC schematic diagram is displayed in Fig. 1.

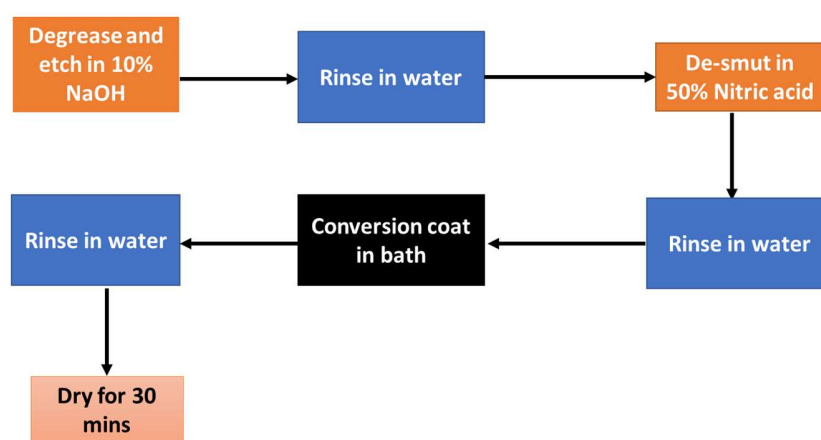


Figure 1: Schematic diagram of CC.

Corrosion exposure tests

Triplicate separate electrodes were treated for 3 min each in the coating solutions, rinsed in water, allowed to dry, and some of them were overcoated with lacquer. Lacquer coating was performed by the specimen's immersion in a 50 mL bottle of lacquer, at a right angle, withdrawn as immersed, and allowed to dry, for 48 h. Bare and lacquer-coated specimens were cross-hatched, and some of them were exposed angled at 30°, as stipulated in ASTM G50-20, to natural atmospheric weather. Other similarly treated specimens were exposed to a 3.5% NaCl solution, for 168 h. 6061 Al without CC were the control samples. The specimens were examined at intervals, with naked eye and photography, after adhesive tape application, using Japanese industrial paint adhesion testing method, as described in [10, 16].

Electrochemical examinations

The corrosion behavior of 6061 Al coated for 3 min each in the various CC baths, with uncoated control samples, was determined through PDP and EIS measurements. Following ASTM G59-97 (2020) [26], PDP measurements were performed in a conventional three-electrode cell, using computer-controlled potentiostat/galvanostat (Autolab PGSTAT 302N). A Pt foil, Ag/AgCl in 3 M KCl, and CC and uncoated Al 6061

samples were employed as CE, RE and WE, respectively. The WE area exposed to 3.5% NaCl was approx. 1 cm². Prior to E sweeps, the electrodes were allowed to corrode freely for about 30 min, to attain OCP. After this, OCP steady state, corresponding to E_{corr} of the WE, was obtained. Tafel plot data were acquired within a scan range of $E = E_{\text{corr}} \pm 250$ mV, at a SR of 10 mV/s⁻¹. Employing the same electrochemical cell, EIS for similarly treated samples was carried out at OCP, by superimposing a sinusoidal A of 5 mV amplitude, at frequencies from 0.01 Hz to 10⁵ Hz. EIS data were analyzed with FRA 32 software. R_{ct} and CPE were obtained from Nyquist plots.

Results and discussion

Coating development and gravimetric analysis

The growth patterns of the coatings in VO₄ and HSCE/VO₄ baths were similar. They initially developed at a fast rate, which slowed down at 30 s of IT, after their initial deposition over the macroscopic substrate surfaces.

Within 30 to 50 s, the coating weight decreased, showing thinning of the precursor coating materials, to allow electron tunneling for growth to start at the coating/metal interface, as discussed in [27], and described by other authors [28, 29]. Further development occurred, and the maximum coating weight achieved after 600 s was 3 and 4 mg, respectively, in VO₄ and HSCE/VO₄ coating solutions, as shown in Fig. 2a and b. The color changes were mid-tan yellow mixed with purple and greenish, beyond the initial lustrous metallic finish of the untreated and cleaned 6061 Al samples. Color changes of this nature, which became darker, normally indicate coating development and growth.

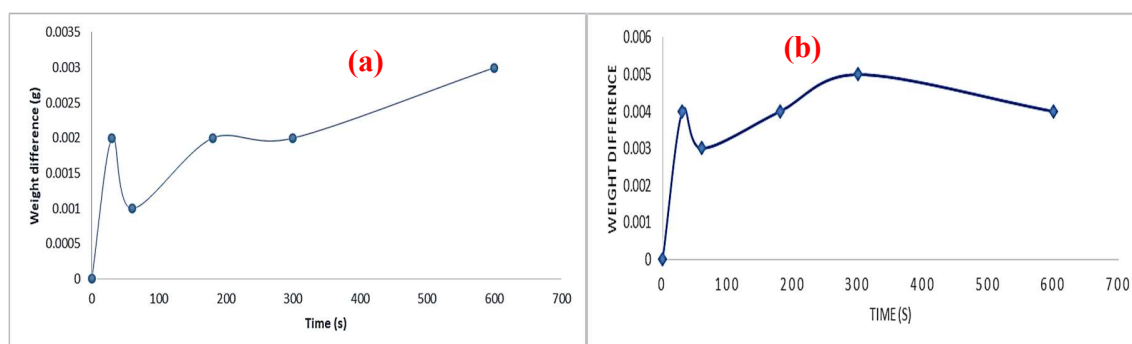


Figure 2: Growth rate for 6061 Al in (a) VO₄ and (b) HSCE/VO₄ coating baths.

CC formation and development at room temperature usually follow the well-established activation of Al by fluoride, being assisted by other species in the coating solution. Electrons are released through complex formation with Al. The released electrons are then taken up by V [V] ions, to gradually form [IV], [III] and [II] ions, as discussed by [1, 18]. A complimentary cathodic reaction involving HER naturally took place, increasing the substrate's interfacial pH. Thus, the hydrated oxides and/or hydroxides of the several reduced V ions were deposited as the initial coating

materials. Further coating growth continued at the coating/substrate interface, through electron tunneling, as discussed earlier.

The coating formation and development can be summarized by Eqs. (1-3):



Other V oxides/hydroxides were also formed, which gave rise to the various colors observed on the coatings: blue, for V (IV), when V (V) picked by one electron; and green, for V (II), when V (V) picked 3 electrons.

Atmospheric and 3.5% NaCl solution corrosion exposure tests

From naked eye observations, lacquer-coated 6061 Al showed some signs of dip whitish coloration, after 168 h exposure to the natural environment in the North Central region of Nigeria. The coloration, as several authors explained [10, 12, 16], is due to moisture absorption by the lacquer polymeric material. None of the exposed samples showed paint delamination, after atmospheric exposure, and tape pull-off adhesion tests.

However, lacquer-coated specimens exposed to NaCl solutions revealed, to the naked eyes, changes in their coloration, whereas bare CC samples showed slight discoloration to a lighter shade of mid-tan yellow, before exposure regimes. Corrosion incidences were not found, even in the deliberately inscribed scratches, which implied the CC good corrosion protective barrier and smart protection [30, 31], through stifling reactions by oxyanions in VO_4 , as well as other inhibitors in the HC. In its turn, the uncoated 6061 Al suffered massive pitting corrosion episodes after 168 h, in the salt solution, as shown in Fig. 3a, as against Fig. 3b, which revealed CC sample corrosion-free surface, after a similar exposure test.

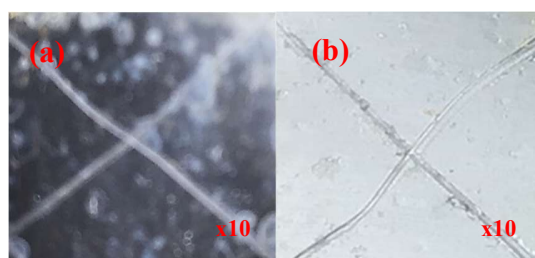


Figure 3: Samples of (a) bare 6061 Al and (b) CC, after 168 h exposure in a 3.5% NaCl solution.

From these observations, it can be safely inferred that the CC provided a protective barrier against corrosion, and improved paint adhesion over the 6061 Al substrate in harsh media. The coatings adequately provided the known two major functions of CC; improved CR and paint adhesion.

Electrochemical characteristics

Fig. 4 displays PDP curves of bare 6061 Al and coated samples in a 3.5% NaCl solution, while Table 1 presents PDP parameters. It is generally known that CC do influence the corrosion behavior of Al alloy substrates.

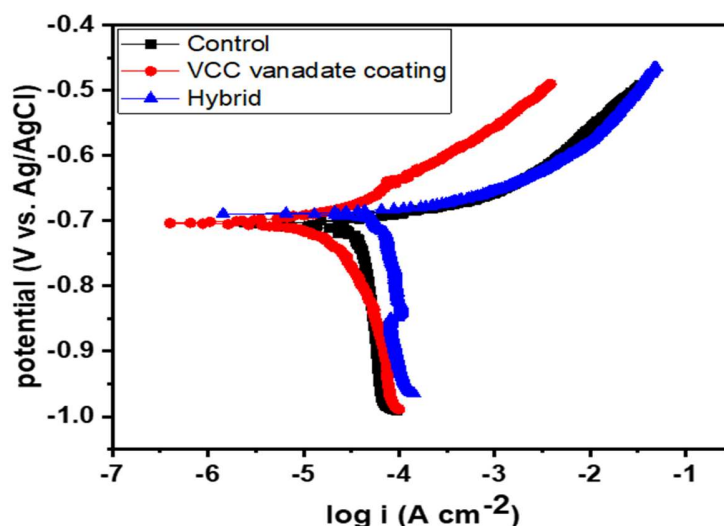


Figure 4: PDP curves for bare 6061 Al, VO₄, and hybrid VO₄/HSCE CC on 6061 Al.

Table 1: Polarization parameters for the samples in a 3.5% NaCl solution.

Sample	β_a (V/dec)	β_c (V/dec)	E_{corr} (V)	I_{corr} (A/cm ²) $\times 10^{-6}$
Control	0.030	0.788	-0.704	36.640
VCC	0.932	0.424	-0.703	24.934
Hybrid	0.271	0.779	-0.690	33.275

Compared with the polarization process of bare 6061 Al, the coated samples curves revealed shifts towards positive E_{corr} , and decreasing i_{corr} . It is well known that E_{corr} , a thermodynamic quantity, is a measure of the propensity of a metal to corrode, and i_{corr} reveals kinetics information [32]. Therefore, higher E_{corr} value indicated a lower possibility of corrosion, and lower i_{corr} implied slower rates of corrosion. However, the linear relationship between i_{corr} and corrosion rates suggests that its values better describe the electrochemical resistance of the tested samples. From Tafel extrapolation, bare Al, VO₄, and VO₄/HSCE had i_{corr} values of 36.640×10^{-6} (maximum), 24.934×10^{-6} , and 33.275×10^{-6} A/cm², respectively. Thus, i_{corr} values for VO₄ and hybrid VO₄ were lower than for bare 6061 Al. This implied a slower rate of corrosion on the CC substrates than that of the bare Al substrate (control). E_{corr} values increased from about -0.704 V, for bare Al, to about -0.690 V, for HC, while VO₄ had -0.701 V. This indicated that bare Al was more prone to degenerate in a Cl⁻ environment, due to the corrosion reaction, unlike the CC samples. The lower E_{corr} value for the CC from VO₄ was due to imperfections associated with crack morphologies [6, 16], while the HC that incorporated organic compound additives

usually had less severe cracks, due to the formation of metal-organic complexes [1, 20, 33] that protect it more from the environment. Although [19, 1] have found that, on the addition of organic compounds to CC solutions, marked improvements in CR are usually observed, [1] has not employed a V coating solution without tannic acid. They have only indicated a marked 12-fold higher CR than untreated 6063 Al. This may be due to the formation of metal/organic complexes which, in most cases, have reduced the usual mud cracking patterns on CC. These river-bed cracking morphologies, as described by [3, 6, 16], are recognized to be the weak point in coatings through which corrodent from the environment comes in contact with the substrate. Also, in some cases, the organic compound supplies additional inhibitors to complement those originally present in VO_4 coating, such as V reducible metal ions in IV, IV, and III oxides [1, 18]. However, in this instance, with HSCE, such improvement in CR was not seen. It has been shown that the purple coloring material in HSCE is stronger as a CI than its organic acid counterparts [25]. In this work, it was seen that the extract's bright purple color, after being mixed with the VO_4 coating solution, reduced to a lighter shade, by V oxyanions oxidizing actions. This suggested a reduction in the extract's inhibitive properties. Hence, the hybrid solution and, by extension, the coating formed thereof, were stripped of some colored, active inhibitor species that would have added to the coating's corrosion performance.

The CC and bare 6061 Al electrochemical behavior was also examined by EIS measurement in a 3.5 wt.% NaCl solution. The semi-circular loop diameter in Nyquist plots is related to the corrosion rate. In Fig. 5a, the larger diameter indicates slower electrochemical activities at the metal/solution interface [34]. The semicircle diameters for the specimens were in the order: bare Al < HSCE < VO_4 . The increases in the Nyquist loops were partly due to the protective barrier functions of the coating, and to its oxyanions inhibiting effects [35]. However, as expected, some oxyanion inhibitor species, which should have been in the hybrid, reacted with the coloring matter in the extract and oxidized it, depleting the overall inhibitor sample in the coating. From the foregoing, it is herein suggested that the HC solution mixing should be at the point of application on the metal substrate, as performed for $\text{M}_2\text{MoO}_4/\text{HSCE}$ [19], or be employed as a final rinse operation. This will be much easier during roller coating operations. From Fig. 5a and Table 2, R_{ct} was the lowest for uncoated 6061 Al (116 ohm/cm²), followed by HSCE/ VO_4 coating (1825 ohm cm²), while VO_4 had the largest R_{ct} (3434 ohm/cm²) hence being the least electrochemically active and, thus, having the highest CR.

Fig. 5b shows Bode plots obtained for the uncoated substrate and CC specimens, where two-time constants can be seen. The relaxation process at high-intermediate frequencies, associated with VO_4 coatings features, presented a phase angle (ϕ) close to -80° , which indicates a capacitive behavior with good dielectric properties. That is, CC have the ability to charge, avoiding the ionic flow of the corroding solution [30, 31, 33]. Other specimens displayed similar characteristics, but with lower phase angles, since their capacitive properties can be inferred to be poorer. In addition, as the frequency decreased, the slightly dropped phase angle gave rise to a second relaxation process. This should be related to Cl^- penetration through the coatings to the metal substrate, due to inherent flaws in them [33].

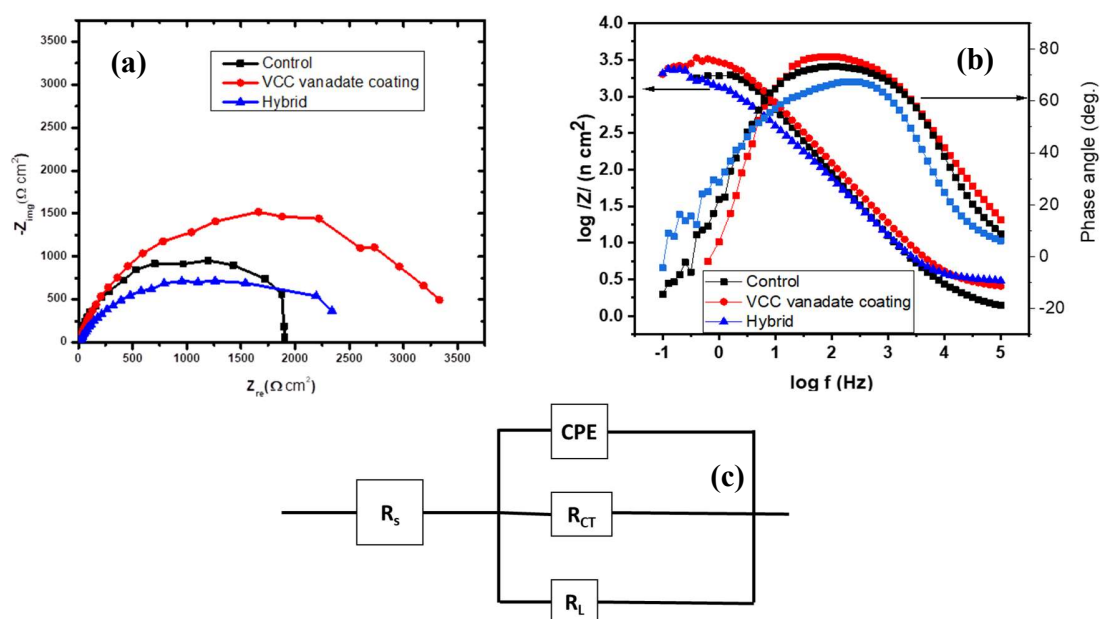


Figure 5: (a) Nyquist plots for bare 6061 Al and samples coated with VO_4 and hybrid VO_4 /HSCE in a 3.5% NaCl solution; (b) Bode plots of the various specimens; and (c) equivalent circuit diagram for the samples.

Table 2: EIS parameters for CC and bare Al samples in a 3.5% NaCl solution.

Sample	R_s (Ω/cm^2)	R_{ct} (Ω/cm^2)	CPE ($\mu\text{F}/\text{cm}^2$)
Control	1.23	116.3	0.23
CC with V	2.54	3434	0.25
HC	3.02	1825	0.52

The equivalent circuit for 6061 Al samples in 3.5% NaCl is shown in Fig. 5c, where R_s is the solution resistance between RE and WE, in series with a first CPE, and in parallel with a second resistance (R_c), which represents the coating's properties. This is in series with a second parallel sub circuit, which corresponds to interactions through the flawed regions of the coating between the substrate and the saline solution employed in this study. This represents C_{dl} and R_{ct} associated with the corrosion process, and it also fits for bare 6061 Al, with expected porous oxide/hydroxide films present on its surface. Their thickness is in the region of those of the CC films, which had 100-300 nm, albeit more flawed than them.

Conclusions

CC from HSCE and VO_4 were herein tested on 6061 Al in a 3.5% NaCl medium. Corrosion protection afforded by the coatings was in the order: $VO_4 > CC > \text{bare Al}$. The i_{corr} values were 36.640, 24.934, 33.275 ($\mu\text{A}/\text{cm}^2$), for bare Al, and HC from VO_4 and HSCE/ VO_4 , respectively. These values were validated by their R_{ct} of 116.3, 3434 and 1825 Ω/cm^2 , respectively. The higher R_{ct} values, the higher the samples' CR.

The coatings, within the exposure limits adopted and electrochemical tests employed in this investigation, had high CR, and improved lacquer adhesion on 6061 Al. The alloy was massively inflicted with various sizes of pits, after IT for 168 h, in a 3.5% NaCl solution. The CC specimens were free of pitting corrosion incidences after similar exposure regimes.

Bode plots revealed that CC had capacitive behavior with good dielectric properties, thus, the ability to charge, avoiding the ionic flow of the corroding solution species. Bode plots also revealed a second relaxation episode at low frequencies, associated with Cl⁻ ingress at flaws in the coating.

CC from HSCE/VO₄ can be adapted to roller coating operations in the metal finishing industries. The roller coating process can be slightly modified, to allow for a final rinse with HSCE or mix with VO₄, at the point of contact with the metal to be coated. Thus, VO₄ and HSCE/VO₄ are promising replacements for CrO₄²⁻ in CC formulations/baths.

Authors' contributions

M. Oki: research idea. **M. Oki, P. P. Ikubanni, A. A. Adediran, O. S. Adesina, A. A. Adeleke:** materials; samples preparation. **P. K. Egba, H. I. Nwachukwu, R. P. Ojediran:** further laboratory experiments on prepared samples, to obtain required data. **A. A. Adediran, O. S. Adesina, A. A. Adeleke:** samples' microstructure interpretation. **M. Oki, P. P. Ikubanni, A. A. Adediran:** data analyses; first draft of the manuscript. All authors contributed to the scientific discussion of the manuscript.

Abbreviations

AgCl: silver chloride

Al: aluminum

ASTM: American Society for Testing and Materials

CC: conversion coating/coated

C_{dl}: double layer capacitance

Ce: cerium

CE: counter electrode

CI: corrosion inhibitor

Cl⁻: chloride

CPE: constant phase element

Cr (III): trivalent chromium

CrO₃: chromium trioxide

CrO₄²⁻: chromate

Cr (VI): hexavalent chromium

CR: corrosion resistance

Cu: copper

E: potential

E_{corr}: corrosion potential

EDS: energy dispersive spectroscopy

EIS: electrochemical impedance spectroscopy

Fe: iron
FT-IR: Fourier transform-infrared
HC: hybrid coating
HER: hydrogen evolution reaction
HNO₃: nitric acid
HSCE: *Hibiscus sabdariffa* calyx extract
I_{corr}: corrosion current density
IT: immersion time
KCl: potassium chloride
La: lanthanum
M₂MoO₄: molybdate
Mg: magnesium
Mn: manganese
Mo (VI): molybdenum vi oxide
MS: mild steel
NaCl: sodium chloride
NaOH: sodium hydroxide
Na₃VO₄: sodium vanadate
Nd: neodymium
OCP: open circuit potential
PDP: potentiodynamic polarization
Pr: praseodymium
R_{ct}: charge transfer resistance
RE: reference electrode
R_p: polarization resistance
SEM: scanning electron microscopy
Si: silicon
SR: scan rate
Ti: titanium
WE: working electrode
V: vanadium
VO₄: vanadate(3-) (vanadium oxoanion)
Y: yttrium
Zn: zinc
Zr: zirconium

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