Corrosion behavior of aluminum in molten hydrated salt phase change materials for thermal energy storage

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Abstract
The corrosion behavior of aluminum 1060 in hydrated salt phase change materials (PCM) melts comprised of Na₂HPO₄·12H₂O - Na₂SO₄·10H₂O was investigated through electrochemical tests as a function of pH. The pH of PCM medium was adjusted by adding H₂SO₄ or NaOH. Electrochemical impedance spectroscopy reveals the existence of concentration difference layer at aluminum/PCM interface ascribed to the adsorption of PCM species and the formation of aluminum oxides. The observed anodic branch of DC polarization exhibits potential independence which is ascribed to the formation of surface oxide film and the accumulation of hydrogen molecules inside surface pores. The oxide film formed at neutral condition is characterized as the most compact and corrosion resistant while as the environmental pH shifts away from 7 the oxides/aluminum dissolution is accelerated and more aluminum 1060 substrate is exposed.

1. Introduction
Among various thermal energy storage techniques, latent heat storages, particularly hydrated salt phase change materials (PCM), have attracted much attention due to the lower phase transition temperature and higher heat storage capacity. Researches attained so far have shown that hydrated salt PCM can not only balance the mismatch between the limited energy supply and increasing social demands but also improve the capacity and storage capacity. Researches attained so far have shown that hydrated salt PCM can not only balance the mismatch between the limited energy supply and increasing social demands but also improve the capacity and storage capacity. Researches attained so far have shown that hydrated salt PCM can not only balance the mismatch between the limited energy supply and increasing social demands but also improve the capacity and storage capacity. Researches attained so far have shown that hydrated salt PCM can not only balance the mismatch between the limited energy supply and increasing social demands but also improve the capacity and storage capacity. Researches attained so far have shown that hydrated salt PCM can not only balance the mismatch between the limited energy supply and increasing social demands but also improve the capacity and storage capacity. Researches attained so far have shown that hydrated salt PCM can not only balance the mismatch between the limited energy supply and increasing social demands but also improve the capacity and storage capacity.
others for PCM storage. In order to retard the PCM induced corrosion, our recent work introduced four kinds of Schiff base composites to the PCM medium working as effective inhibitors for aluminum corrosion [20]. Nevertheless, the corrosion issue of Al-PCM system is still not fully addressed and more realistic operating conditions should be considered before it can be extensively applied.

Aiming to better understand the corrosion mechanisms of Al-PCM system, the present work is carried out by changing the pH value of composited Na$_2$HPO$_4$·12H$_2$O and Na$_2$SO$_4$·10H$_2$O PCM medium. The dissolution process of Al-1060 is studied through electrochemical measurements including electrochemical impedance spectroscopy (EIS) and DC polarization measurements. The morphologies of specimen surface are characterized by means of optical metallography (OM), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). Compositions of surface films were further investigated by grazing incidence x-ray diffraction (GIXRD) analysis.

2. Experimental

2.1. Materials

The studied inorganic hydrated salt PCM composite was prepared in chemical purity of Na$_2$HPO$_4$·12H$_2$O and Na$_2$SO$_4$·10H$_2$O with a composition ratio (wt%) of 9:1, which has been reported in our pervious works as an efficient thermal energy storage medium [17–19]. The prepared PCM was mix and melted at 60 °C by keeping magnetic stirring in a thermostatic water bath. The pH value of fresh melt was 9 according to pH meter. The pH of PCM medium were adjusted by adding H$_2$SO$_4$ or NaOH and five pH values (2, 4, 7, 9 and 11) were chosen in the present study. During tests, the electrochemical cell was kept suspending in the thermostatic water bath with temperature controlled at 60 ± 1 °C.

Commercial aluminum 1060 (Al-1060) sheet with Al (wt%) > 99.6% were prepared as the working electrodes. Specimens were first machined into round discs having 14 mm diameter and 3 mm thick and then welded with copper wire and later mounted in araldite, exposing a 1.540 cm$^2$ circular surface area in contact with corrosive electrolyte. Before commencing test, specimen surfaces were polished successively to 1500 grit SiC paper, then degreased in alcohol and ultrasonically cleaned in deionized water.

2.2. Electrochemical measurements

The electrochemical measurements were carried out through PARSTAT 2273 potentiostat (Princeton Applied Research, US) with a conventional three-electrode cell using a platinum spade as the auxiliary electrode and a saturated calomel electrode (SCE) with Luggin capillary as the reference electrode. Before starting each measurement, the open circuit potential ($E_{ocp}$) of electrode was allowed to stabilize for 1 h. All the potentials referred in the present paper are in reference of SCE. After attaining the system equilibrium, electrochemical impedance spectroscopy (EIS) test was performed at open circuit potential under AC perturbation of 5 mV in amplitude with frequency ranging from 10 mHz to 100 kHz. For potentiodynamic polarization measurement, specimen was polarized from 250 mV (SCE) below open circuit potential towards anodic potential under 1 mV s$^{-1}$ scan rate. Each experiment was performed three times to ensure the data reliability.

2.3. Surface analysis

After DC polarization measurements, samples were gently cleaned in deionized water in order to remove the attached PCM salts. Microstructural characterizations were detected under an optical microscope and the further analyzed by a scanning electron microscope (ZEISS, Germany) equipped with an energy dispersive spectrometer (EDS) under voltage of 10 kV. The chemical compositions of corroded sample surface were characterized by GIXRD (X’Pert Pro MRD, Netherland) using Co-K$_{α}$ radiation with incident angle of 0.5 degree.

3. Results and discussion

3.1. Electrochemical impedance spectroscopy measurements

Figure 1 displays the EIS results of Al-1060 in studied PCM melts. From figure 1 (a), the Nyquist response under each pH condition is featured similarly over the whole frequency range by a capacitive loop at high frequency (HF) region followed by an inductive loop at medium frequency region and a second capacitive loop at low frequency (LF) region. However, all capacitor loops act as depressed semicircles without being centered at the real axis of complex plan ($Z_{oc}$), designating a clear deviation from ideal behavior. In molten salt system, this deviation phenomenon is highly associated with the non-uniform electric field existed at metal/PCM interface resulting from the roughness of film grown on the electrode surface [21].
Similar Nyquist responses of aluminum electrode in alkaline environments have been widely discussed [22–26]. The origin of HF capacitor loop could be ascribed to the formation of surface oxide layer or to the pre-existing surface oxide [22–26]. According to Brett [22, 23], the occurrence of HF capacitive loop is a manifestation of the interfacial charges transportations and the formation of oxide layer. During the charge transfer process, oxidation reactions take place where metal cations are initially generated at metal/oxide interface and then tend to migrate across the oxide layer driven by the high electric field strength into the oxide/PCM interface where they are further oxidized to higher valence state [27]. A broader HF capacitive arc signifies a better effect of surface barrier in obstructing the charge transfer process [28]. It is noteworthy that the diameter of HF capacitor loop reaches the largest in the case of pH 4 and pH 7, approximately three times as compared with high acidic (pH 2) or in high alkaline (pH 11) medium, indicating a relative outstanding surface resistance existed in moderately acidic and neutral conditions.

The appearance of second capacitor loop assigns to the dissolution of surface oxide film [29, 30]. From figure 1(a), the diameter of characteristic low frequency loop varies with pH change, being maximized in the neutral environment and tending to reduce as the pH changing away from 7. It signifies that the property of aluminum surface oxide film is affected by the environmental pH value. The film formed in neutral PCM medium is featured by the largest LF arc which translates to a better thermodynamic stability. By contrast, dramatic diminishments of low and high frequency loops are observed in both pH 2 and 11 cases, suggesting the weak protection of the oxides grown on electrode surface. This reflects the amphoteric nature of aluminum that it can be readily dissolved either in highly acidic or highly alkaline environments [31–33].

In addition, it is also observed that between the two capacitive loops there is an inductive loop grown at medium frequency region. This inductive response has been reported in many researches [22–26, 34, 35]. Its origin is highly relevant to the existence of aluminum oxides and commonly ascribed to the surface or bulk relaxation of the intermediates into the oxide layer [29]. In our cases, the adsorption of intermediate species, such as Al\(^{3+}\), Al\(^{2+}\) and Al(OH)\(_4\)\(^{-}\), can also result in the inductive response.

The characteristic of two time constants, as indicated in Nyquist plot by two capacitive arcs, were also evidenced in each $|Z|$ against log frequency diagram (figure 1(b)) by two measured linear relationship portions which own negative slopes of about $-1$. At the low frequency limit, the resistive behavior $|Z|$ is dominated by polarization resistance ($R_p$) across the Al/PCM interface, specially being the largest in the case of pH 7 and particularly small in the cases of pH 2 and 11. This indicates a stronger surface resistance against mass transfer in
neutral condition possibly related to the growth of a more protective oxide film at Al/PCM interface. The twotime-constant behavior has also been confirmed by the phase angle curve (figure 1(c)), in which two peaks were
given rise at HF and LF regions respectively relating to two capacitive responses. Notably, the HF phase angle
peak reaches the maximum value of around 65 in two cases, i.e., pH 4 and pH 7, with the peak width covering the
widest frequencies ranging from 100 kHz to 10 Hz, identifying the existence of a relatively thick or less
defective surface layer formed at Al/PCM interface as compared to it formed at other pH conditions [16, 28].

Equivalent electrical circuit (EEC) was proposed to further evaluate the impedance plots and more
quantitative results were extracted. Constant phase element (CPE) was introduced in the EEC simulating the
non-ideal capacitive behavior which is resulted from the heterogeneous oxides grown on the electrode surface.
The electrical impedance of a CPE can be calculated through equation (1) [36].

\[ Z_{CPE} = \frac{1}{Y_0 (i\omega)^{-n}} \]  

in which \( Y_0 \) represents the modulus; \( \omega \) and \( n \) are the angular frequency and the deviation parameter, respectively.
The ideal capacitor behavior is considered as \( n = 1 \). From figure 2, the applied EEC consists of seven elements.
CPE\(_1\) represents the double electrical layer capacitance at oxide/PCM interface and \( R_s \) is the electrolyte
resistance. The aluminum oxide layer is represented by a resistor \( R_{ox} \) and a capacitor CPE\(_2\), considering the
resistance of charge transportation inside oxide and the dielectric nature of the oxide layer, respectively. In series
with the \( R_{ox}\)-CPE\(_2\) component, an \( R_{ct} \) is applied representing the charge transfer resistance. Besides, an inductor
L and the relative resistor \( R_L \) are introduced, accounting for the surface relaxation and adsorption course of
intermediates in the oxide layer. Fitted results of these circuit elements are listed in table 1. Accordingly, the
polarization resistance \( R_P \) is computed through equation (2).

\[ R_P = \frac{R_{ct} R_L}{R_{ct} + R_L} + R_{ox} \]  

Moreover, the value of double layer capacitance \( C_{dl} \) in the EEC is calculated from CPE parameter by equation (3).

\[ C_{dl} = Y_0^{1/n} R_{ct}^{(1-n)/n} \]  

Table 1. Impedance parameters for Al-1060 in PCM melt with pH variation.

| pH  | 2    | 4    | 7    | 9    | 11   |
|-----|------|------|------|------|------|
| \( R_s (\Omega \ \text{cm}^2) \)  | 2.359 | 2.538 | 2.733 | 2.836 | 3.087 |
| \( \text{CPE}_1 (Y_0/\Omega^{-1} \ \text{S} \ \text{cm}^{-2}) \)  | 2.02 E-5 | 1.68 E-5 | 1.62 E-5 | 2.57 E-5 | 3.16 E-5 |
| \( n_1 \)  | 0.931 | 0.940 | 0.942 | 0.933 | 0.926 |
| \( C_{dl} (\text{F cm}^{-2}) \)  | 1.13 E-5 | 1.10 E-5 | 1.07 E-5 | 1.62 E-5 | 1.77 E-5 |
| \( R_s (\Omega \ \text{cm}^2) \)  | 20.33 | 82.33 | 78.78 | 60.37 | 22.99 |
| \( L (\text{H cm}^2) \)  | 0.463 | 2.361 | 5.481 | 0.4194 | 0.536 |
| \( R_L (\Omega \ \text{cm}^2) \)  | 16.72 | 77.49 | 60.65 | 39.57 | 13.01 |
| \( \text{CPE}_2 (Y_0/\Omega^{-1} \ \text{S} \ \text{cm}^{-2}) \)  | 3.38 E-2 | 1.96 E-2 | 3.38 E-2 | 4.37 E-2 | 8.31 E-2 |
| \( n_2 \)  | 0.849 | 0.918 | 0.975 | 0.897 | 0.831 |
| \( R_{ox} (\Omega \ \text{cm}^2) \)  | 10.79 | 43.44 | 57.96 | 36.94 | 9.00 |
| \( R_{ct} (\Omega \ \text{cm}^2) \)  | 19.96 | 83.36 | 92.23 | 60.84 | 17.31 |

Figure 2. Equivalent electrical circuit applied to model the experimental impedance results.
From table 1, it can be seen that the value of CPE1 is quite smaller (three orders of magnitude) than CPE2, which indicates the presence of a concentration different layer at Al/PCM interface. Since concentrations of HPO$_4^{2-}$, H$_2$PO$_4^-$, PO$_4^{3-}$ and SO$_4^{2-}$ are sufficiently high in the molten PCM medium, it is adequate to propose that these electrolyte anions can be strongly adsorbed on the positively charged electrode surface during polarization thus contributing to the formation of interfacial concentration different layer. Generally, the variation of $C_{dl}$ represents the property change of dielectric film formed on the electrode surface. From table 1, a decreasing of $C_{dl}$ is observed as the environmental pH shifts from either highly acidic or highly alkaline to neutral condition. The more $C_{dl}$ is decreased, the thicker the barrier film is formed in terms of the expression of Helmholtz model (equation (4)) where the value of $C_{dl}$ is inversely proportional to the film thickness $d$ [16, 26].

$$C_{dl} = \frac{\varepsilon_0 \varepsilon}{d}$$

in which $S$ represents the surface area of electrode, $\varepsilon_0$ is the vacuum permittivity and $\varepsilon$ is the local dielectric constant.

In particular, the phenomenon of interfacial concentration difference can be significant when a porous oxide layer is grown on the Al-1060 surface. As one of the dominate species in the studied PCM, the incorporation of phosphates ions into the aluminum oxide layer is highly likely. Literature survey [37–40] shows that phosphates can make strong bonds with Al surface and positively influence the corrosion property of oxide film mainly through two ways; formation of an adsorption layer at oxide/PCM interface, thus preventing the penetration of aggressive anions; incorporation into the Al oxide film in the form of aluminum phosphates, healing the surface film by plugging the defects. Another main PCM specie, SO$_4^{2-}$ ions, also show potential to participate in the competitive adsorption at oxide/PCM interface and promote the growth of oxides by chemical adsorption[33]. The formation of aluminum sulfate is possibly favored in alkaline medium [33]. Besides, aluminum hydroxides can also be formed at Al/PCM interface under continuous attack of OH$^-$ ions. The growth of these surface oxides is witnessed from the origin of LF Nyquist arc. The corresponding $R_{ox}$ reveals the difficulty of transportation of species inside oxides and its value shows a considerable difference (from 9.00 to 57.96 $\Omega$ cm$^2$) with pH changes. The highest $R_{ox}$ is observed at pH 7, suggesting the formation of a more protective oxide barrier at neutral condition. Similar trend is found in $R_{p}$ variation. According to the theoretically derived Pourbaix diagram, pure aluminum gets immunized in the aqueous electrolyte within protective oxide barrier at neutral condition. Similar trend is found in $R_{p}$ variation. According to the theoretically derived Pourbaix diagram, pure aluminum gets immunized in the aqueous electrolyte within protective oxide barrier at neutral condition. The dissolution process of Al-1060 can be explained based on the point defect model [41–44] that the charge carriers in the oxide film are designated as oxygen vacancies and aluminum vacancies which are spontaneously generated in the oxide film and directed through the film, contributing to the formation of film. The electrochemical processes occur at Al/oxide interface can be expressed as the generation of oxygen vacancy $V_o^{2+}$ (ox) (equation (5)) and the annihilation of aluminum vacancy $V_{Al}^{3-}$ (ox) (equation (6)).

$$Al_{Al}(m) = Al_{Al}(ox) + 2/3 V_o^{2+}(ox) + 3e^-$$

$$Al_{Al}(m) + V_{Al}^{3-}(ox) = Al_{Al}(ox) + 3e^-$$

where $Al_{Al}(m)$ presents the aluminum atom in metal site and $Al_{Al}(ox)$ is the aluminum atom in oxide film site. Meanwhile, reactions proceeding at the oxide/PCM interface include the filling of oxygen vacancy (equation (7)) as well as the appearance of aluminum vacancy (equations (8) or (9)).

$$H_2O + V_o^{2+}(ox) = O_2(ox) + 2H^+(aq)$$

$$Al_{Al}(ox) = Al^{3+}(aq) + V_{Al}^{3-}(ox)$$

$$H_2O(ad) = O_2(ox) + 2/3 V_{Al}^{3-}(ox) + 2H^+(aq)$$

where $O_2(ox)$ is the oxygen atom in oxide film site. As the result, oxygen vacancy (equation (5)) diffuses outwardly to oxide/PCM interface and consequently facilitates the oxide growth via the incorporation with adsorbed water molecular (equation (7)), while aluminum vacancy (equations (8) or (9)) diffuses inwardly to Al/oxide interface where they will be consumed and in return assists the oxide growth (equation (6)). In acidic environments, the aluminum dissolution processes are accordingly given in the form of equations (10) and (11) with dissolution steps controlled by the complexation reaction between the hydrated cation and the electrolyte anion (equation (11)) [24, 27, 45]. Moreover, the alumina film is dissolved through equation (12).

$$Al^{3+} + H_2O = [AlOH]^{2+} + H^+$$

$$[AlOH]^{2+} + X^- = [AlOHX]^+$$
\[ \text{Al}_2\text{O}_3 + 6\text{H}^+ = 2\text{Al}^{3+} + 3\text{H}_2\text{O} \]  \hspace{1cm} (12)

However, direct aluminum dissolution, where \text{Al}^{3+} ions are directly released upon electric field-assistance from the oxide lattice into the PCM (equation (8)), can hardly occur in alkali medium due to the fact that \text{Al}^{3+} ions are not thermodynamically stable in alkaline condition. Pyun and moon et al\cite{43, 44, 46} pointed out that the generation of aluminum vacancy in alkali medium is mainly accounted for the electrochemical process of adsorbed water molecule on the oxide film, as modeled in equation (9). In this manner, hydroxides are electrochemically formed on aluminum surface upon the penetration of hydroxyl ions across the oxide film to the Al/oxide interface (equation (13)).

Some of these oxides may deposit and incorporate to the growth of film while the remainder chemically dissolves in the form of aluminate ions in later step (equation (14)) under the continuous hydroxyl attack at the oxide/PCM interface. Meanwhile, alumina oxide film is consumed through equation (15). By contrast with acidic dissolution, the electrochemical process in alkaline medium contains consecutive formation and breakdown of the aluminum oxide film, in which aluminate ions rather than aluminum ions participate.

\[
\begin{align*}
\text{Al} + 3\text{OH}^- &= \text{Al(OH)}_3 + 3\text{e}^- \\
\text{Al(OH)}_3 + \text{OH}^- &= \text{Al(OH)}_4^- \\
\text{Al}_2\text{O}_3 + 2\text{OH}^- + 3\text{H}_2\text{O} &= 2\text{Al(OH)}_4^- 
\end{align*}
\]

(13)  \hspace{1cm} (14)  \hspace{1cm} (15)

Besides the above principles, the abundant PCM species, \text{HPO}_4^{2-}, \text{H}_2\text{PO}_4^-, \text{PO}_4^{3-} \text{and SO}_4^{2-} anions, also make essential contributions in the generating of surface oxide layer during the aluminum dissolution process, in which the precipitation of \text{AlPO}_4, \text{H}_2\text{O} is highly likely\cite{19, 39}. The corrosion process and product property can be consequently affected by the incorporation of phosphorus through the following. Firstly, the penetration of \text{H}_2\text{O}/\text{OH}^- can be retarded by phosphates ions by means of competitive adsorption on electrode surface. Secondly, phosphorus contributes to the formation of oxide layer in the form of phosphate precipitates which in return slow down the ion mobility between electrode surface and bulk PCM significantly. Furthermore, according to Venables 1984\cite{47}, the disintegrating rate of oxide film which contains phosphorus is correspondingly dominated by the dissolution rate of phosphates, which signifies a better oxide film stability with a larger phosphorus incorporation.

Moreover, the electrons generated from overall anodic reactions will be consumed immediately by cathodic process mainly through hydrogen evolution reaction (equation (16)); especially through equation (17) when the environmental \text{pH} value is below 4\cite{48}.

\[
\begin{align*}
3\text{H}_2\text{O} + 3\text{e}^- &= 3/2 \text{H}_2 + 3\text{OH}^- \\
2\text{H}^+ + 2\text{e}^- &= \text{H}_2 
\end{align*}
\]

(16)  \hspace{1cm} (17)

3.2. Polarization measurements

Figure 3 shows the monitored OCP curves of Al-1060 exposed in molten PCM of different \text{pH} values. It is noticed that upon the exposure time the measured OCP shows a positive rising before reaching a relatively steady status in the cases of \text{pH} 4, 7, 9 and 11. However, there is no evident shift of OCP measured from \text{pH} 2 medium. Generally, the positive displacement of OCP with time is attributed to the acceleration of cathodic process or the inhibition of anodic process at the metal/solution interface\cite{49}. The former seems less possible in the present case due to the absence of necessary incorporation of alloy impurities, while the later is related to the growth of surface oxide film, which better explains the phenomenon\cite{49, 50}. Especially for the specimen immersed in moderately acidic (\text{pH} 4) and neutral medium (\text{pH} 7), the OCP commences with a rapid increase in the initial 800 s, which is likely indicative of a fast film formation on Al-1060 electrode surface. As environmental \text{pH} increasing from 2 to 11, the equilibrium OCP values show a tendency to drop from \(-0.86\) to \(-1.21\) \text{V}_{SCE}, which is similar to the aluminum behavior reported by Wysocka et al\cite{51}. This resultant negative shift of OCP with environmental \text{pH} could be attributed to the change of activation or the transformability of the aluminum oxide film due to the increment of aggressive \text{OH}^- anions, causing the dissolution of aluminum into aluminates (equations (14) and (15))\cite{52}.

Potentiodynamic polarization curves obtained for Al-1060 in the PCM medium with \text{pH} variation are displayed in figure 4. Polarization parameters are extracted from figure 4 and presented in table 2, including Tafel slopes ($\beta\alpha$, $\beta\beta$), corrosion current density ($i_{corr}$), corrosion potential ($E_{corr}$) and the average current density in current plateau region ($i_a$). $i_{corr}$ is derived by extrapolating the anodic and cathodic Tafel branches of each polarization curve to $E_{corr}$. With the decrease of environmental \text{pH}, the corrosion potential of Al-1060 ($E_{corr}$) shifts to more noble values, which is consistent with the previous OCP observation, indicating the changes of Al-1060 surface film. However, the course of each polarization curve is similar during the whole anodic process which is in reasonable agreement with the Al-1060 behavior reported previously\cite{19}.

In the initial polarization region, up to 250 mV versus $E_{corr}$, the measured anodic current density climbs exponentially as applied potential increasing. This potential range is identified as activation dissolution region in...
which the corrosion rate of Al-PCM system is dominated by the oxidation process of aluminum [51, 53]. It is noted that a large \( i_{\text{corr}} \) is observed at both pH 2 and 11 conditions, approximately four times greater than that observed at pH 4, 7 or 9, indicating the mass active aluminum dissolutions at extreme pH conditions. Above the activation dissolution region, the measured current density shows relative independence of the applied potential, exhibiting a long current plateau in the rest of measurement without any observed sharp current transient. Although all observed current plateaus look like conventional passivation behavior, the observed current density \( i_p \) at each pH condition shows a much large quantity, about two orders of magnitude greater than the normal passive current density \( (\sim 10 \, \mu A \, cm^{-2}) \) [54]. On the other hand, if aluminum were truly passivated in the PCM medium, the Nyquist response at LF observed from figure 1(a) would own a nonterminating radius. In
our case, with the applied voltages shifting to more positive, the overall aluminum dissolution process is speeded up and thus the growing of corrosion products layer on Al-1060 electrode surface is promoted. Together with the concentrated molten salts environment where free solvent molecules are relatively less, a blocking effect on the transportation of reactants at Al/PCM interface can be achieved and consequently witnessed from the independence of current densities to applied voltages. Therefore, in this observed anodic plateau region, the overall corrosion process is expected to be controlled by the diffusion rate of oxidants from reaction plane into the bulk PCM \[21, 51\]. Hence, the entire anodic branch is considered as two sub-region, i.e., initial activation controlled reaction region and the followed long diffusion controlled reaction region. It is noted that the measured \(i_p\) shows the minimum at pH 4 among all pH conditions and it tends to increase as the environmental pH changing away from 4. The lower \(i_p\) observed in moderately acidic medium, even though it is still in large quantity (0.65 mA cm\(^{-2}\)) and a surface immunity cannot be achieved, gives the hint of comparatively less electrochemical activities ongoing on at Al/PCM interface. It should be noticed that the electrochemical activities herein involve not solely metal dissolution but also oxide film formation/dissolution, since the measured current density in current plateau region is representative of overall current flow during the polarization process. Different from pH 4, 7 or 9 case, the current plateau obtained from both pH 2 and 11 cases shows a slightly upward swing along with considerable \(i_p\), which is indicative of the weakening of blocking effect to current flow against the applied electric field in highly acidic or alkaline medium, possibly ascribed to the lack of protectable surface oxides.

Moreover, the observation of released gas bubbles on the aluminium surface during polarization tests elucidated that the cathodic reaction in the Al-PCM system is partially hydrogen evolution reaction (equations (16) and (17)).

### 3.3. Surface morphology and corrosion product analysis

Optical microscopy observations of Al-1060 surfaces after dynamic polarized in PCM medium with pH variation are shown in figure 5. The surface morphologies obtained in different pH conditions exhibit pore-like features in addition to the specimen polarized in neutral medium where the Al-1060 surface is blurrered with a whitish layer which finely covers the substrate beneath. Similar surface pores on aluminum electrode have been reported by \[55\]. This structural porosity is highly related to the massive hydrogen evolved on the aluminum surface based on equations (16) and (17). During the polarization process, Al-1060 surface is positively charged. As the applied potential stepwise increasing, the interfacial charge transfer is speeded up thus giving rise to the increment of hydrogen evolution rate and facilitating the formation of hydrogen molecules on the electrode surface.
It is also noticed that with the environmental pH value shifting to highly acid (pH 2) or alkali (pH 11), some surface pores become significant in size along with recognizable boundary being featured as cavities (figures 5(a) and (e)). These discrete visible cavities are representative of acceleration of rapid aluminum dissolution, which is in the form of Al$^{3+}$ and [AlOH]$^{2+}$ in acidic medium; in the form of Al(OH)$_3$ in alkaline medium, and consequent hydrogen evolution activities on the surface, as confirmed by the EIS measurements (figures 1(a) and (b)) where evidently low values of $R_p$ are observed at pH 2 and 11 designating the readily mass transportations at Al/PCM interface. Moreover, the clear boundaries exposed along the cavity also give the hint that the attached oxide film which could serve as a physical barrier for mass transfer is extremely thin.

Microstructures of corroded Al-1060 surfaces were further characterized under SEM as shown in figure 6. Figure 6(a) displays a relatively clean Al-1060 surface with densely arranged cavities, suggesting the extensive inward penetration of ions from bulk PCM and great loss of surface oxide film at pH 2. EDS analysis confirmed the poor existence of oxides by the detection of merely 1% oxygen element while approximate 98% aluminum of surface as shown in figure 6(a). In this extreme acid medium, surface dissolutions take place in such a rapid manner as indicted earlier by the measured low $R_p$ and high $i_p$ (∼4.9 mA cm$^{-2}$) that fairly no oxide film can be existed. By contrast, as environmental pH increases from 2, aluminum dissolution process is relatively slowed down and corroded Al-1060 surfaces are observed with porous attachments, resembling the presence of surface oxides film.

In moderately acid condition (figure 6(b)), abundant pores are distributed irregularly and the whole surface is featured by rough and loose structure. Composition analysis of this porous surface reveals the existence of a relatively large percentage of oxygen (over 50%) which likely indicates the formation of aluminum oxides. The presence of 5% P gives the hint of the incorporation of phosphate deposits in the corrosion layer. The high surface corrosion resistance as well as low $i_p$ observed at pH 4 from electrochemical measurements could be explained by this extensive structural porosity with the formation of surface oxides. During the electrochemical process, anodic and cathodic reactions are always combined with each other on Al-1060 surface via competing for available reaction sites. The hydrogen molecules formed during cathodic process become easily trapped in the propagating pores and considerably accumulated in this highly pored surface structure, occupying the active reaction sites, thereby causing the plugging effect to current flow. Together with the growth of surface oxide film, the overall corrosion resistance of Al-1060 in moderately acid condition shows the improvement.

Interestingly, the Al-1060 surface polarized in neutral condition is observed with appreciable adhered whitish deposits (figure 6(c)), covering most of the neutral surface and consequently making the metal substrate being scarcely seen. Different from the observation in acidic or alkaline conditions, no surface pore could be found under such thick deposits. EDS inspection further reveals that the thick film mainly consists of O, Al, and P with the majority of oxygen (>60%). This large quantity of incorporated oxygen is indicative of active electrochemical activities and accordingly heavily oxidation of surface film which could be the explanation for the relatively high $i_p$ (∼0.98 mA cm$^{-2}$) obtained from anodic current plateau of dynamic polarization (figure 4). Likewise, thickening of the surface film could be expected during the stretching of current plateau from where the film is supposed to thicken in order to keep a constant electric field according to the measured constant current density. Although the film mentioned here is not a truly passive film, otherwise $i_p$ should maintain at micro ampere level, the origin of LF capacitance arc observed from EIS measurement convinces the...
commencement and growth of film, which serves as a physical barrier and contributes to the polarization resistance of Al-1060 at LF limits. Finely covered by this thick film, the beneath metal substrate is therefore protected from the penetration of aggressive electrolyte anions and the overall corrosion rate is slowed down.

From figure 6(d), the corroded surface morphology of specimen subjected to PCM medium at pH 9 exhibits flake-like deposits and dense-micro pores. As discussed in previous work [19], these surface discontinuities characterize the continuous aluminum/oxide dissolution in alkaline environment, mainly through equations (13)–(15). Elemental analysis of corroded surface shows that the ratio of Al to O atoms reaches over 3 in the case of pH 9 which is indicative of a weak protection of surface oxides and a large area of exposed aluminum substrate. Moreover, small amount of attached deposit was found on the surface, owning the similar morphological porosity as the surface film favored in pH 7 condition. These partially formed deposits are likely the representative of localized pH reduction around reaction site resulting from the rapidly local consumption of OH\(^-\) ions while the relative slow replenishment of them from bulk PCM. With the increment of environmental hydroxyl ions (pH 11), the specimen is convinced to suffer more severe damage as shown in figure 6(e) from which metal substrate is clear exposed with densely distributed cavities. A similarly large percentage of Al (~97%) has been detected by EDS as in the case of pH 2, suggesting the certain breakdown of oxide barrier with the large exposure and massive loss of aluminum substrate in extreme pH conditions.

It is worth mentioning that an appreciable quantity of P was detected from the deposits formed in pH 7 case, approximately two times larger than that found in pH 4 case or in pH 9 case, indicating the more successful survival of phosphates in neutral medium and their consequent contribution to the growth of a denser oxide film onto the Al-1060 surface. Furthermore, the relatively less percentage of sulphur (<1%) detected from the corroded surface indicates the less inwards penetration of SO\(_4^{2-}\) ions at oxide/PCM interface, which is consistent with Porosini’s [7] and García’s [12] observations.

The sensitivity of grazing incidence x-ray diffraction (GIXRD) for detecting crystalline layer formed in nm-range ensures the feasibility to further analyze the chemical composition of surface corrosion layer produced in various pH environments. Figure 7 shows the GIXRD results from corroded Al-1060 samples in pH 4, 7 and 9 PCM medium. The neglect of surface analysis in the case of pH 2 and 11 herein is due to the large exposure of Al substrate (>95%) and rarely existence of surface film in extreme pH conditions as revealed by EDS detection (figures 6(a) and (e)). From figure 7(a), the pattern is representative of two substances, i.e., Al and Al\((H_3PO_4)_3\)\(\cdot\)nH\(_2\)O. The absence of Al\(_2\)O\(_3\) peaks indicates that the natural alumina barrier is totally consumed in the pH 4 medium while phosphates deposits are later formed on the corroded Al-1060 surface serving as the barrier for mass transfer. Combined with the highly porous corroded surface morphology which readily gets hydrogen molecules stuck inside, the plugging effect to electron flow is therefore reached and the overall corrosion resistance of Al-1060 surface has been improved in the moderately acidic PCM medium. At neutral condition (figure 7(b)), in addition to the weak signal of aluminum substrate, the composition of surface film is mainly characterized by peaks of Al\(_2\)O\(_3\), Al\((OH)_3\), Al\((H_3PO_4)_3\)\(\cdot\)nH\(_2\)O and Al\(_2\)(SO\(_4)_3\)\(\cdot\)nH\(_2\)O. The presence of alumina accompanying multiple salt precipitations reveals the duplex property of surface film where a compact
featureless Al₂O₃ layer is expected at the inner part while the thick porous surface coverage, clearly shown from SEM (figure 6), acts as the outer film arising from the formation and accumulation of salt precipitations including Al(OH)₃, Al(HₙPO₄)ₙ·nH₂O and Al₃(SO₄)₃·nH₂O. The observed alumina could be related to the less aggressiveness of PCM species to Al-1060 surface at neutral environment, resulting in the partially conservation of this nature surface oxide. Another possibility for the occurrence of alumina film could be ascribed to the inward migration and dissociation of hydroxyl ion into protons and O²⁻ during the hydration processing of outer film [56]. By the substitution of OH⁻ ions, O²⁻ ions potentially rest in the oxide lattices, thus the growth of the pure alumina film could be achieved. It can be noticed from the thick oxide layer and diversity of corrosion products that neutral environment is relatively friendly to the Al-1060 surface and instead of direct loss of aluminum into the bulk PCM most of the Al element survive in the form of salt precipitations which serve as a physical barrier and contribute to hinder the further surface dissolution.

At pH 9 (figure 7(c)), except Al substrate, the detected composition of corroded surface mainly comprised of Al(OH)₃, Al(HₙPO₄)ₙ·nH₂O and Al₃(SO₄)₃·nH₂O, which is similar to those salt precipitations found at pH 7. However, no Al₂O₃ has been detected on the surface. The absence of Al₂O₃ suggests the completely destroy of this inner compact nature oxide film in the PCM medium under OH⁻ penetrating. As the result of rapid aluminum dissolution, heavy hydration is throughout the film thickness leading to the local departure of barrier layer and hence a low corrosion resistance is reflected from the impedance diagram at pH 9.

4. Conclusions

The corrosion property of Al-1060 in composite PCM melts of Na₂HPO₄·12H₂O - Na₂SO₄·10H₂O was investigated electrochemically with surface analysis. Results reveal that the corrosion property of the studied PCM is highly related with pH and the following conclusions are drawn:

1. A concentration difference layer is formed between the Al-1060 surface and PCM melts attributed to the adsorption effect of PCM species, i.e., phosphate and sulfate ions, and the formation of surface oxides.

2. As the environmental pH shifts away from neutral (pH 7), the anodic dissolution of Al-1060 in PCM medium speeds up, the exposure area of aluminum substrate is increased and the overall corrosion resistance of Al-1060 is reduced.

3. The anodic current plateau observed from DC polarization is ascribed to the presence of surface oxide film and plugging effect of hydrogen molecules inside surface pores.

4. The oxide film is featured as the thickest and most compact at neutral condition mainly consisting of Al₂O₃, Al(OH)₃, Al(HₙPO₄)ₙ·nH₂O and Al₃(SO₄)₃·nH₂O which serves as a physical barrier, retards the interfacial mass transfer and hinders the further Al-1060 dissolution in the PCM.

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