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2020

Lai, C. Q., Chay, J. C., & Kanaujia, P. K. (2020). Precise dynamic control of the mechanical and self-healing properties of an electrolytic cell with soluble porous anode. *Advanced Engineering Materials*, 22(6), 1900833-. doi:10.1002/adem.201900833

<https://hdl.handle.net/10356/143181>

<https://doi.org/10.1002/adem.201900833>

This is the accepted version of the following article: Lai, C. Q., Chay, J. C., & Kanaujia, P. K. (2020). Precise dynamic control of the mechanical and self-healing properties of an electrolytic cell with soluble porous anode. *Advanced Engineering Materials*, 22(6), 1900833-, which has been published in final form at doi:10.1002/adem.201900833. This article may be used for non-commercial purposes in accordance with the Wiley Self-Archiving Policy
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Advanced Engineering Materials

Precise Dynamic Control of the Mechanical and Self-Healing Properties of an Electrolytic Cell with Soluble Porous Anode*Chang Quan Lai*, Jie Cheng Chay, Pawan K. Kanaujia*

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Keywords: adaptive, cellular structure, variable stiffness, metal foam, self-healing

Engineering products are currently designed to operate under a fixed set of conditions, but the demands of a dynamic environment may occasionally exceed these specifications, resulting in technical failures. Materials with properties that can be modulated in real-time allows the functionality of a product to be dynamically tuned to meet these changing requirements. Having a single versatile product meet multiple needs also eliminates the necessity for multiple parts with dedicated functionalities, conserving space, material and energy. Here, we demonstrate how a material with electrically tunable mechanical properties can be achieved using an electrolytic cell with porous copper foams for electrodes. By controlling the voltage polarity, current density and process duration, copper metal can be reversibly deposited or etched from the foam in a precise and deterministic manner without changing its nominal volume or temperature. The resultant change in relative density, in turn, alters the modulus, strength and energy absorption characteristics of the foams over a range of 2 orders of magnitude. By excessively depositing material at the interface of separate foam pieces, the system was shown to possess self-healing characteristics as well. Lastly, a demonstration of real-time mechanical property modulation in a product prototype was carried out.

MAIN TEXT

The performance of engineering products is inherently dependent on the properties of its constituent materials. Because these properties are mostly fixed for each material, the range of requirements that the engineering product can satisfy is consequently very narrow. The environment that these engineering parts operate in, however, can be very dynamic, requiring quick and substantial property modifications for optimal performance. For instance, to effectively attenuate acoustic noise,^{[1]–[3]} impact^{[4]–[7]} or seismic waves,^{[8][9]} materials with stiffnesses and strengths that can be temporally varied are needed. Similarly, tumor cell migration rates can be controlled in real time by hydrogels with variable stiffness.^{[10][11]} Having materials with dynamic mechanical properties would also allow for the reconciliation of soft robotics, which has the advantages of dexterity and interacting safely with delicate bodies,^{[12]–[15]} with conventional hard robotics, which is needed to maintain and transmit large loads,^{[12][16]} within a single machine. Moreover, having a versatile product that can meet a wide range of requirements eliminates the need for multiple specialized parts with dedicated functions, such as functionally graded materials,^{[4][17]} thus reducing energy and material wastage, leading to a positive ecological impact.

One of the easiest methods to induce changes in mechanical properties is to spatially compact a given structure. A biological body does this with muscular contractions, for instance, in a human tongue and elephant trunk,^[12] while structural foams can be infused with magnetic particles, either in the struts^[2] or in the pores,^[6] so that the material will stiffen in the presence of a magnetic field. However, a constant energy input is required to maintain this property change and the accompanying alteration in volume may be undesirable, especially if the material is part of an assembly with tight tolerances.

An alternative method that has been explored involves heating/ cooling a material in order to induce a phase change.^{[18][19]} For a low-melting-point alloy (*e.g.* Field's metal), this

change in phase is between a solid and liquid, which can lead to a modulus variation over 4 orders of magnitude.^[19] In the case of shape memory polymers, the phase change occurs when they are heated above their glass transition temperature and 2-3 orders of magnitude change in flexural rigidity of these beams have been demonstrated.^{[20][21]} Although the change in stiffness can be very large using these techniques, the property variation is essentially binary, since it is difficult to control and maintain the relative amounts of stiff and soft material at the melting or glass transition temperature. Furthermore, the temperature change involved may not be ideal for applications involving sensitive environments (*e.g.* biomedical settings).

It has also been shown recently, that the application of an electrochemical potential to a nanoporous gold foam can cause the adsorption of a sub-monolayer of oxygen and accumulation of electrons onto its surface, increasing its stiffness through modifications of the surface stress.^[22] The adsorbed oxygen could also pin dislocations, increasing the flow stress of the foam.^[23] The range of modification demonstrated, however, was rather low – only 8% for the modulus^[22] and 2 times for the flow stress.^[23] On the other hand, hydrogels crosslinked with photosensitive groups can exhibit up to an order of magnitude difference in modulus in the presence of light, but the highest value achieved was only ~ 2 kPa, limiting their use to non-structural applications.^[10]

To circumvent these limitations, we introduce an alternative setup described in **Figure 1a**, which is commonly used for the electrolytic refining of metals such as Cu and Ni.^[24] In this electrolytic cell, the electrodes are made up of a non-inert metal (Cu, for this study), so that the application of a potential bias will cause the metal to dissolve at the anode due to oxidation, and get redeposited at the cathode through reduction of the metal ion. In such a system, when an open-cell Cu foam (20 – 25 PPI), acting as a structural element, is used as a cathode, the deposition of Cu will cause its trusses to thicken, thereby stiffening and strengthening the foam (**Figure 1b**). To weaken the foam, the polarity of the voltage bias can be simply reversed, so that the structural Cu foam is now the anode, and the accompanying anodic etching process

results in a thinning of the foam struts (**Figure 1b**). The improved surface area to volume ratio of the porous foam electrodes, compared to solid electrodes, is essential for expediting the deposition/ etching process. For brevity, we will refer to the system as ECSPA (Electrolytic Cell with Soluble Porous Anode) in the following.

One important advantage of the ECSPA setup is that the energy requirements for the above processes are minimal. Firstly, the reversible potential of the system in **Figure 1a** is zero, since the anode and cathode are composed of the same material.^[24] Practically, a small voltage ($< 1\text{V}$) is required to overcome the resistance of ion movement in the electrolyte, which amounted to $\sim 1\ \Omega$ in our experimental setup (Supplementary Information). Secondly, unlike the case with magnetic^{[2][6]} and certain phase change materials,^{[20][21]} once deposition/ etching of the foam has taken place, the foam is permanently strengthened/ weakened, and no additional energy is necessary to maintain this change.

The effectiveness of ECSPA is clearly shown in **Figure 1c**, which documents the substantial changes in the mass and relative density (up to 5 times) of the Cu foam under cathodic deposition/ anodic etching without affecting its nominal volume ($< 10\%$). The added mass can be precisely controlled through the current density and process duration, which is evident from the excellent agreement between the experimental data points and the dashed theoretical trendlines obtained using

$$\Delta M = \frac{J A m t}{n F} \quad , \quad (1)$$

where ΔM refers to the change in mass, J refers to the nominal current density, A refers to the nominal surface area of the Cu foam, m refers to the molar mass of Cu, t refers to the process duration, n refers to the valency of the Cu ion in the electrolyte ($= 2$ for Cu^{2+}) and F refers to Faraday's constant (96500 C/mol). The change in relative density, $\Delta\rho/\rho_s$, can be obtained with

$$\Delta \frac{\rho}{\rho_s} = \frac{1}{\rho_s} \left(\frac{M_0 + \Delta M}{V_0 + \Delta V} - \frac{M_0}{V_0} \right) \quad , \quad (2)$$

where ρ refers to the mass density of the foam, ρ_s refers to the mass density of the foam material (8.95 g/cm³),^[25] M_0 refers to the mass of the starting foam, which was kept constant at 0.65g, V_0 refers to the nominal volume of the starting foam (20 mm x 20 mm x 5 mm) and ΔV refers to the change in nominal volume after processing. From **Figure 1c**, however, it can be observed that $\Delta V/V_0$ is negligible and therefore, Equation (2) can be rearranged to give

$$\frac{\frac{\Delta \rho}{\rho_s}}{\frac{\rho_0}{\rho_s}} \approx \frac{\Delta M}{V_0 \rho_0} = \frac{\Delta M}{M_0} \quad , \quad (3)$$

where $\rho_0 (= M_0/V_0)$ refers to the mass density of the starting foam. Equation (2) - (3) shows that the normalized change for the mass and relative density was the same because the electrolytic process took place without any significant change to the nominal volume of the foam.

This gain in relative density, in turn, led to a change in the modulus, E , strength, σ , and energy absorbed per unit volume, Q_{30} , of the foam in the form of

$$\frac{E}{E_s} \propto \left(\frac{\rho}{\rho_s} \right)^{1.8} \quad , \quad (4)$$

$$\frac{\sigma}{\sigma_s} \propto \left(\frac{\rho}{\rho_s} \right)^{1.9} \quad , \quad (5)$$

$$\text{and} \quad Q_{30} \propto \left(\frac{\rho}{\rho_s} \right)^{1.9} \quad . \quad (6)$$

The modulus, E_s , and strength, σ_s , of pure Cu was taken to be 120 GPa and 45 MPa respectively.^[25] Energy absorption was calculated for strain = 30%, which is after yielding and before structural densification. These trends in Equations (4) – (6) appear to be independent of the applied current density (**Figure 1c – 1f**), at least for the range investigated here. The power law indices for Equations (4) and (5) are reasonably close to the respective values of 2 and 1.5 predicted by Gibson and Ashby previously.^{[26][27]}

Taken together, **Figure 1c – 1f** shows that by using ECSPA, the mechanical properties of the foam can be modulated over a range of at least 2 orders of magnitude, with reasonably good precision and accuracy ($\sim \pm 0.1$ order of magnitude). Compared to other techniques of

modulating stiffness,^[28] ECSPA exhibits a good combination of maximum achievable modulus and range, as measured by the modulus ratio (*i.e.* ratio of maximum to minimum modulus) (**Figure 2a**). In fact, only 3 materials reported in the literature (shaded region in **Figure 2a**) displayed better maximum modulus and range characteristics. However, these come at the cost of resolution – ECSPA materials can adjust their moduli to any value within the reversible range, while the other 3 materials, which depend on phase transitions, only exhibited binary modulus values (**Figure 2b**).^{[19][29][30]} Such fine control of modulus is necessary for certain applications, such as those that involve the control of acoustic or elastic waves.^{[1][3][31]} Moreover, there is much room for optimizing the performance of ECSPA materials. For instance, the maximum achievable modulus can be easily improved by replacing the Cu foams with Ni foams, or by carrying out co-deposition of ceramic particles^[32] during the stiffening and strengthening phase of the process.

The change in mechanical properties using ECSPA is also reversible (**Figure 3**). As a demonstration, different foam samples were subjected to ≤ 2 full cycles of cathodic deposition (D) and anodic etching (E), starting either with deposition first (**Figure 3a**) or etching first (**Figure 3b**). Because the mechanical tests were destructive, a separate sample had to be used for each processing condition.

Despite some small inter-sample variability, it can be observed that the stress-strain curves were essentially the same for samples that had the same net number of deposition or etching processes *e.g.* 1D and 2D1E both had 1 net D. The changes in mechanical properties as a result of the cyclic treatment are plotted in **Figure 3c**, which shows that the stiffness, strength and energy absorption properties of the foams can be reproducibly and reversibly modulated with an electrical current.

The key to reversibility in an ECSPA system is the retention of the Cu foam topology during the deposition or etching processes. In other words, struts within the foam must not be thickened to the point where new joints are formed and similarly, they should not be thinned to

the point where some struts become broken. When that happens, the microstructural geometry of the foam changes, leading to a different set of relative density – property relationships. If reversibility is not a requirement, however, then the range of property modification can be greatly expanded, basically to the limits of the solid metal and liquid electrolyte, which have vastly different mechanical properties.

The encouraging results in **Figure 3** suggests that an ECSPA material can be repeatedly modified for multiple use, although more evidence is needed to confirm that the same reproducibility will hold up over a large number of cycles, as small changes to the foam geometry for each deposition/ etch cycle will add up to be quite significant over time. These changes can be significantly influenced by the original surface roughness of the foam struts (*e.g.* field concentration effects at sharp edges)^{[33][34]} and operating parameters such as current density, duration of deposition/ etching, electrolyte composition, temperature, pH etc., which are known to influence the thermodynamics and kinetics (*e.g.* diffusion-limited or surface-reaction-limited reaction rates) of electrochemical processes.^{[32][34]–[37]} A more detailed follow-up study focusing on the reliability of the ECSPA system for extended cyclic usage will be necessary to clarify these relationships.

Beyond precise, reversible modulation of mechanical properties over a large range, ECSPA also confer the Cu foams self-healing/ regenerative capabilities. To demonstrate this, we placed 2 separate 20 mm x 20 mm x 5mm Cu foam samples in contact with each other and performed cathodic deposition at a nominal current density of 0.75 mA/mm² for different durations. It was found that as the deposition duration increased, the seam between the 2 samples, indicated by blue arrows in **Figure 4a**, became less visible and both the tensile stiffness and tensile strength of the repaired sample improved (**Figure 4b**).

The mechanical properties of the repaired samples, however, were much worse than control samples that were never separated but had been subjected to the same cathodic deposition process. This is because the struts of the 2 separated samples did not match up

perfectly with each other, resulting in the narrowing of the strut cross-section at the healed interface (see magnified view of interface for 8H in **Figure 4a**). Therefore, upon tensile loading, the repaired sample failed cleanly along this weakened fault line, rather than through the jagged paths of the control samples (**Figure 4a**).

To truly enable a product to meet dynamic requirements, the changes in the mechanical properties of the material must be take place *in situ*, without having to extract the material from the product for processing. In **Figure 5a - b**, we present one possible design that can achieve this. In this design, a central tube made of Cu foam, held steady by solid polymeric caps (modulus = 1.1 GPa) at its ends, formed the load bearing structure in the cell. It was surrounded by a concentric layer of counter electrode, made of Cu foam, that acted as the material reservoir for transferring material to and from the central Cu foam. The 2 separate foams were submerged in CuSO₄/H₂SO₄ electrolyte that was held in place by a thin polymer wrap (thickness ~ 50 µm) that had no significant load bearing capabilities. The foams were connected to an external DC power supply using two insulated copper leads. **Figure 5b** summarizes these details in a cross-sectional diagram of the cell, while **Figure 5c** shows an actual self-contained ECSPA system undergoing quasistatic compression test (strain rate ~ 10⁻⁴/s).

As a demonstration, the central foam providing the structural support was strengthened after every 2% of compressive strain with a nominal current density of 0.3 mA/mm² for 20 min (each instance is indicated with blue arrow in **Figure 5d**). During the cathodic deposition onto the central foam, the compression test was paused, so that the compressive strain remained constant for the duration of the deposition. The control sample was subjected to the same stoppages, without any processing taking place during the 20 min period.

Comparing the stress-strain curve obtained with that of a control cell where deposition was not carried out, it can be seen that the elastic moduli of the cells were initially the same up to ~ 0.8% strain. This is expected as no cathodic deposition was carried out for either cell at this point. However, one of the cells was slightly weaker, as it began to deviate from the elastic

regime at a stress of 0.35MPa (red line), compared to the other, which only yielded at 0.55 MPa (green line). At 2% strain, the weaker system was strengthened through cathodic deposition so that there was a sudden increase in the stress it was able to sustain for strain > 2%. After the first strengthening procedure, the originally weaker cell (red line) was able to sustain a similar load as the other cell (green line) from 2% to 4% strain. At 4%, another cathodic deposition was carried out and once again, there was an obvious increase in the stress that the strengthened system could sustain after that. From 4% - 6%, the mechanical properties of this cell overtook that of the control and the difference was amplified after yet another cathodic deposition performed at 6% strain.

In summary, we have demonstrated how an electrolytic cell with soluble porous anode (ECSPA) can be used to dynamically tune the mechanical properties of a metal foam. The mechanical properties were modulated over 2 orders of magnitude with good precision and minimal energy. The modifications took place without any significant change in temperature and nominal volume of the foam, and were shown to be reversible. The unique ECSPA system also provided the added advantage of self-healing characteristics. Finally, a prototype that can perform such property modulation *in situ*, during a compression test, was presented as well.

Experimental Section

Electrolyte Preparation: 50 mL electrolyte containing 0.8 M anhydrous Cu (II) Sulphate (Sinopharm Chemical Reagent Co.) and 1.5 M Sulphuric Acid (95%, 1L, VWR Chemicals) was prepared at room temperature by dissolving 6 g of CuSO₄ in 46 ml of deionized water and 4 ml of H₂SO₄.

Sample Preparation: Cu foam sheets (20-25 PPI, 5 mm thickness) were purchased from a commercial source (LaTech™, Singapore) and diced into samples. Each sample was 20 mm x 20 mm samples with a standardized weight of 0.65 g, unless otherwise stated. The counter

electrodes for each sample was a 130 mm x 70 mm Cu foam diced from the same sheet as the samples. The counter electrode was folded into a cylindrical roll and fitted into a 100 ml glass beaker, with the sample arranged in the center. The mismatch in electrode sizes was designed to ensure that sufficient material would be available in the counter electrode for cathodic deposition onto the sample. The electrodes were connected to a DC Power Supply (Digimess® HY3003-3) using alligator clips. When the sample was connected to the positive terminal, it acted as the anode while connection to the negative terminal allowed cathodic deposition to take place on the sample. All processes were carried out at room temperature. The relative density of the samples was calculated based on measurements of the sample mass and dimensions.

Characterization: Characterization of mechanical properties of the foam was conducted using a uniaxial testing machine (Shimadzu AGS-X) fitted with a 10 kN (etched samples) or 50 kN load cell (deposited samples) and the appropriate fixtures for compressive and tensile tests. The strain rate used was $\sim 10^{-3}$ /s for all samples, except for the self-contained ECSPA setup, where the strain rate was 10^{-4} /s. Surface morphologies of the samples were captured using a wide-zoom Stereo Microscope (Olympus SZX16).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This work was performed with the assistance of funding provided by the Temasek Research Fellowship.

Received: ((will be filled in by the editorial staff))

Revised: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

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Figure 1. (a) A schematic illustration of the ECSPA system and its operating principle. (b) Photos of the Cu foams after cathodic deposition and anodic etching. The starting foam sample, with relative density (ρ/ρ_s) of 0.03 is also shown. (c) A plot of the normalized change in mass, relative density and volume with respect to the product of current and duration, which is a measure of the total number of electric charges that flowed through the circuit. (d) Plot of relative compressive modulus (E/E_s) and absolute compressive modulus (E) vs. relative density (ρ/ρ_s) for different current densities. E_s for Cu was taken as 120 GPa.^[25] (Inset) A copper foam sample undergoing quasistatic compression test (strain rate $\sim 10^{-3}$ /s). Scale bar = 10 mm. (e) Plot of relative compressive strength (σ/σ_s) and absolute compressive strength (σ) vs. relative density for different current densities. σ_s was taken as 45 MPa.^[25] (f) Plot of energy absorbed per unit nominal volume at 30% strain vs. relative density for different current densities. Control in (d) – (f) refers to the untreated starting foam.

Figure 2. (a) Chart of maximum effective elastic modulus vs. modulus ratio for the various techniques used to control material stiffness, as reported in the literature.^[28] The materials with better maximum achievable modulus and range than ECSPA materials are highlighted in the shaded region. (b) Chart of moduli reported for ECSPA materials, bistable electroactive polymers,^[29] thermoplastic shape memory polymer (SMP)^[30] and low melting point alloy.^[19]

Figure 3. (a) Engineering stress-strain plots (compressive) of samples that underwent different number of deposition (D) and etching (E) processes. 1D and 1E refer to 1 instance of deposition and 1 instance of etching respectively, at a current density of 0.15 mA/mm^2 for 45 min. (Inset) Cu foams with 0 (*i.e.* 1D1E & 2D2E) [left] and 1 (*i.e.* 1D & 2D1E) [right] net instance of deposition. Scale bar = 10mm. (b) Engineering stress-strain plots of samples that underwent different number of deposition (D) and etching (E) processes. (Inset) Cu foams with 0 (*i.e.* 1D1E & 2D2E) [left] and 1 (*i.e.* 1E & 2E1D) [right] net instance of etching. Scale bar = 10mm. (c) Plots showing the temporal variations of physical and mechanical properties of the Cu foam with changes in the polarity of the applied current density. The solid orange trend corresponds to the stress-strain curves in (a) while the dashed blue trend corresponds to those in (b).

Figure 4. (a) Images of a single (Control) and 2 separate pieces (Repaired) of Cu foam that were subjected to 4H, 6H and 8H of cathodic deposition at a current density of 0.75 mA/mm^2 . Images of the samples before (above) and after (below) tensile testing in the horizontal axis at strain rate $\sim 10^{-3}/\text{s}$ are shown. The blue arrow indicates the original interface between the 2 separated pieces. (Inset) Magnified view of the seam between the 2 samples after 8H of cathodic deposition. (b) Engineering stress-strain curves (tensile) obtained for the various samples.

Figure 5. (a) Schematic illustration of a self-contained ECSPA system. See Supplementary Information for more details on the dimensions of the cell. (b) Cross-section of the self-contained ECSPA system. (c) Image of an actual self-contained ECSPA system. (d) Compressive stress-strain plot (red) of an ECSPA system that had its inner Cu foam periodically subjected to cathodic deposition every 2% strain (each instance indicated by a blue arrow). The deposition was carried out at a current density of 0.3 mA/mm^2 for 20 min each time while the compression test was suspended. The control setup (green trend) was subjected to the same pauses, but no cathodic deposition was carried out. Dotted circles highlight the sudden increase in stress that the cell can bear after each cathodic deposition to the inner Cu foam.

An electrolytic cell with non-inert metal foam electrodes allows material to be electrochemically transferred from the anode to the cathode, leading to reversible thickening or thinning of the foam struts. This can be used to precisely and reversibly tune the mechanical properties of the metal foam over a large range (> 2 orders of magnitude) in real-time and confers self-healing properties as well.

Keyword: Smart Materials

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Precise Dynamic Control of the Mechanical and Self-Healing Properties of an Electrolytic Cell with Soluble Porous Anode

Supporting Information

Precise Dynamic Control of the Mechanical and Self-Healing Properties of an Electrolytic Cell with Soluble Porous Anode*Chang Quan Lai*, Jie Cheng Chay, Pawan K. Kanaujia***1. I-V Measurements of ECSPA Setup**

Figure S6. I-V measurements of a typical ECSPA system (data points) and the fitted trend (red line). The resistance of the setup can be computed from the inverse of the gradient, giving a value of 1.1 Ω .

2. Assembly and Testing of Self-Contained ECSPA System

Figure S7. (a) Schematic cross-section of the self-contained ECSPA prototype with full dimensions. The central Cu foam providing structural support to the system was a 30 mm x 45 mm Cu foam sheet (thickness = 5 mm) rolled into a cylinder. The counter electrode, placed concentrically on the outside, was a similar cylinder folded from a sheet of 50 mm x 120 mm Cu foam (thickness = 5 mm). The caps were 3D printed from Grey Resin using Form 2 (Formlabs, USA), which has an elastic modulus measured to be ~ 1 GPa. (b) Plot of strain vs. time, showing the alternating sequence of processing and compressive testing. The test was carried out using Shimadzu AGS-X fitted with a 10 kN load cell, at a strain rate of $\sim 10^{-4}$ /s.