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COMPETING ELECTROCHEMICAL AND CHEMICAL DISSOLUTION OF ALUMINUM IN PHOTOPOLYMERIZED ACRYLIC HYDROGELS

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ABSTRACT. Dissolution of aluminum in acrylic hydrogels was studied in printed ultra-thin galvanic cells, in open circuit potential, when only chemical corrosion occurred, and in the presence of external current flow, when the aluminium anode was electrochemically dissolved. By the appropriate design of the Al/hydrogel interface we were able to control the rate of electrochemical dissolution, a process driven by the applied voltage (upon short-circuiting the galvanic cell), and to avoid spontaneous chemical dissolution (and thus, maximizing the shelf life of devices in the absence of current flow). Aluminum anodes (thickness of 30-90 nm) were used in conjunction with a graphite or MnO_2 cathode. Photopolymerized acrylic gels with incorporated inorganic or quaternary ammonium salts served as the supporting electrolyte. The appearance of the first localized chemical damage of the surface defined the shelf life of the cell, and typically was on the order of days. The choice of anion and cation incorporated in the hydrogel affected both the electrochemical and chemical dissolution of aluminum.

Keywords: aluminum dissolution, aluminum anode, acrylic hydrogel, ultra thin galvanic cell, electrochemistry of aluminum.

INTRODUCTION

Over the past decade the organic electrochemistry of aluminum, an intermediately reactive metal, has developed dynamically [1-15]. Studies on the anodic behavior of Al in organic solutions with different electrolytic salts [1-9] and in ionic liquids [10, 11], respectively, were triggered by the use of Al as current collector in Li^+-ion batteries and the need for attenuating the corrosion of Al in such galvanic cells. By contrast, Yu et al. [2] and Licht et al. [12-14] studied galvanic cells equipped with Al anodes, attempting to increase the electrochemical activity of Al in organic media. Given that Al is electrochemically

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passive in most organic electrolytes, specific solution phase activators (e.g., dissolved Hg, In, Ga, Sn, or Bi salts) are required [12]. Other research addressed Al corrosion in non-aqueous and mixed aqueous-organic media [15].

In this paper we investigate the behavior of Al in hydrogel media. We report data on the chemical and electrochemical dissolution of Al in ultrathin galvanic cells, in which the supporting electrolyte is either an inorganic or a quaternary ammonium salt, incorporated in a gel type polymer. Gels are obtained by photopolymerizing mixtures with one or two acrylic-type monomers, with water present in the system (hydrogels). We examine the dissolution rate of Al, when an external short is applied to the galvanic cell, and we are able to prevent (or minimize) the dissolution of Al in the open circuit mode. To the best of the authors' knowledge this is the first account on the electrochemical behavior of aluminum in a hydrogel system.

Presence of the thin, highly adherent native aluminum oxide layer prevents Al dissolution in many environments [16]. Chemical dissolution of Al is noticed when microscopic perforations of the natural protective oxide layer allow for the localized damage of the metal surface. For our purposes, the first localized dissolution of Al defines the *shelf life* of the cell; in the examined systems it typically is on the order of days. Electrochemical dissolution, as opposed to chemical dissolution, occurs only upon short-circuiting the galvanic cell; this causes the perforation of the protective oxide layer, and, hence, the flow of an external current.

Ellipsometry performed on 30-90 nm Al films revealed a variable thickness of the natural oxide layer over the surface, in the range of 1.8-24.8 nm, values in agreement with the average thickness of the oxide film reported in the literature [17].

Several components of the gel electrolyte in contact with the Al surface affect the rate of its electrochemical and chemical dissolution: the identity of the anion and cation present in the gel, the degree of cross-linking, the polymerization time, and the storage conditions. Therefore, we discuss these effects in detail.

RESULTS AND DISCUSSION

Choice of the supporting electrolyte

For the proper selection of the supporting electrolyte we considered: (i) the solubility of the salt in one particular photopolymerizable mixture (inorganic salts were incorporated in the hydrogels), (ii) total ionic strength in the hydrogel (the higher the ionic strength, the better the electrochemical activity); and (iii) reactivity of the anion (Cl^- ions attacked Al, while phosphates and tetraborate protected the metal) [18]. As revealed by gravimetric data (Table 1), the identity of the anion in the hydrogel affected significantly the rate of both the electrochemical and chemical dissolution of aluminum.

In the halide series (each at the same concentration) we found that: I^- inhibited the polymerization (as irradiation likely generated free iodine atoms) [19]; with F^- both chemical and electrochemical dissolutions proceeded very slowly (i.e., galvanic cells with F^- had extended shelf life, and the electrochemical dissolution rate was approximately the same as the chemical dissolution rate); with Cl^- present in the gel, the lifetime of galvanic cell decreased five fold as compared to Br^-; surprisingly, the electrochemical dissolution with Br^- was just slightly slower than with Cl^- (less by only 20%). Chloride ion is the main environmental factor, which accelerates pit initiation [20], which accounts for the much greater chemical dissolution rate in the presence of Cl^-.

Table 1: Effect of anions and cations present in the hydrogel on the dissolution rate of Al (data recorded in the two-electrode ultrathin system)

Salt Concentration	**Investigated Ion**	**Electrochemical Dissolution Rate** [μg cm^{-2} s^{-1}]	**Chemical Dissolution Rate** [μg cm^{-2} s^{-1}]
Potassium halides (0.88 *M*)	F^-	3.10×10^{-2}	3.10×10^{-2}
	Cl^-	27.9	1.57×10^{-2}
	Br^-	23.2	3.36×10^{-3}
	I^-	Interfered with the polymerization	
Other potassium salts (0.44 *M*)	NO_3^-, ClO_3^-, SO_4^{2-}, $H_2PO_4^-$, HPO_4^{-2}, PO_4^{3-}, $B_4O_7^{2-}$	$5 \times 10^{-5} - 2 \times 10^{-3}$	$< 10^{-5}$
Chlorides (0.48 *M*	Li^+, Na^+, K^+, Rb^+, Cs^+	17.6 ± 2.4	$(1.42 \pm 0.04) \times 10^{-2}$

Polyatomic anions, such as NO_3^-, ClO_4^-, HPO_4^{2-}, $H_2PO_4^-$, PO_4^{3-}, and $B_4O_7^{2-}$ were virtually inert; they did not sustain either chemical or electrochemical dissolution (in each experiment the cation was K^+). Current density, recorded upon short-circuiting the ultrathin galvanic cells, corresponds to the electrochemical dissolution rate of Al. Current delivered by the system over time, with various anions in the hydrogel, is displayed in Figure 1a. Nitrate was the least active, yielding maximum current values of less than 10 μA, which lasted just for a few seconds, the current decaying fast after ca. 10 s. While HPO_4^{2-} and PO_4^{3-} showed 7-9 fold greater initial currents than NO_3^-, they were still unable to sustain a constant current, which would correspond to a uniform dissolution rate of Al. Hence, polyatomic anions are not useful in the supporting electrolyte (despite the corrosion inhibiting properties of several of them, which would defer chemical dissolution of Al). When fast electrochemical dissolution is desired, Br^- exhibits the most favorable properties (Table 1): its electrochemical activity is close to that of Cl^- (only 17% less), and in the meanwhile it allows for an extended shelf life of the device (4.7 times longer than in the presence of Cl^-).

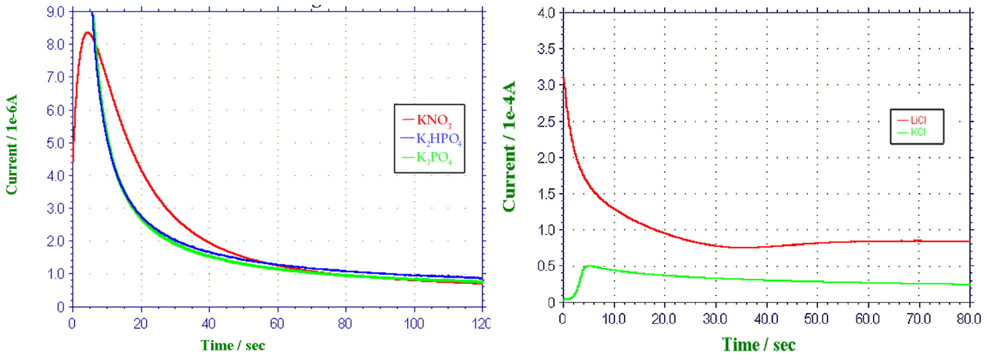

Figure 1. (**a**) Effect of anions on the electrochemical dissolution of Al in acrylic acid/ acrylonitrile copolymers: comparison of NO_3^-, HPO_4^{2-}, and PO_4^{3-}; (**b**) Cation effect on the electrochemical dissolution of Al: comparison of Li^+ (top curve) and K^+ (bottom curve). All experiments were performed with ultra thin galvanic cells (displayed schematically in Figure 3).

When comparing cations immediately after short-circuiting the device, Li^+ showed greater electrochemical dissolution rate than K^+ (Figure 1b), while Na^+ was approximately 40% less active (not shown). Over the long term (200 h) the average dissolution rate became identical for Li^+ and K^+: 102 ng h^{-1}. With CsCl incorporated in the hydrogel, an initial current of 60 μA was recorded over 300 s (a value intermediate between Li^+ and K^+), and then it dropped fast to 10 μA, within 100 s to (graph not shown). Multivalent cations were not useful, as they affected the texture of the hydrogel. Slow chemical dissolution is desirable; therefore, from the cations in Table 1, K^+ is the best choice. However, when fast electrochemical dissolution is attempted, Li^+ salts are the most efficient.

From these studies, best cations were K^+ (for slow electrochemical dissolution) and Li^+ (for fast electrochemical dissolution). When combined with bromide (the most convenient anion), they provided the best salts for being used in hydrogels.

In order to determine the optimal concentration of the supporting electrolyte, we tested the activity of hydrogels, which contained increasing salt concentrations. Electrochemical dissolution rate of Al increased with increasing KCl or KBr content up to 5.5-6.4 wt.%, and then it diminished, probably due to ion pairing. Ion pairs are poor charge carriers, as they do not possess a net charge and stay solvated. Therefore, the conductivity of the hydrogels decreased, and the corrosion current depleted. At high salt concentrations (9.3-11.6 wt.%) charged triplets were formed, and the current increased, again. Unlike ion pairs, triple ions do possess a net charge, and can act as charge carriers. Similar behavior of electrolytes is known in solvents with low dielectric constant [21]. Hence 5.5-6.0 wt.% represents the optimal concentration of the salt in the hydrogel.

These studies on ion effects revealed that while the chemical dissolution rate primarily depends on the adsorption of active anions and the destruction of the natural protective Al_2O_3 layer [22], the electrochemical dissolution is affected by the radius and mobility of the anions. Consequently, the viscosity of the hydrogel and thickness of the hydrogel layer influence to a considerable extent the electrochemical process. In most cases, it has proven an extremely difficult task to identify a system in which electrochemical dissolution can be driven efficiently, while keeping an extended shelf life of the battery via inhibiting spontaneous chemical dissolution.

Selection of monomers and setting the pH of the hydrogel

When keeping the supporting electrolyte concentration constant in the polymer (6.0 wt. %), the corrosion of Al matrices was 10 fold faster in poly(acryloyloxyethyl trimethylammonium chloride), which contains bound charged groups, as compared to acrylic acid/acrylonitrile copolymers, which becomes an ionic conductor via adding a salt to the gel. The looser texture and higher water content of the former hydrogel may allow for an easier migration of the ions, securing by this a better conductivity of the polymer matrix. As a general rule, the recorded current density decreased with decreasing water content of the hydrogel, its lowest value of 5 $\mu A\ cm^{-2}$ being observed in the absence of water. We addressed the effect of water content on the polymer matrix in an earlier paper [23].

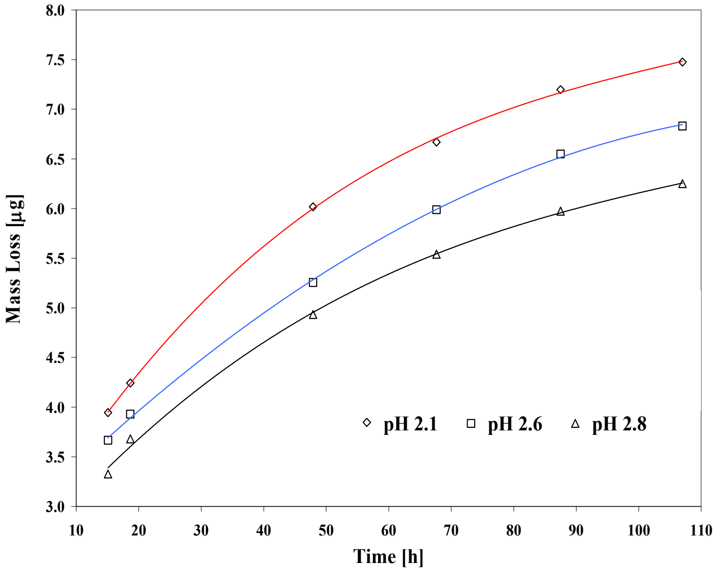

Figure 2. Electrochemical dissolution (mass loss) of Al over time at acidic pH values: bottom line – pH 2.1, middle line – pH 2.6, top line – pH 2.8.

Mass loss of Al over time in contact with hydrogels of decreasing pH value is shown in Figure 2. As the hydrogel becomes more acidic, the system is moved away from the passivity zone of Al (pH 4.0-8.6, according to the Pourbaix diagram [24]). Thus, the electrochemical activity of Al is enhanced and the corrosion rate increases; the average corrosion rate is 38.7 ng h^{-1} at pH 2.8, 40.1 ng h^{-1} at pH 2.6, and 48.6 ng h^{-1} at pH 2.1. Acidic pH values below pH 3.8 are favorable for fast electrochemical dissolution [24]. By setting the pH value we were able to fine-tune the rate of the dissolution process.

CONCLUSIONS

The use of supporting electrolytes incorporated in UV-cured acrylic-type gels allowed for a new approach toward the organic electrochemistry of aluminum. In addition to the chemical identities of the anion and cation, and the selection of the monomer, water content and the pH value of the hydrogel have proven critical to controlling the electrochemical activity of aluminum. Aluminum anodes were active in ultrathin galvanic cells with gel type electrolytes. Driving the electrochemical dissolution, while inhibiting or delaying spontaneous chemical dissolution appears to be an extremely demanding task.

EXPERIMENTAL SECTION

Materials. Gel-type electrolytes were prepared according to previously reported procedures [25, 26]. Typically, hydrogels contained 30-50 wt.% of water and an inorganic salt, such as alkali halides: LiCl, NaCl, RbCl, and CsCl (99+% each, Aldrich), and KCl (Spectro pure, SPEX Industries, Inc.). Several other salts were tested: Na^+ and K^+ chlorates, bromides, nitrates, sulfates, phosphates, hydrogenphosphates, and dihydrogenphosphates (all from Aldrich). For preventing the formation of Al/O_2 batteries, prior to polymerization the curable mixture was degassed with Ar for 15 min [23].

Electrochemical measurements. Electrochemical measurements were conducted with screen-printed ultra thin galvanic cells (Wisconsin Labels Associates, Peachtree City, GA), equipped with Al anode (surface area of 0.20-0.75 cm^2 and thickness of 30-90 nm). Ultrathin galvanic cells operate with Al anode and MnO_2 or graphite cathode; the hydrogel serving as the ionic conductor, is sandwiched between the electrodes (Figure 3). Model 660a Electrochemical Workstation (CH Instruments, Austin, TX) was utilized, measurements being performed under a Faraday cage, at 298.2 ± 0.1 K, thermostated with a Model RTE-210 thermostat (Neslab Instruments, Inc., Newington, NH).

Surface examination. The thickness of the natural protecting Al_2O_3 layer on the surface of Al thin films was determined by ellipsometry with a Model Compel ELC-10 ellipsometer (InomTech Products, Inc., West Hartford, CT), data processing being performed by means of the software supplied by the manufacturer. Microscopic perforations of the natural protective oxide layer on Al were observed with a stereo magnifier (Bausch & Lomb, magnification 10) and a stereo microscope (Fisher Micromaster®, magnification 400). The thin cell design included a red-colored substrate beneath the thin Al layer to facilitate detection of localized perforations.

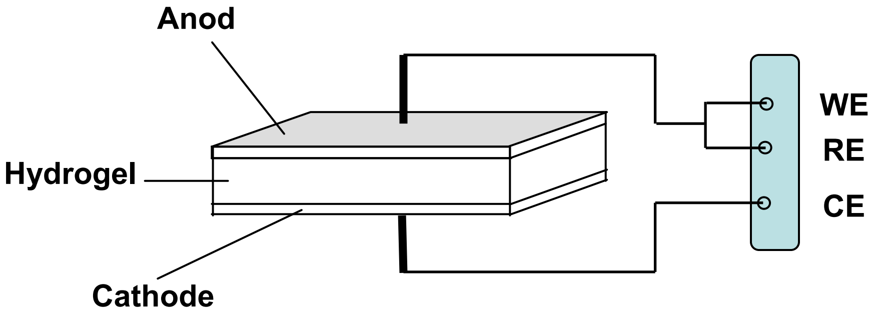

Figure 3. Schematics of the ultra thin galvanic cell setups used for testing of Al in hydrogel electrolytes (Anode: metallic Al; Cathode: graphite or MnO_2; Hydrogel: acrylic polymer; WE – working, RE – reference, and CE – counter electrodes)

Gravimetric method. Dissolution of Al was monitored by gravimetric method, i.e., the weight loss over time of the ultrathin galvanic cell.

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