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Pulsed aluminum battery

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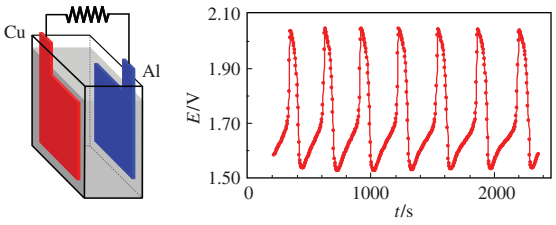
Pulsed aluminum batteries were developed in the course of ongoing research in technomimetics. They can amplify external electrical trigger signals, leading to potential applications as components of electrochemical computing systems and self-powered sensors. Periodic changes in the modified surface film on aluminum electrodes likely play a critical role in pulsing and trigger amplification of aluminum batteries.



Keywords: aluminum battery, trigger, amplifier, layered double hydroxide.

Dedicated to the memory of Nikolay S. Zefirov (1935–2017) whose relentless curiosity inspired the research beyond ordinary.

Aluminum is an attractive anode material for electrochemical devices.[1] This ubiquitous industrial metal has a gravimetric energy density approaching 70% that of lithium, and a favorable environmental profile.[2,3] A new approach in the technology of specialty aluminum batteries entails construction of pulsed electrochemical systems.[4] Digitally controlled pulsed devices currently dominate modern electronics due to their high efficiency (above 90%) and precise power output control in pulse frequency modulation and pulse width modulation modes.[5] Although direct application of the principles of pulsed electronics for electrochemical devices is a difficult task,[6] it can be accomplished by employing electrochemical systems operating in the deep non-equilibrium regime.[7,8]

Numerous experiments with various types of aluminum batteries have shown that some of them are capable to operate in a stable pulsed mode. For feasibility studies, we selected alkaline aluminum batteries with complex electrolytes containing small amounts of lithium salts as pulse inducers and stabilizers in hypochlorite catholyte, and electrocatalytic[9] copper cathodes. These pulsed aluminum batteries have simple experimental design† and high theoretical voltage[11] (Scheme 1) along with good stability of the pulsed mode.

$$2\,Al + 8\,OH^- \rightarrow 2\,Al(OH)_4^- + 6\,e^- \quad \text{(anode; } E^0 = 2.34\text{ V)}$$

$$3\,OCl^- + 6\,e^- + 3\,H_2O \rightarrow 3\,Cl^- + 6\,OH^- \quad \text{(cathode; } E^0 = 0.81\text{ V)}$$

$$2\,Al + 3\,OCl^- + 3\,H_2O + 2\,OH^- \rightarrow 2\,Al(OH)_4^- + 3\,Cl^- \quad \text{(overall; } E^0 = 3.15\text{ V)}$$

Scheme 1 Electrochemical reactions in alkaline hypochlorite aluminum batteries.

Pulsed alkaline hypochlorite aluminum batteries with above mentioned design are capable of spontaneous transition from continuous to pulsed mode after a short induction period (Figure 1). The highest peak voltages in these batteries are in the range of 2.0–2.2 V, which is typical for traditional alkaline hypochlorite aluminum batteries.[11,12]

One of the distinctive features of these pulsed aluminum batteries is relatively low oscillation frequency, which is in the single-digit mHz range at ambient temperatures. In this respect, the closest analog of pulsed aluminum batteries is iron/sulfuric acid electrochemical system with oscillations in this frequency range.[13] As expected, the shape and frequency of pulsed oscillations are affected by the electrolyte composition, temperature, and other environmental variables. Higher concentrations of the base (NaOH) lead to wider pulses, whereas

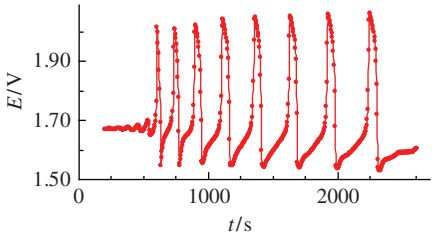


Figure 1 An electric output of the pulsed aluminum battery in transition from continuous to pulse mode.

† All experiments were performed in standard electrochemical cells equipped with 7×20 mm aluminum anodes (0.2 mm thickness) and 30×80 mm copper cathodes (0.3 mm thickness). The complex electrolyte was prepared from 50 ml of commercial sodium hypochlorite solution (1.1 M of sodium hypochlorite), 0.43 g of lithium chloride (0.2 M electrolyte concentration, unless otherwise specified), and 2.0 g of sodium hydroxide. Concentrations of sodium hypochlorite in commercial hypochlorite solutions were monitored by UV-VIS spectroscopy (λ_{max} = 293 nm, ε = 360 dm^3 mol^{-1} cm^{-1})[10] in 0.1 N NaOH. The electrodes were fully immersed in the electrolyte, and the air-exposed conductor parts as well as opposite sides of the electrodes were covered by a protective adhesive tape. The 3.3 kΩ load resistors were used in all experiments. The temperature of the electrolyte was measured by a thermocouple thermometer and maintained within the 18–21 °C range. The stability of electric potential of the copper cathode (+0.63 ± 0.05 V *vs.* Ag/AgCl) was periodically checked using a reference Ag/AgCl electrode.

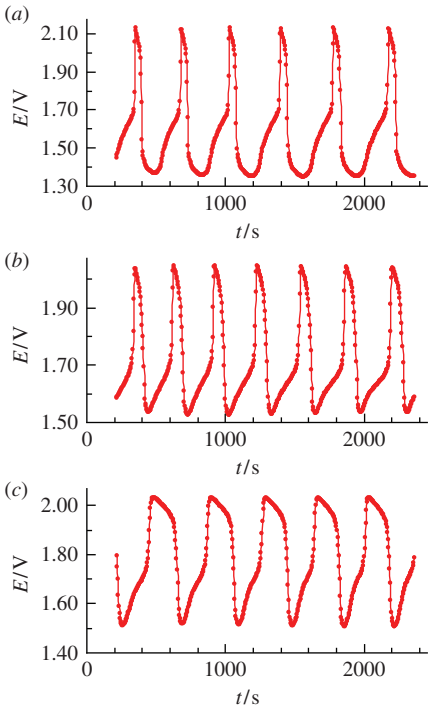


Figure 2 Various pulse curves produced by pulsed aluminum batteries: (*a*) 0.2 M LiCl at 20 °C; (*b*) 0.15 M LiCl at 21 °C; (*c*) 0.1 M LiCl at 19 °C.

higher concentrations of the oscillation inducer and stabilizer (LiCl) give the opposite effect. Decreasing temperature reduces pulsing frequency. Some typical pulse curves are presented in Figure 2.

Coherence[13] (also called global coupling)[14] of electrochemical processes leading to pulsed behavior is of paramount importance for pulsed electrochemical systems. Essentially, the observed periodicity requires that the whole electrode should be in-phase during the oscillatory transformations, and some form of phase information transfer should exist between the different areas of the electrode.[13] The simplest way to establish the nature of this phase information transfer is to create a physical barrier separating two areas of the electrode, or to investigate the behavior of two identical metal electrodes immersed with spatial separation in the electrolyte mixture. In the abovementioned iron/sulfuric acid system,[13] the physical barrier separation results in emergence of two independent oscillators leading to an unequivocal conclusion that in this case the phase information is being transmitted *via* electrolyte.

Pulsed aluminum electrochemical systems presented here behave differently. Physical barrier separation of two areas of an aluminum electrode does not produce any notable effect on the pulse sequence, and this divided electrode shows the same oscillatory pattern as the non-divided one. The same is true for batteries with two separate aluminum electrodes in close proximity to each other with direct electric connection. Removal of the electric connection turns them into two independent oscillators with no phase correlation between the pulse sequences. These experiments demonstrate that the pulse phase information in aluminum anodes is being transmitted *via* electric connections between the different areas of the electrode.

Perhaps the most interesting feature of the pulsed aluminum batteries is their capability of pulse triggering by applying external stimuli. Such external stimuli can be addition of small amounts of a catalyst (*e.g.*, $KMnO_4$), or, more conveniently, application of a short electric pulse with the proper polarity above the certain voltage threshold. In the latter case, power amplification of the trigger signal is possible (Figure 3). However, the power amplification coefficient is only in the high

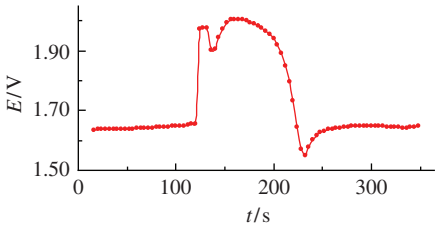


Figure 3 Trigger response in the pulsed aluminum battery with the alkaline hypochlorite electrolyte containing 0.15 M LiCl at 19 °C. The response was triggered by a short (10 s) external pulse (1.97 V) at the 120 s time point.

single-digit range, which is relatively low compared to modern semiconductor devices. In addition, there is a notable delay between the incoming trigger signal pulse and the amplified response pulse, which somewhat limits the utility of these systems for trigger signal amplification. Nevertheless, the big advantage of electrochemical pulse amplifiers is their autonomous nature, since they do not require any external power sources to operate.

External triggering of electric pulses in pulsed aluminum batteries allows a facile control of an electric output in pulse frequency modulation mode (Figure 4). These devices also demonstrate good tolerance to minor impurities and retain adequate functional stability with anodes constructed from recycled aluminum of at least 95% purity. The quantitative computer modeling of pulsed aluminum batteries can be done within van der Poy's relaxation oscillator theoretical framework.[15]

The exact mechanism of the observed spontaneous and triggered pulse behavior of aluminum batteries is not fully understood at this time. The required presence of lithium salts in the electrolyte lends some credence to a hypothesis that this phenomenon is related to the formation of surface-modifying film of lithium aluminum layered double hydroxide (LDH). This compound is produced during dissolution of aluminum in alkaline solutions containing lithium salts.[16] LDH has a layered structure, with lithium cations embedded in holes of gibbsite-type aluminum hydroxide layers and charge-compensated by counter-anions between the aluminum hydroxide framework layers (Figure 5).[17] These counter-anions are only loosely

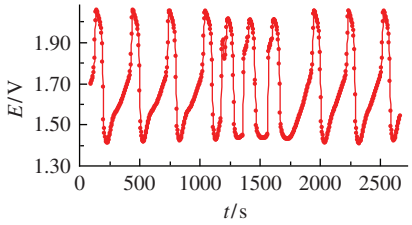


Figure 4 Pulse frequency modulation in the pulsed aluminum battery at 21 °C. The three middle voltage peaks were triggered by applying short (10 s) external electric pulses (1.85 V).

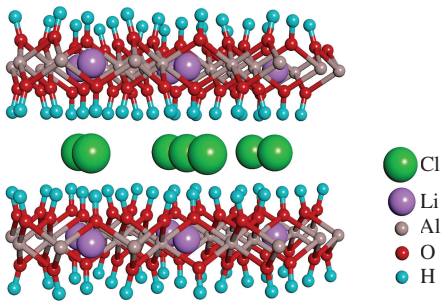


Figure 5 The X-ray structure of lithium aluminum layered double hydroxide $LiAl_2(OH)_6Cl$.

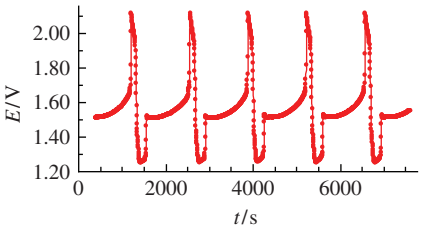


Figure 6 Pulse curves produced by the pulsed aluminum battery with the 0.2% Cu–Al alloy electrode at 18 °C.

connected with the rigid aluminum hydroxide nanosheet framework, and can be easily interchanged with various anions in the electrolyte.[18] To some extent, similar exchange may occur between the lithium cations in the aluminum hydroxide layers and other cations present in the electrolyte.[19] The compositional and structural[20] changes within the LDH surface film affected by the electrode potential are likely the cause of observed oscillatory processes in pulsed aluminum batteries. This hypothesis is further confirmed by an observation that the established oscillations continue in a fresh alkaline electrolyte without lithium salts, albeit for a relatively short period of time.

The complexity of electrochemical processes in pulsed aluminum batteries is underscored by the observation that small (<1%) amounts of manganese and iron metals in aluminum electrodes provide substantial stabilizing effect on the pulsed regime. It is also notable that small amounts of cooper (<0.5%) significantly alter the pulse shape and frequency (Figure 6).

In summary, this research demonstrates a feasibility of pulsed aluminum batteries capable of trigger signal amplification and digital electric output control in pulse frequency modulation mode. Potential applications of these devices include components of autonomous electrochemical computing system and sensors. Although the exact mechanism of spontaneous oscillations and trigger signal amplification in pulsed aluminum batteries remains not fully understood at this time, the periodic compositional and structural changes of the surface-modifying film of lithium aluminum layered double hydroxide likely play a critical role in these processes.

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