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Supporting Information for

PVA-FeCl$_3$ composites as substrate and packaging materials for the controlled degradation of non-degradable metals in transient electronics

Neeru Mittal,[a#] *Tae-Min Jang,*[b#] *Suk-Won Hwang,* [b,c,d,]* *Markus Niederberger* [a,]*

[#] These authors contributed equally to the work

[a] Laboratory for Multifunctional Materials, Department of Materials, ETH Zürich, Vladimir-Prelog-Weg 5, 8093 Zurich, Switzerland.

[b] KU-KIST Graduate School of Converging Science & Technology, Korea University, Seoul, 02841, South Korea

[c] Department of Integrative Energy Engineering, Korea University, Seoul, 02841, South Korea

[d] Center for Biomaterials, Biomedical Research Institute, Korea Institute of Science and Technology (KIST), Seoul, 02792, South Korea

*Email: dupong76@korea.ac.kr; markus.niederberger@mat.ethz.ch

Methods

Materials

Polyvinyl alcohol (PVA) was purchased from Sigma-Aldrich with the following weight average molecular weights (M_w) and degrees of hydrolysis: M_w of 9.000-10.000 g·mol^{-1}, 80% hydrolyzed; M_w of 31.000-50.000 g·mol^{-1}, 98-99% hydrolyzed; and M_w of 85.000-124.000 g·mol^{-1}, >99% hydrolyzed. Ferric chloride ($FeCl_3$, 97%) and hydrochloric acid (HCl, 37%) were purchased from Sigma-Aldrich.

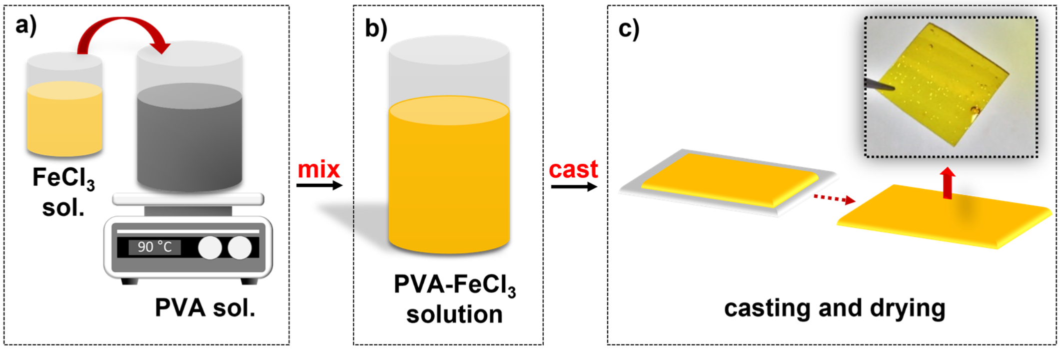
Fabrication of polydimethylsiloxane (PDMS) mold

A 10:1 mixture of PDMS elastomer (SYLGARD 184 A, Dow Corning, Midland, USA) and curing agent (SYLGARD 184 B, Dow Corning, Midland, USA) was poured into a petri dish (20 g for thin and 60 g for thick films), degassed inside a desiccator under vacuum and then cured at 60 °C for 2 h or at ambient conditions to obtain PDMS mold.

Fabrication of pure PVA and PVA- $FeCl_3$ films

The fabrication process of PVA-$FeCl_3$ films is illustrated in **Scheme S1**. Firstly, a 10 wt.% PVA solution was prepared by dissolving 2 g of PVA in 20 mL distilled water, followed by adding 10 µL of HCl to expedite the dissolution process. The solution was stirred at 90 °C for 3 h, then cooled to room temperature and stirred overnight. After that, the desired amount of $FeCl_3$ was pipetted from 30 wt.% (w/w) $FeCl_3$ aqueous solution and added to the PVA solution. To maintain the fixed volume for all solutions, the calculated amount of distilled water was added, followed by stirring for another 1 h. The chemical composition of PVA-$FeCl_3$ films and the notation used in the study are presented in **Table S1**. The solution casting method was used to fabricate polymer composite films. 500 and 1000 µL of different concentrations of PVA-$FeCl_3$ solutions were carefully drop-cast into the PDMS mold (1.8 cm long, 1.8 cm wide, and 1 cm thick) to obtain ~25 µm thin and ~100 µm thick films, respectively. The solution was dried under ambient conditions for 48 h to obtain films that were carefully peeled off from the mold and stored in sealed bags under normal conditions for further experiments.

During the preparation of pure PVA films, PVA with different weight average molecular weights and hydrolysis degrees was used, while for obtaining PVA-$FeCl_3$ films, PVA with a weight average molecular weight of 9,000-10,000 $g \cdot mol^{-1}$ and hydrolysis degree of 80% was only utilized. For experiments concerning the dissolution behavior of pure PVA films with different hydrolysis degree and molecular weights, a hydrophilic blue dye was added to the PVA solution that upon drying provided blue PVA films. This was done to get a more accurate dissolution time for these films which was difficult to achieve with transparent PVA films.



Scheme S1: Schematic illustration of the fabrication process of PVA-$FeCl_3$ composite films.

Fabrication of transient electronics

Patterned traces of ~100 nm thick Cu and ~80 nm thick Al metal films were deposited using magnetron sputtering (DC/RF sputtering system KVS-2004, Korea Vacuum tech) and electron beam evaporation (VER5004, SNTEK) methods on different substrates, including glass, PDMS, and PVA-$FeCl_3$ films. The deposition conditions used for Cu were 150 W, 10 mTorr, 10 sccm Argon, and 10 min deposition time, while for Al they were 0.05 $nm{\cdot}s^{-1}$, 0.3-0.4 V, 50-70 mA, and 10^{-6} torr. The shadow mask for the metal sputtering methods was prepared by cutting the desired pattern on a PDMS stamp. The Cu films for the LEDs experiment were deposited using magnetron sputtering with a high resolution (20 µm) stencil mask on a glass substrate. Conductive silver epoxy (ELCOAT A-200, 2 components, heat-cured at 150 °C for 20 min) was used for attaching LEDs and conductive wires to the Cu film. Thick films (100 µm) of PVA-2% $FeCl_3$ and PVA-15% $FeCl_3$ were attached to copper films through Van der Waals interaction between the glass substrate and composite films. The digital photograph showing the device setup used for the LEDs experiment to demonstrate the transience kinetics of metal dissolution using PVA composite films is shown in **Figure S5**. For the other transience experiments, the metal films are either deposited on PDMS substrates and then covered/encapsulated with PVA-$FeCl_3$ composite films as packaging material or metal films are direct deposited on PVA-$FeCl_3$ composite substrates.

Transient behavior of films

Transiency of polymer films in distilled water was monitored using a charged couple device (CCD) camera (Canon EOS 700D). The PVA films with a fixed size and almost similar thicknesses were cut and then their transience behavior was monitored inside a Petri dish containing distilled water.

The dissolution behavior of Cu (area 25 mm^2) and Al (area 25 mm^2) metallic films deposited on glass or PDMS substrate and encapsulated with PVA-15% $FeCl_3$ films was initiated by pipetting a drop of water (volume ~20 µl) onto the PVA film. The entire dissolution process was recorded using a charged couple device (CCD) camera (Canon EOS 700D) and a high resolution optical microscope (Eclipse LV100nd, Nikon).

Characterization

Scanning electron microscopy (SEM) analyses were performed on a DSM 982 Gemini instrument (Zeiss). Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy equipped with a single reflection ATR attachment with diamond crystal was used for this study (LabRam ARAMIS IR2, HORIBA JOBIN YVON). Samples were placed directly on the ATR crystal, and scans were recorded with a spectral resolution of 4 cm^{-1} at room temperature for all samples. Before each measurement, the samples were dried at 60 °C for 48 h. X-ray diffraction (XRD) patterns were obtained on SmartLab, Rigaku diffractometer in reflection mode using Cu Kα radiation (45 kV, 200 mA). The samples were scanned in the range of 10-70° with a step of 0.01° per second. To monitor the degradation products formed during the transience test of thin Cu film using PVA-15% $FeCl_3$ as encasing material, the grazing incidence angle X-ray diffraction (Bruker D8 micro-source) analysis was conducted. The thickness of both PVA and PVA-$FeCl_3$ films was obtained on Dektak-XT, Bruker.

Supporting Figures

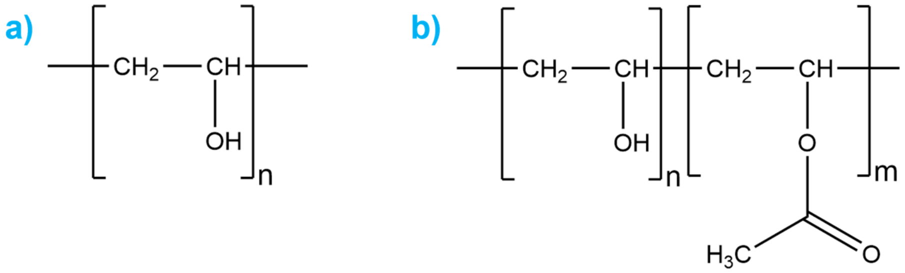


Figure S1. Representative chemical structure of a) fully hydrolyzed and b) partially hydrolyzed PVA.

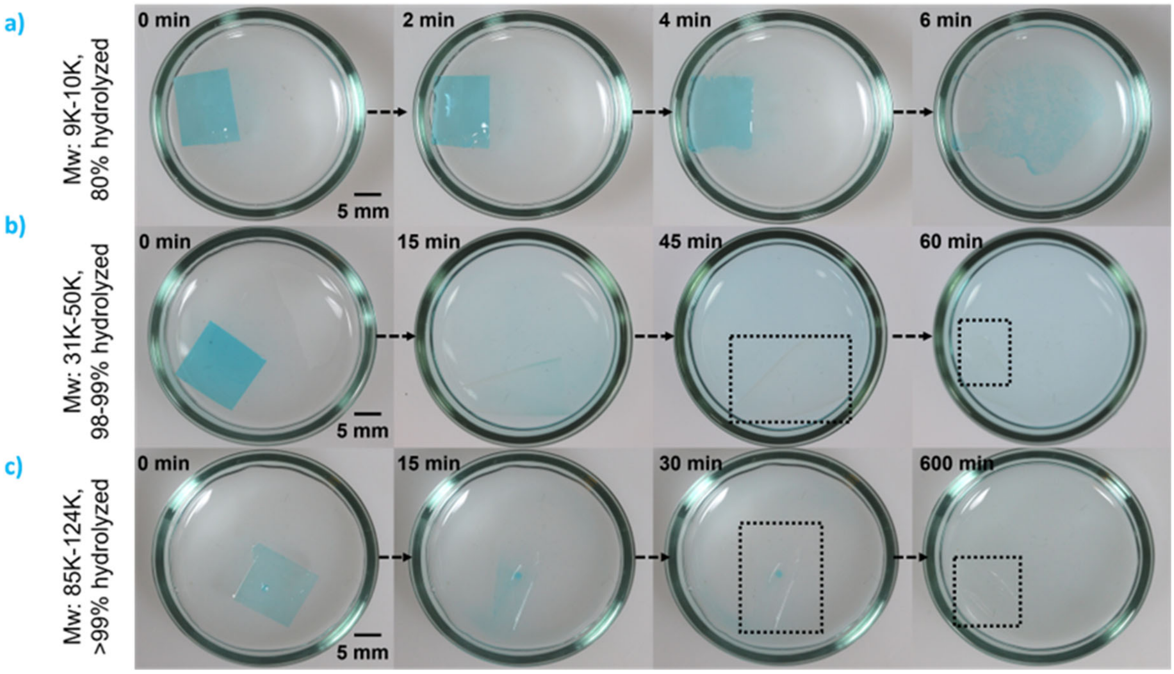


Figure S2. Digital photographs showing the time-dependent dissolution of PVA films (25 μm thick) with different degrees of hydrolysis and molecular weights in distilled water.

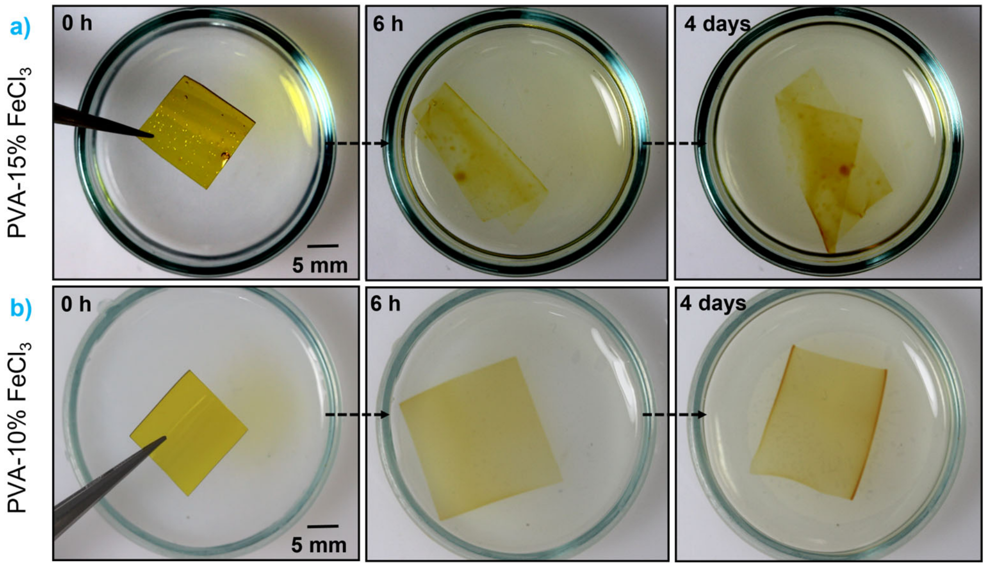


Figure S3. Digital photographs showing the time-sequential dissolution in distilled water of a) PVA-15% FeCl$_3$ and b) PVA-10% FeCl$_3$ films with *Mw* of 31,000-50,000 g·mol^{-1} and 98-99% degree of hydrolysis.

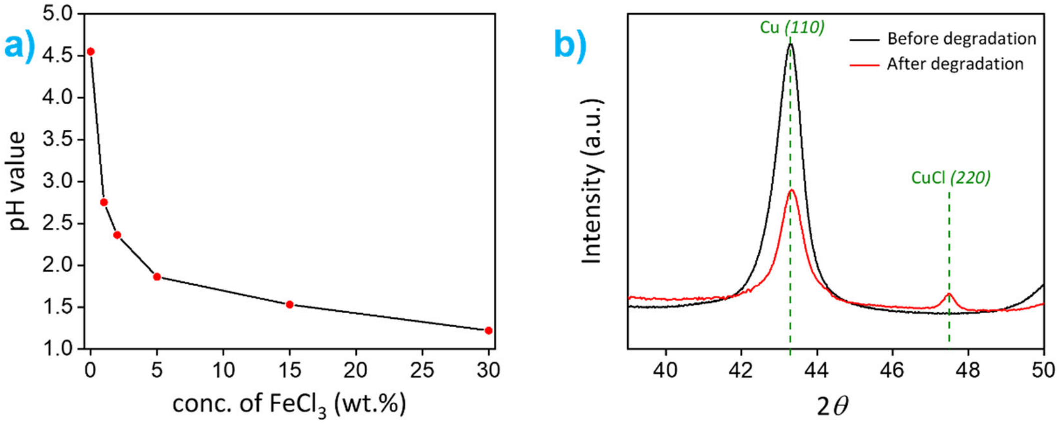


Figure S4. a) The pH values obtained after dissolving PVA-FeCl$_3$ films in distilled water with different additive concentrations. b) The grazing incidence angle X-ray diffraction patterns of Cu film obtained before and after the dissolution process using PVA-15% FeCl$_3$ as packaging material.

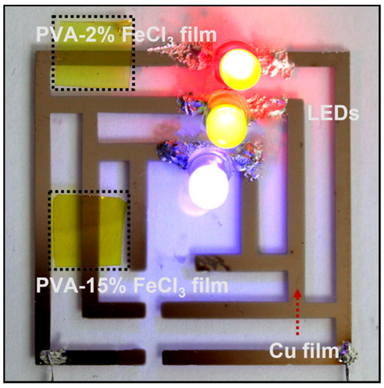


Figure S5. Digital photograph showing the device setup used for the LEDs experiment. Here, the designed circuit consists of three LEDs connected in parallel to the Cu film/electrode. The Cu electrode to red and blue LEDs is partially encapsulated by PVA films containing 2 wt.% and 15 wt.% $FeCl_3$. The experiment is carefully designed to present tunable transience kinetics of PVA-$FeCl_3$ films for the degradation of non-transient Cu metal.

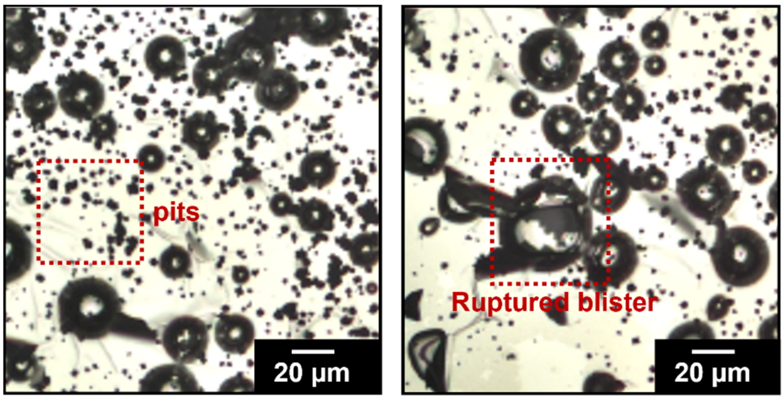


Figure S6. Optical microscopy images showing pits and a ruptured blister formed during the water-triggered dissolution of thin Al film encapsulated with PVA-15% $FeCl_3$ film.

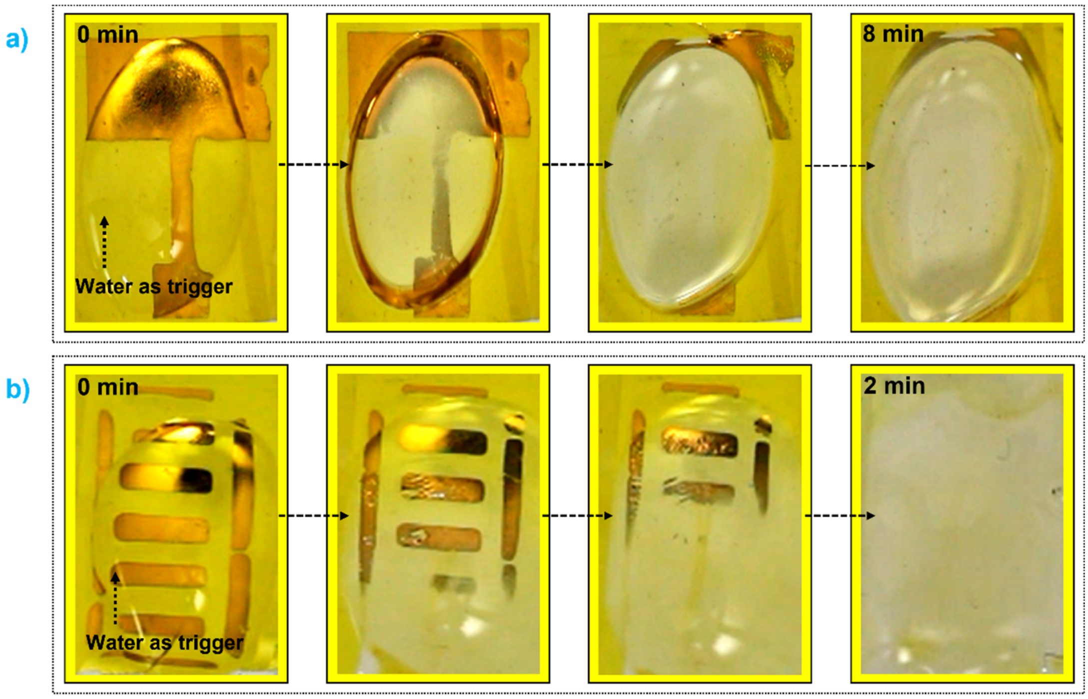


Figure S7. The digital photographs showing the water-triggered dissolution behavior of Cu films (100 nm thick) in different patterned designs a) current collector and b) battery, directly deposited on PVA-15% $FeCl_3$ substrate.

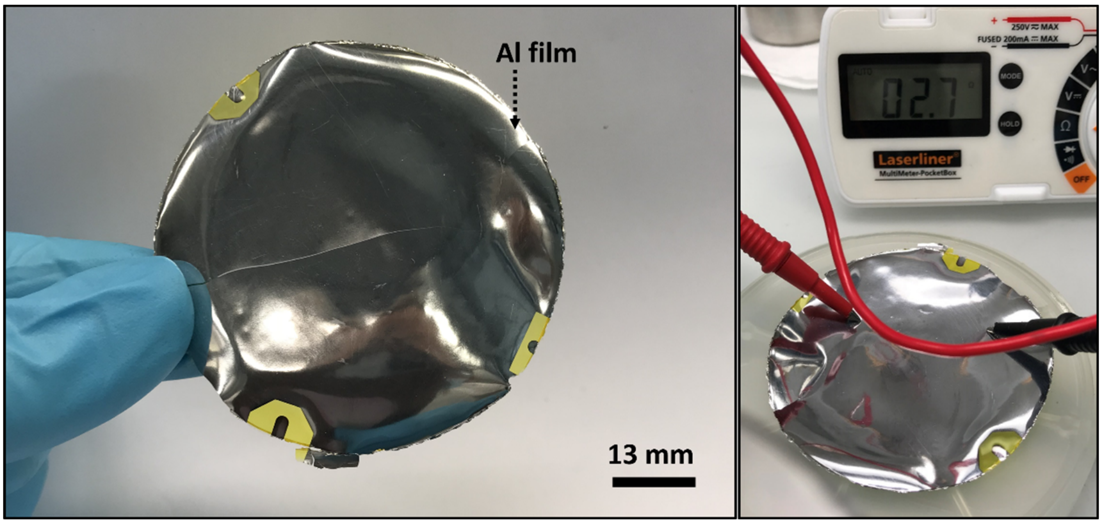
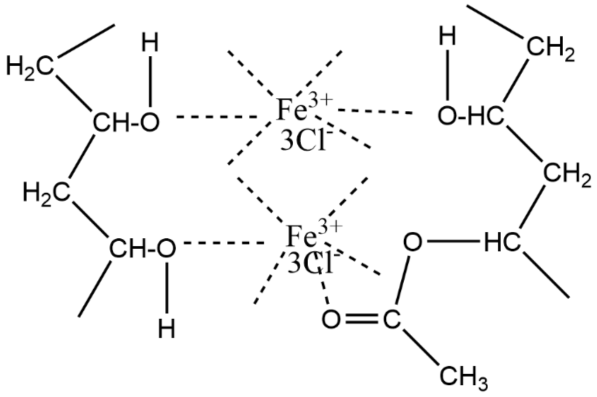


Figure S8. Digital photographs of the PVA-15% $FeCl_3$ film coated with metallic Al (100 nm thick) and its electrical resistance measured by a multimeter.



Scheme S2. Scheme showing the possible chemical interactions between the electron donor groups of PVA and Lewis acid, $FeCl_3$.

Supporting Tables

Table S1. Sample name and chemical compositions of the synthesized PVA-$FeCl_3$ films.

Sample name	PVA (g)	$FeCl_3$ (g)	Weight ratio (PVA:$FeCl_3$)
PVA	2	0	100:0
PVA-1% $FeCl_3$	2	0.02	100:1
PVA-2% $FeCl_3$	2	0.04	50:1
PVA-15% $FeCl_3$	2	0.3	~7:1
PVA-30% $FeCl_3$	2	0.6	~3:1