

Received:
9 June 2017

Revised:
12 July 2017

Accepted:
19 July 2017

Cite as: Zhiyuan Zhu,
Kequan Xia, Zhiwei Xu.
Triggered degradation of 250
μm-thick Mg targets using acetic
acid for transient electronic
applications.
Heliyon 3 (2017) e00366.
doi: [10.1016/j.heliyon.2017.
e00366](https://doi.org/10.1016/j.heliyon.2017.e00366)



CrossMark

Triggered degradation of 250 μm-thick Mg targets using acetic acid for transient electronic applications

Zhiyuan Zhu, Kequan Xia, Zhiwei Xu *

Institute of Marine Electronics, Zhejiang University, No.1 Zheda Road, ZhouShan, 316021, China

*Corresponding author at: Zhiwei Xu, Zhejiang University, Institute of Marine Electronics, No.1 Zheda Road, Dinghai district, Zhoushan, Zhejiang Province, China, 316021.

E-mail address: xuzw@zju.edu.cn (Z. Xu).

Abstract

Transient electronics are becoming a hot topic due to the rapid development of bioelectronics, self-destructive devices and environmental sensors. This letter reports a novel scheme for triggering degradation of 250 μm-thick Mg target using acetic acid regarding transient electronics applications. The triggered transience has also been demonstrated using commercial vinegar. To achieve programmable transience as well as device protection, polypropylene carbonate (PPC) was investigated as passivation layer. The proposed method has demonstrated simplicity, high safety, low cost and low trigger temperature.

Keywords: Materials science, Materials chemistry, Electrical engineering

1. Introduction

Transient electronics are an emerging class of advanced electronics with the ability to disintegrate in a controlled manner [1, 2, 3, 4, 5], which has broad applications in implantable, environmentally friendly, and hardware secure devices, such as marine sensors. Current demonstrations of transient electronics include the destruction of various materials and device, such as Si [1], SiGe and Ge [6], metal [5], diode [4], brain sensor [2], etc. The transience is introduced using water [7], acid [4], ultraviolet (UV) [8], and microfluidic [9]. Particularly, acid-catalyzed

transience is of special interest as the transience occurs on demand without requirement of UV exposure. C. W. Park et al. [4] reported thermally triggered transient electronics based on protective wax that contain encapsulated methanesulfonic acid (MSA) microdroplets. Once heated, the wax melts and releases MSA that then degrades electronics. However, the use of super acid (e.g. MSA) requires carrier with strong acid resistance (e.g. wax). It also poses safety and cost concerns.

On the other hand, Mg and its alloy are useful in various application fields [10, 11, 12]. Especially, Mg has been widely used in transient electronics due to its advantages of easy processing, rapid rates of hydrolysis and biocompatibility [5]. Most of the reports use ultra-thin Mg film to demonstrate the transience as ultra-thin Mg film can be easily dissolved. For instance, 300 nm thick Mg electrode is used to demonstrate photo triggerable transient electronics [4]. However, various applications require different Mg thicknesses. For instance, the thickness of the magnesium electrode for fluidic battery paper chip is around 100 μm [13]. The application for Mg electrode with thickness of hundreds of microns necessitates more difficult challenges when attempting to introduce transience property. Therefore, it is significant to develop triggering mode for Mg target with thickness of hundreds of microns and achieves high safety, simplicity and low cost.

Acetic acid is a weak acid which, however, can dissolve Mg target [5, 14, 15]. Acetic acid enjoys the benefit of low cost, availability, and low toxicity. Therefore, acetic acid is widely used in commercialized products (e.g. vinegar), which is appealing to achieve cost-efficient and facile transience. Despite the above advantages, there has been no report on investigation of acetic acid in transient electronics application to the best of our knowledge.

In this paper, we report a novel scheme for triggering degradation of 250 μm -thick Mg target using acetic acid. Glacial acetic acid (GAA) and vinegar were utilized to trigger degradation. We also propose cascaded triggering modes that annihilate electronics in programmable manner. The proposed approach is beneficial to build large scale cascaded transient electronics for time programmable disintegration with advantages of simplicity, high safety, low cost and low trigger temperature.

2. Experimental

The Mg specimens were cut into 4 mm \times 4 mm pieces with a thickness of 250 μm in this study. In order to achieve rapid degradation, two groups of Mg specimens (10 samples for each group) were placed in GAA (4 ml) and commercial vinegar (4ml, containing 3 wt% acetic acid) for degradation, respectively. The triggering process is schematically illustrated in Fig. 1a. The application of transient electronics in harsh environment requires packaging passivation layer, which is able to provide temporary protection when without stimulus. However, it is

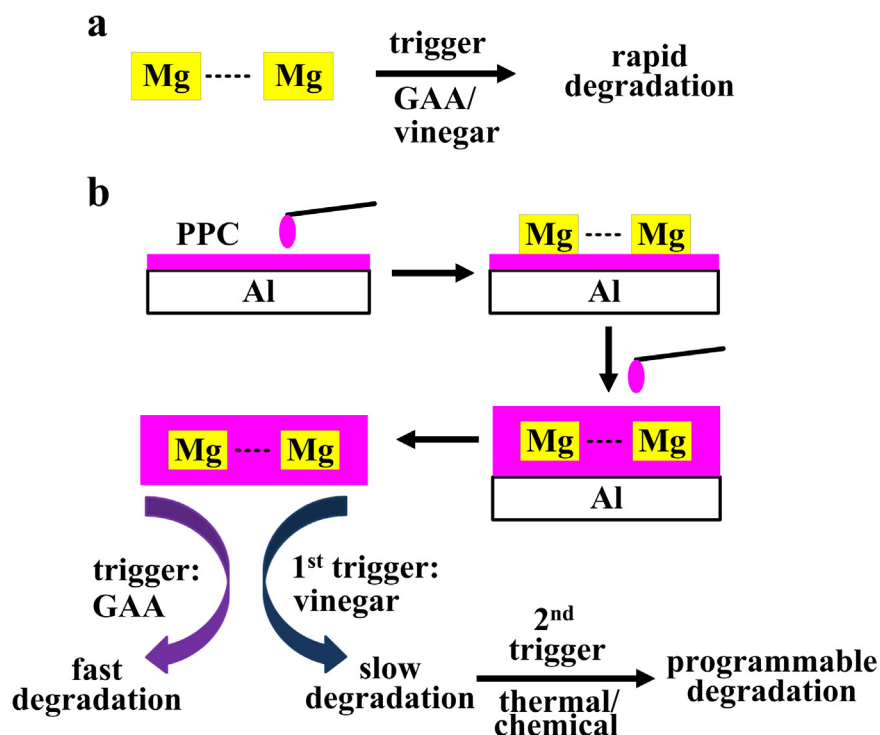


Fig. 1. Schematic representation of transience triggering process (a) Without PPC passivation layer (b) With PPC passivation layer.

expected to undergo degradation when triggered. Polypropylene carbonate (PPC) was investigated as temporary protection layer in this letter. PPC is a biodegradable green polymer that is able to protect metal surface from oxidation in ambient air [16]. More importantly, the glass transition temperature (T_g) of PPC is near room temperature ($T_g \approx 25^\circ\text{C}$ to 45°C) [17, 18, 19], which is beneficial for enabling low transience-triggering temperature.

The PPC polymers (QPAC 40) used in this study were obtained from Empower Materials Inc., New Castle, Delaware and have a molecular weight of 196 kg/mol. The PPC dissolves in acetone under constant stirring to form a 20 wt% solution. As is schematically illustrated in Fig. 1b, the PPC solution was dropped onto Al substrate. Then, the Al substrate with PPC coating was baked at 60°C for 15 min to remove acetone. Ten Mg specimens ($4\text{ mm} \times 4\text{ mm}$, $250\text{ }\mu\text{m}$ -thick) were placed with PPC coating, followed by PPC solution dropping on Mg surface. The samples were baked at 60°C for 15 min. After Al substrate was removed, a continuous PPC layer containing 10 Mg specimens was formed for degradation analysis. The degradation process was proposed as follows. Rapid degradation was achieved for GAA trigger. In contrast, when vinegar was used as first trigger, slow degradation was obtained. After thermal/chemical stimuli were applied as the second trigger, programmable degradation was achieved.

3. Results and discussion

The dissolution state of Mg specimens was checked after triggering. The dissolution time is averaged from 5 groups of Mg specimens and shown in Fig. 2a. The error bars represent one standard error, which is calculated by dividing the standard deviation by the square root of number of measurements. For Mg specimens without PPC passivation, the dissolution time for GAA and vinegar trigger is 14 min and 10 min, respectively. It is observed that the initial reaction rate for GAA is much slower than that of vinegar, which can be attributed to incomplete ionization and explains the difference of dissolution time for GAA and vinegar. The rapid degradation triggered by vinegar provides a simple and cost-effective scheme for achieving transient electronics.

However, when PPC passivation layer was applied, the dissolution time for vinegar trigger (7 days) is much longer than that without PPC passivation, which indicates that the PPC is able to protect transient electronics in harsh environment. It also implies that a second triggering process is needed. On the other hand, for Mg specimens with PPC passivation, the dissolution time for GAA trigger is 16 min, which shows no significant increase of dissolution time than that without PPC passivation. This result shows that GAA can effectively destroy the PPC passivation and then trigger the transience.

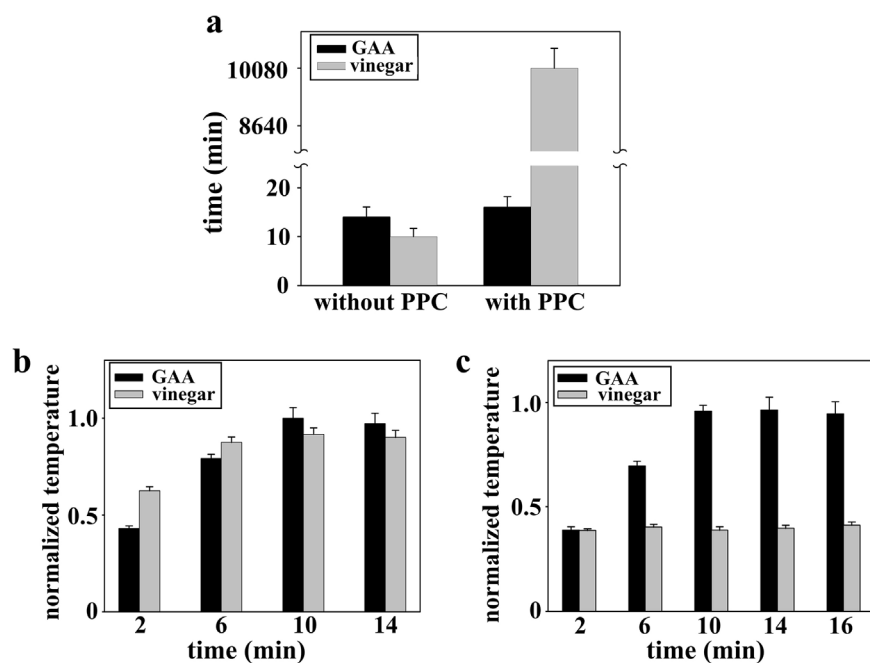


Fig. 2. The dissolution state of Mg specimens after triggering (a) The dissolution time without and with PPC passivation (b) The normalized temperature to trigger with PPC passivation (c) The normalized temperature to trigger without PPC passivation.

The temperature of solution was monitored by thermometer during triggering process. The temperature sensors are in physical contact with the solution being sensed and use conduction to monitor changes in temperature. The normalized temperature to trigger is averaged from 5 samples and illustrated in Fig. 2b and Fig. 2c. Fig. 2b shows the normalized temperature to trigger when PPC passivation was not applied. At the initial reaction stage of 2 min, the temperature of GAA is lower than that of vinegar, which indicates slow reaction rate due to incomplete ionization of GAA. The temperature of GAA increased dramatically as the reaction continues. This can be attributed to increased reaction rate as moisture is absorbed into GAA.

Fig. 2c shows the normalized temperature to trigger when PPC passivation was applied. The temperature of vinegar shows no significant difference among the measured time. It is obvious that PPC passivation can provide temporary protection for Mg specimens from reaction with vinegar. On the other hand, the highest temperature of GAA is almost the same as that shown in Fig. 2b. This result confirms that GAA is able to destroy PPC passivation layer and react with Mg specimen.

Intensive discussion has been carried out to investigate the interaction between PPC and acetic acid. Previous research has shown that a small amount of acetic acid can be used in PPC separation [20]. In contrast, excessive GAA and vinegar were applied in this study. It is noted that vinegar contains large amount of water and PPC is insoluble in water, which corresponds with the fact that PPC residue was observed in vinegar after triggering. It is possible that the acetic acid of vinegar interacts with PPC passivation layer, resulting in vulnerable spot in PPC layer (e.g. pinholes). Thus, the acetic acid penetrates the PPC passivation layer, slowly dissolving the Mg specimens.

On the other hand, a clear sticky solution was formed after dissolution when GAA was used as a trigger. After a small amount of water is added to the formed solution, stable emulsions were observed, indicating the precipitation of PPC. It can be concluded that GAA completely dissolve the PPC passivation and react with Mg specimens during the triggering process.

The above analysis has shown a long dissolution time for vinegar trigger (7 days) when PPC passivation layer was applied. In order to achieve programmable degradation, a second triggering process is required. For second thermal triggering process, the vinegar solutions containing Mg specimens were placed on hotplate at surface temperature of 35-90 °C. For second chemical triggering, chemical trigger (1 ml) was added into vinegar solution containing Mg specimens. The dissolution time of second thermal/chemical triggering is averaged from 5 samples and illustrated in Fig. 3.

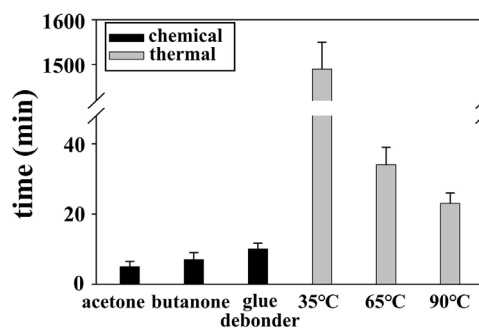


Fig. 3. The dissolution time of second thermal/chemical triggering.

As shown in Fig. 3, the dissolution time decreased significantly with temperature increasing for thermal triggering process, which can be attributed to increased interaction between acetic acid and PPC. Compared with ref. [4], a lower trigger temperature of 35 °C is achieved due to the low Tg of PPC.

For chemical triggering process, the PPC passivation was dissolved by chemical triggers. Thus, the Mg specimens reacted with acetic acid and disappeared. The shortest dissolution time of 5 min was achieved using pure acetone as chemical

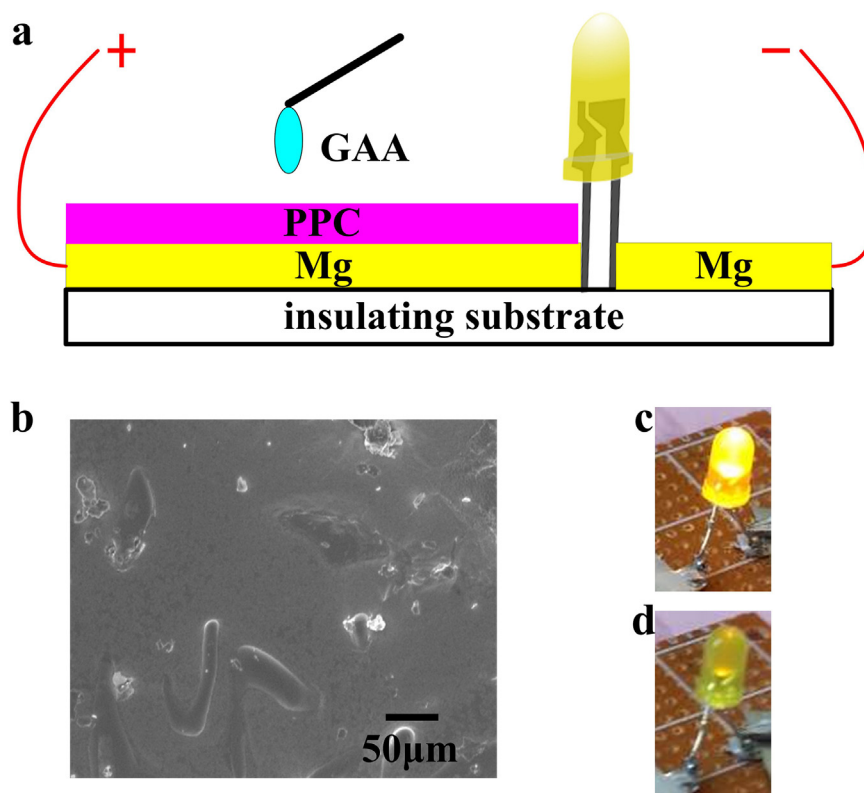


Fig. 4. Demonstration of GAA triggering process (a) Schematic of the GAA triggering process (b) SEM image of PPC (c) The LED image before triggering (d) The LED image after triggering.

trigger. In contrast, a commercial glue debonder, which contains acetone and butanone, was used as chemical trigger. The dissolution time is 11 min. The potential application of commercial daily products (e.g. vinegar, glue debonder) in transient electronic further decreases the cost and improves the operability. The experiments suggest that PPC passivation layer is of crucial importance for achieving time programmable disintegration.

GAA triggered destruction of an electronic device was demonstrated with PPC coating. As is schematically shown in Fig. 4a, the device was composed of one light emitting diodes (LEDs) in parallel with Mg electrodes. The Mg traces connected yellow LEDs were partially coated with approximately 40 μm -thick PPC. The scanning electron microscope (SEM) image of PPC is shown in Fig. 4b. After connected to power source, the LED operated normally (Fig. 4c). Small volume of GAA (0.1 mL) is dropped onto Mg surface with PPC coatings every 1 hour. After 8 hours, the yellow LED dimmed (Fig. 4d).

4. Conclusion

A novel scheme for triggering degradation of transient electronics using acetic acid is reported. GAA and vinegar were utilized to dissolve the probe metal. To achieve programmable transience as well as device protection, PPC was investigated as passivation layer. The reported method has the benefit of simplicity, high safety, low cost and low trigger temperature. The investigation of controllable degradation of 250 μm -thick Mg target is significant for Mg-based transient electronics using Mg alloy.

Declarations

Author contribution statement

Zhiyuan Zhu: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Kequan Xia: Performed the experiments; Wrote the paper.

Zhiwei Xu: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Funding statement

This work was supported by the Fundamental Research Funds for the Central Universities.

Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

References

- [1] S.W. Hwang, H. Tao, D.H. Kim, et al., A Physically Transient Form of Silicon Electronics, *Science* 337 (6102) (2012) 1640–1644.
- [2] S.K. Kang, R.K. Murphy, S.W. Hwang, et al., Bioresorbable silicon electronic sensors for the brain, *Nature* 530 (2016) 71–76.
- [3] S.W. Hwang, J.K. Song, X. Huang, et al., High-performance biodegradable/transient electronics on biodegradable polymers, *Adv. Mater.* 26 (23) (2014) 3905–3911.
- [4] C.W. Park, S.K. Kang, H.L. Hernandez, et al., Thermally Triggered Degradation of Transient Electronic Devices, *Adv. Mater.* 27 (25) (2015) 3783–3788.
- [5] L. Yin, H.Y. Cheng, S.M. Mao, et al., Dissolvable Metals for Transient Electronics, *Adv. Funct. Mater.* 24 (5) (2014) 645–658.
- [6] S.K. Kang, G. Park, K. Kim, et al., Dissolution chemistry and biocompatibility of silicon-and germanium-based semiconductors for transient electronics, *ACS Appl. Mater. Interfaces* 7 (17) (2015) 9297–9305.
- [7] M.A. Brenckle, H. Cheng, S. Hwang, et al., Modulated degradation of transient electronic devices through multilayer silk fibroin pockets, *ACS Appl. Mater. Interfaces* 7 (36) (2015) 19870–19875.
- [8] H.L. Hernandez, S.K. Kang, O.P. Lee, et al., Triggered transience of metastable poly (phthalaldehyde) for transient electronics, *Adv. Mater.* 26 (45) (2014) 7637–7642.
- [9] C.H. Lee, S.K. Kang, G.A. Salvatore, et al., Wireless microfluidic systems for programmed, functional transformation of transient electronic devices, *Adv. Funct. Mater.* 25 (32) (2015) 5100–5106.
- [10] Y. Hayasaki, T. Hasumura, T. Fukuda, et al., Synthesis of magnetic alloy-filling carbon nanoparticles in super-critical benzene irradiated with an ultraviolet laser, *Heliyon* 2 (9) (2016) e00171.
- [11] J. Zhang, C. Gu, J. Tu, Robust Slippery Coating with Superior Corrosion Resistance and Anti-Icing Performance for AZ31B Mg Alloy Protection, *ACS Appl. Mater. Interfaces* 9 (12) (2017) 11247–11257.
- [12] C.S. Roberts, *Magnesium and its Alloys*, Wiley, USA, 1960.

- [13] Y. Koo, S. Jagannathan, Y. Yeoheung, High performance magnesium anode in paper-based microfluidic battery, powering on-chip fluorescence assay, *Biomicrofluidics* 8 (5) (2014) 054104.
- [14] V.H. Agreda, *Acetic Acid and its Derivatives*, CRC Press, Boca Raton, Florida, USA, 1992.
- [15] A. Basile, *Acetic Acids: Chemical Properties, Production & Applications*, Nova Science Publishers Inc, New York, USA, 2014.
- [16] Z.Y. Zhu, M. Yu, O. Phillips, et al., Bonding of copper surface in ambient air using propylene carbonate as passivation layer, *J. Micro/Nanolith. MEMS MOEMS* 14 (3) (2015) 034504.
- [17] S.D. Thorat, P.J. Phillips, V. Semenov, et al., Physical properties of aliphatic polycarbonates made from CO₂ and epoxides, *J. Appl. Polym. Sci.* 89 (5) (2003) 1163–1176.
- [18] Q. Zhu, Y.Z. Meng, S.C. Tjong, et al., Thermally stable and high molecular weight poly (propylene carbonate)s from carbon dioxide and propylene oxide, *Polym. Int.* 51 (10) (2002) 1079–1085.
- [19] T.J. Spencer, P.A. Kohl, Decomposition of poly (propylene carbonate) with UV sensitive iodonium salts, *Polym. Degrad. Stab.* 96 (4) (2011) 686–702.
- [20] X. Jing, M.R. Salick, T. Cordie, et al., Electrospinning Homogeneous Nanofibrous Poly(propylene carbonate)/Gelatin Composite Scaffolds for Tissue Engineering, *Ind. Eng. Chem. Res.* 53 (22) (2014) 9391–9400.