



# Aluminum corrosion mitigation in alkaline electrolytes containing hybrid inorganic/organic inhibitor system for power sources applications



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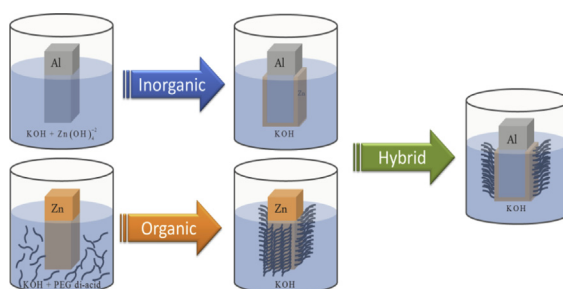
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## HIGHLIGHTS

- Hybrid ZnO/PEG di-acid inhibitor for Al alkaline power sources was developed.
- Al corrosion rate reduced by more than one order of magnitude.
- Al corrosion inhibition occurs due to mitigation of the cathodic reaction.
- The formed protective layer is being regenerated during rest periods.
- The hybrid inhibitor markedly increases the Al-air battery discharge capacity.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The severe corrosion accompanied with hydrogen evolution process is the main obstacle preventing the implementation of Al as an anode in alkaline batteries. It impairs the functionality of alkaline battery, due to a drastic capacity loss and a short shelf life. The possibility to reduce Al corrosion rate in alkaline solution with the use of hybrid organic/inorganic inhibitor based on poly (ethylene glycol) di-acid (PEG di-acid) and zinc oxide (ZnO) was examined in this work. A correlation between an Al corrosion rates and the concentrations of both PEG di-acid and ZnO in alkaline is shown. Selecting 5000 ppm PEG di-acid and 16 gr/l ZnO provides substantial corrosion protection of Al, reducing the corrosion rate in a strong alkaline solution by more than one order of magnitude. Moreover, utilizing the same formulation results in increase in Al-air battery discharge capacity, from 44.5 (for a battery utilizing only KOH in the electrolyte) to 70 mAh/cm<sup>2</sup> (for a battery utilizing ZnO/PEG di-acid hybrid inhibitor in the electrolyte). The morphology and composition of the Al electrode surface (studied by SEM, EDS, and XRD) depend on PEG di-acid and ZnO concentrations.

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## 1. Introduction

Aluminum (Al) is the most abundant metal in the earth crust [1,2]. Due to its physical and chemical properties, Al is considered as a highly attractive energy source. Low atomic weight (28.98 gr/mol) and tri-valence oxidation of Al yields a low gram-equivalent weight

(8.99) and ultra-high specific gravimetric capacity (2.89 Ah/g). Only lithium have slightly higher electrochemical equivalent of (3.86 Ah/g), while the theoretical specific volumetric capacity of Al is the highest amongst metallic fuels (8.04 Ah/cm<sup>3</sup>) [3]. These advantages, as well as the low price per energy unit increase the attractiveness of Al as an anode material in battery systems, and more specifically, in alkaline metal–air batteries [3–8].

The major obstacle of applying Al in alkaline based batteries lies in its high corrosion rate in the electrolyte (Fig. 1Sa and Video 1S) [2,3,9–17]. Furthermore, Al corrosion in alkaline solution is accompanied by high rate hydrogen evolution, which may result in battery electrolyte leakage [11]. These aforementioned phenomena significantly reduce Al alkaline battery capacity and its shelf life [3,18–20]. Two approaches have been suggested to reduce Al corrosion rate in alkaline: the first was substitution of pure Al with Al alloys and the second, focused on corrosion inhibition.

Supplementary video related to this article can be found at <http://dx.doi.org/10.1016/j.jpowsour.2015.03.048>.

Numerous researchers studied the effect of various alloying elements, such as Mg, Zn, Pb, Sn, Ga, In, Mn, Ti, Bi, Te, Hg, Tl, etc. on Al corrosion rate in alkaline solutions [2,9,11,18,21–34]. They mainly focused on binary alloys, although ternary and quaternary alloys were studied, as well. However, despite a large body of research, this approach was not proven successful. Inhibition protection of Al anode in alkaline solutions has been also the objective of much research. Zinc oxide (ZnO) was discovered as one of the most effective Al corrosion inhibitors in alkaline solutions. It was shown by Zaromb for pristine and amalgamated Al (99.5 wt.%) more than 50 years ago [35]. It was also shown that ZnO reduces Al corrosion rate, while it does not affect the anodic characteristic (current density and over-potential) of Al [35]. Much weaker inhibition effect than ZnO was established with polyaniline [36], methanol [37], hydroxytryptamine [38] dimethyl amine epoxy propane [39] and sodium silicate [40]. It was also reported that the protection effect of these inhibitors might be improved by the addition of haloid ions to the alkaline solution [41].

While ZnO is considered as the most potent Al corrosion inhibitor, its sole implementation does not reduce the Al corrosion rate in alkaline solutions to the desired level (allowing Al usage as an anode in alkaline batteries). In order to improve ZnO inhibition effect, Wang et al. studied the combined effect of ZnO and polyethylene glycol (PEG) in a 4 M KOH on Al corrosion [42]. The unmodified PEG was already being used as a Zn corrosion inhibitor in alkaline batteries [43–48]. Albeit, the application results were insufficient, as surface evaluation of the Al electrode after OCP (open circuit potential) exposure did not reveal the presence of a protective zinc layer over the electrode surface. While comparing the inhibition properties of PEG and PEG di-acid [ $\alpha,\omega$ -Bis(2-carboxymethyl)polyethylene glycol] we concluded that PEG di-acid is a superior inhibitor and one of the most efficient corrosion inhibitor for Zn corrosion in a strong alkaline solutions [43–47]. It was suggested that PEG di-acid efficiently binds to ZnO surface (covering the zinc surface in the alkaline media) via the carboxylic acid end groups [43,44].

In this work, we report on a substantial reduction in Al corrosion rate in alkaline electrolytes. These results were obtained by a successful application of both ZnO – PEG di acid hybrid inhibition system in KOH solutions (Fig. 1Sb). A suggested model calls for the electrodeless deposition of metallic Zn on the aluminum surface and a subsequent protection of the deposited zinc layer by adsorbed PEG di-acid linked to the formed ZnO (covering the metallic zinc). We report here on Al surface characterization in the presence of PEG di-acid/ZnO hybrid composition in a strong alkaline solution and the effect of this hybrid inhibitor composition on Al–air batteries discharge.

## 2. Experimental

### 2.1. Materials and chemicals

The electrolytes used in this study were 5 M KOH additive-free, as a based solution and, the same alkaline based solution containing ZnO (Merck) and  $\alpha,\omega$ -Bis(2-carboxymethyl)polyethylene glycol (PEG di-acid, Sigma–Aldrich, molecular weight of 600 gr/mol) as additives. The 5 M KOH solution was prepared by dissolving KOH flakes (Bio-Lab Ltd.) in deionizer water (DI, 18.2 M $\Omega$ cm, Millipore System). The concentrations of ZnO in the 5 M KOH solutions were 1, 5 and 16 g/l, while PEG di-acid concentrations were varied between 10 and 5000 ppm (10, 100, 1000 and 5000 ppm). PEG di-acid was introduced in the appropriate volumes into the KOH–ZnO alkaline solutions from a “mother solution” containing 5% of PEG di-acid dissolved in DI water, achieving the desired inhibitor concentration in the solution.

Specimens for corrosion and electrochemical measurements were cut from aluminum alloy (99.7 wt.%) into a cuboid shapes with a surface area of 3 cm<sup>2</sup>. Prior to the electrochemical and corrosion experiments, the Al electrode surfaces were freshly wet-abraded to a 2400 grit finish, degreased with ethyl alcohol, rinsed with DI water and air dried. Chemical composition of the Al alloy is shown in Table 1.

### 2.2. Electrochemical methods

Electrochemical measurements were performed at a temperature of 25  $\pm$  1 °C with a potentiostat/galvanostat VersaStat (EG&G) in a polypropylene (100 ml) three-electrode electrochemical cell equipped with a working electrode (Al), a reference saturated calomel electrode (SCE) and, a Pt-wire counter electrode. The reference electrode was connected to the solution through a *Luggin–Haber* capillary tip assembly. All potentials presented in the text are given versus SCE. Different electrochemical techniques, such as OCP exposure, potentiodynamic, galvanostatic and linear polarizations were applied in this study. Polarization was applied either upon immersion of the Al specimen (working electrode) into the solutions (additive-free and with ZnO and PEG di-acid), or after a given time period of OCP exposure.

### 2.3. X-ray and surface examination

Aluminum surface structure evaluation was conducted subsequent to a given time (1, 5, 15 and 60 min) of OCP exposure in the electrolytes. Surface studies included X-ray diffraction (Rikagu MiniFlex X-Ray Diffractometer in the Bragg–Brentano geometry), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) (FEI Quanta 200 equipped with EDAX, Oxford Inst.). Cross-sectional evaluation samples were prepared by a dual-beam FIB (focused ion beam) Strata 400 s (FEI) equipped with a field emission gun (FEG) electron source (operated at 30 kV), a Ga<sup>+</sup> ion beam (2–30 kV). The accelerating voltage and current of the incident e-beam was maintained at 10 kV and 2.1 nA, respectively. An incident ion beam accelerating voltage of 30 kV, with current ranging from 21 to 0.46 nA was used during the initial milling. Before preparing the cross sections, the surface of the sample was coated with Pt in the FIB, first by e-beam deposition (10 kV, 2.1 nA)

**Table 1**  
Aluminum anode composition.

Element	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ni	Al
%wt.	0.037	0.26	0.002	0.002	0.007	0.000	0.001	0.005	99.7

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