

Electrochemically Driven Acidification Using 3D PANI Mesh Arrays: A Reagent-Free Approach for Sustainable pH Control

Published as part of ACS Electrochemistry *Special Issue* “Fundamental and Applied Advances in Electrochemical Technologies for Sustainable Water Treatment and Resource Recovery”

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Cite This: *ACS Electrochem.* 2026, 2, 2138–2149



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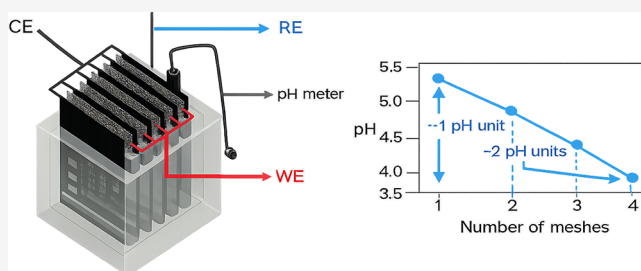
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ABSTRACT: We present a reagent-free electrochemical setup consisting of a newly developed 3D polyaniline (PANI)-coated stainless steel (PANI-SS) mesh array, which enables efficient pH control in both bulk and small-volume aqueous samples. Specifically, a customized electrochemical cell with a total volume of 40 mL hosts multiple PANI-SS meshes connected in parallel as the working electrode, together with a screen-printed carbon counter electrode and an Ag/AgCl reference electrode. The 3D mesh architecture substantially enhances the electroactive surface area, enabling rapid and scalable proton delivery that can be tuned by varying the number of meshes. A single PANI-SS mesh releases $\sim 3 \mu\text{mol}$ of protons upon applying 0.4 V for 200 s, lowering the pH of 40 mL of an NaCl solution from 5.5 to 4.3. Increasing the number of meshes to four further decreases the final pH to 3.4. The system also performs effectively in complex environmental samples such as brackish water, reducing the pH from 7.3 to ca. 3.8. Likewise, it successfully acidifies sediment-seawater suspensions (5% sediment) to the target pH range of 4–5, which is required for certain bioremediation processes. The PANI meshes can be sustainably regenerated through operation in acidic mining leachates, enabling reversible reuse and supporting a circular process. These findings demonstrate the potential of 3D PANI-based systems for efficient, scalable, and environmentally friendly acidification without the use of external chemical reagents.

KEYWORDS: polyaniline, electrochemical acidification, proton pump, sustainable pH control, environmental water samples



INTRODUCTION

The regulation of pH is crucial in numerous fields. It relates to many different aspects and events: it directly impacts bacterial activity and metabolic pathways in biological reactions, but pH is also imperative in certain environmental applications, including wastewater treatment, fermentation processes, and soil remediation. For example, acidic conditions promote bio-based processes such as biohydrogen production, volatile fatty acid production, and bioleaching for metal recovery.^{1–6} Especially, bioleaching, which uses microorganisms to extract metals from waste streams or metal-bearing ores, requires very low pH values for efficient resource recovery.¹ In analytical chemistry, accurate pH control is important because it affects the different chemical forms in which the analyte will be present. In some cases, such as chemical sensing, reaching and maintaining an optimum pH ensures reliable quantification, mitigates interferences, and improves the detection accuracy.^{1–6} For example, pH control facilitates the direct analysis of alkalinity by converting all acid-neutralizing species into

measurable forms.^{7–9} Also, pH creates a suitable condition for the formation of Keggin ions in the electrochemical detection of dissolved inorganic phosphate,^{1,10–13} and it helps suppressing hydroxide interference in ion-selective electrodes (ISEs).^{6,13–15}

Traditionally, the adjustment of pH in real samples relies on the manual or automated addition of strong acids or bases.^{16,17} In essence, it is a reagent-based approach that works at the lab scale but it is challenging to be implemented for real-time measurements and/or in situ applications. The strategy considers a macroscopic dimension, requires regular maintenance, involves the handling of chemical reagents, and generates wastes, raising miniaturization and decentralization limitations together with

Received: March 2, 2026

Revised: June 29, 2026

Accepted: July 27, 2026

Published: August 25, 2026



environmental and economic concerns. Accordingly, research on other means for on-demand control of sample pH, considering sustainable and controllable technologies that do not intrinsically involve the use of reagents, is currently accelerating.^{3,18}

Electrochemical methods applied to certain materials or electrode substrates have emerged as a promising alternative to recreate reagent-based sample acidification. Briefly, the acid or base reagent is substituted by an electrochemistry-driven process able to generate protons (H^+) or hydroxide ions (OH^-).^{3,7} This perspective greatly simplifies the overall workflow, minimizing, in turn, the produced waste and contamination risks. To our understanding, the most outstanding features are wide versatility and implementation with the global system (whether for further analysis or any processing/reaction needed in the sample) that is realistically accessible.³ For example, electrochemical pH control has been integrated into sensing platforms to enhance the analytical performance, but also to mitigate biofouling effects on electrode surfaces.^{9,19,20}

Water electrolysis is the technique that has been most widely proposed for electrochemical pH control of various samples. Its core involves the generation of H^+ or OH^- at the electrode surface by applying a constant potential or current.¹⁴ Read and Macpherson reported that sample pH can be locally adjusted from 6.4 to 2.0 (applying $+66 \text{ A m}^{-2}$) and from 6.4 to 10.0 (-5.8 A m^{-2}) with water oxidation through the boron-doped diamond (BDD) ring electrode.^{21–23} Considering a practical point of view, this actuator combined with an iridium oxide disk electrode can be used for heavy metal ion detection (e.g., Hg^{2+} and Cu^{2+}).²⁴ Another approach for the in situ generation of protons is the electrochemical oxidation of electrodes based on transition metals (e.g., molybdenum).^{25,26} Garçon and co-workers demonstrated that anodic oxidation of molybdenum, when coupled with a proton exchange membrane, enables efficient proton delivery, reducing the pH down to ca. 1 to facilitate subsequent detection of dissolved inorganic phosphate.¹⁰ Both strategies, electrolysis and oxidation of transition metals, require relatively high overpotentials that can lead to side reactions (e.g., hydrogen or oxygen evolution) or the formation of reactive byproducts (e.g., dissolved metal ions). Therefore, the risk of sample contamination and additional presence of interfering events/compounds is rather high, not only compromising a further analysis of the sample but also affecting electrode stability over time and the overall reversibility of the process.⁷ These drawbacks prompted the scientific search for alternative mechanisms and materials permitting more controlled, lower-potential operation.^{3,7,27}

In that context, a promising option is proton-coupled redox-active materials that can reversibly store and release H^+ during redox transitions generated by an applied potential or current. Balakrishnan et al. demonstrated that 4-aminothiophenol covalently attached to an electrode surface could reversibly release protons with minimal side reactions and within the potential window from 0.65 to 0.8 V.²⁸ Rapid pH changes were demonstrated in nanoscale volumes ($\sim 2.5 \text{ nL}$, from 7 to 3). Fomina et al. utilized quinone-based layers in microscale volumes to modulate sample pH (from 4.5 to 7.5) by applying microampere-level constant current.²⁹ These methods primarily induce pH modulation at the electrode surface, restricting acidification to nano and submicroscale volumes due to the limited amount of active material that is available. As a result, the proton storage ability is inherently constrained by the electrode's surface area and material properties.

On the other hand, electrodes modified with the conducting polymers PANI (polyaniline) and PANOA (poly(aniline-co-aminophenol)) were found to exhibit highly reproducible pH modulation capability. In essence, the redox-driven conversion from amines to imines in the backbone of the polymers is connected to H^+ delivery.⁸ The process can occur at ca. 0.4 V, making them suitable for environmental-based applications, including alkalinity detection, dissolved inorganic phosphate analysis, as well as CO_2 and dissolved inorganic carbon imaging.³⁰ Importantly, these concepts were based on sensor-actuator(s) cells in which thin-layer samples were considered (very low volumes in the order of 0.6–35 μL) to maximize the acidification ability. Overall, the use of PANI is more appropriate than other redox-active materials. PANI operates as a bulk-active polymer with a much higher proton exchange density, whereas 4-aminothiophenol and quinone layers are constrained by the poor proton storage ability of 2D surface structures. Then, PANI provides better electronic conductivity and a simpler, more affordable synthesis than PANOA. Furthermore, PANI's excellent structural resilience and stability allow it to be deposited onto three-dimensional substrates, including stainless steel meshes as those herein used, without sacrificing redox efficiency.

Herein, we investigate the capability of PANI to acidify bulk samples, in the order of tens of milliliters. We develop a novel material as well as an electrochemical-based methodology and cell to enable a large-scale application, considering the state of the art of PANI-based acidification. A 3D-printed electrochemical cell incorporates a varying number of 3D PANI-coated stainless steel (PANI-SS) meshes connected in parallel to form a working electrode that can be activated at a constant potential to generate a H^+ release process from the PANI material. The cell can host up to 40 mL sample volume for tuned and effective acidification. Moreover, a sustainable way of regenerating the PANI meshes using acidic mining leachates instead of sulfuric acid was investigated, creating a circular process. With the established approach, brackish water was acidified from environmental pH down to pH 3.8, while sediment-seawater samples obtained from an operative bioreactor reached pH 4.0.

■ EXPERIMENTAL SECTION

Electrode Preparation and Design of the Electrochemical Cell

The acidification system consisted of various PANI-SS meshes connected in parallel as the working electrode (WE), screen-printed carbon counter electrode (SPCE), Ag/AgCl wire as the reference electrode (RE), and a reservoir to allocate 40 mL of sample while being stirred at 150 rpm. The preparation and assembly of each electrode is illustrated in Figure 1a–c.

PANI was electropolymerized onto the commercially available SS mesh ($32 \times 44 \text{ mm}$) using cyclic voltammetry (CV). Then, to maintain the structural integrity of the PANI layer and prevent the mesh edges from contacting the electrochemical cell during installation or removal (thereby minimizing mechanical wear), each PANI-SS mesh was enclosed in a protective frame that secured the mesh edges and facilitated its placement in the cell (Figure 1a). The SPCEs were fabricated by a screen-printing technique with carbon ink on both sides of a 125 μm polyethylene substrate. Since the electrodes were entirely planar, placing them directly into the electrochemical cell could hinder the flow of samples between electrodes even with stirring. Therefore, it was cut into a serpentine pattern (Figure 1b). The commercial Ag wire was cut into a 10 cm piece, then twisted into a helix configuration (3 cm for

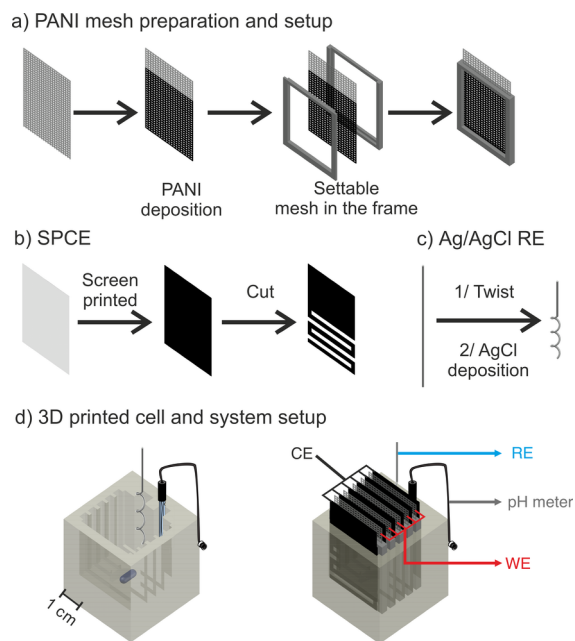


Figure 1. Illustration of the electrodes and the electrochemical cell. (a) Preparation of a PANI-SS mesh fixed in the protecting frame. This will act as the working electrode (WE). (b) Fabrication of the SPCE acting as the counter electrode (CE). (c) Fabrication of the Ag/AgCl wire used as the reference electrode. (d) Design of the 3D-printed cell.

the top untwist part and 3 cm in the twisted part) to increase the surface area of the RE dipped into the sample (Figure 1c). Then, the Ag wire was cleaned and AgCl was electrodeposited in a 0.1 M KCl solution with a current of 1 mA for 5 min to obtain the final Ag/AgCl wire.

The electrochemical cell was designed in AutoCAD for 3D printing using tough-PLA filament and the Ultimaker 3 printer (Ultimaker B.V., Netherlands). Up to 5 PANI-SS meshes, together with a maximum of 6 SPCEs (one more than the number of meshes) and one RE, can be allocated in the sample reservoir. The PANI meshes and SPCEs were alternately arranged, maintaining one additional counter electrode compared to the number of PANI meshes. Notably, the intermesh distance and positioning was maintained constant but depending on the total number to guarantee covering the entire sample space. The Ag/AgCl wire was fixed in a designated pocket on one side of the reservoir. Another empty space next to the first one can accommodate a pH meter for monitoring pH changes in the sample (Figure 1d). Finally, the reservoir contains customized notches to accommodate the PANI meshes.

Preparation of the 3D PANI-SS Meshes

To fabricate a PANI-based mesh for acidification purposes, commercially available SS meshes (0.127 mm diameter wires, model 304, Thermo Scientific) were used as the substrate. Each mesh was cut into a 32 mm × 50 mm piece, cleaned with 95% ethanol, and completely dried under nitrogen gas stream. Electropolymerization was conducted in a 0.1 M aniline/0.5 M H₂SO₄ solution, with the SS mesh serving as the WE and the Ag/AgCl wire as the RE. Three interconnected platinum rods (Model 6.0331.000, Metrohm Nordic AB) were used as the CE, providing sufficient surface area (approximately 23 cm² for 3 CEs) during electropolymerization.

Three electrochemical processes for PANI synthesis on SS meshes were investigated. In any case, the electrochemical process began by monitoring the open circuit potential (OCP, approximately 0.2 V) of the SS mesh for 10 s. Then, a constant potential of 1.1 V (vs Ag/

AgCl) was applied for 10 s to initiate PANI nucleation on the electrode surface in the absence of any stirring. Subsequently, the electrochemical polymerization of PANI was performed under various CV conditions, which are summarized in Table 1. Notably, over 50 scans, the potential window was extended from −0.6 to 1.0 V to ensure sufficient overpotential for monomer oxidation and reprotonation as the film thickened. The optimal strategy was found to be based on two subsequent potential windows from −0.35 to 0.85 V for 50 scans and from −0.6 V to 1.0 V for additional 25 scans. In the three cases, polymerization was carried out under moderate stirring (150 rpm) with a scan rate of 50 mV s^{−1}. These conditions were found to ensure uniform mass transport and homogeneous PANI deposition on the SS mesh. Notably, the optimization of the conditions for PANI electropolymerization was performed on small SS meshes (2 cm × 1 cm) and then translated to those used for the 3D acidification process.

Overall, the synthesis protocol follows established procedures to obtain robust PANI films.^{8,31,32} During CV electropolymerization, film growth increases thickness and resistance, leading to a progressive shift of the redox peaks due to the internal resistance (iR) drop across the film. If a fixed potential window is maintained, these shifts can result in incomplete redox transitions and non-uniform growth. Therefore, the potential window is sequentially expanded to compensate for the increasing resistance and to ensure sufficient effective overpotential for continuous monomer oxidation and proper polymer protonation. This approach enables more uniform film growth and improved mechanical stability compared to a single static window, resulting in thicker and more robust PANI coatings.

Bioleaching Tests with PANI-Acidified Sediment Sample

A set of bioleaching experiments was conducted to assess the difference between the preacidified sediment sample with PANI (pH 4.5) and initial acid addition (pH 4.5) on bioleaching performance. The experiments were conducted in 100 mL glass Erlenmeyer flasks with a working volume of 40 mL. Solid content of the sediment in the flasks was set to 5% (50 g/L) by adding saline water (6 psu). Later, 0.4 g of sulfur was added to the flasks to promote the sulfur oxidation by native sulfur oxidizing bacteria in the sediment. The control set was also prepared, without addition of sulfur. Initial pH of the bioleaching sample set was reduced to pH 4.5 with PANI or HCl. The experiment was run for 18 days with continuous stirring at 180 rpm. As an indicator for microbial activity, both pH and SO₄^{2−} were measured during the experiments. pH was measured with Mettler Toledo FiveEasy™ pH bench meter and SO₄^{2−} concentrations were monitored with ion chromatography (IC) (850 Professional IC Anion, Metrohm, 2.850.2030) equipped with a Metrosep A Supp 5–150/4.0 column (Metrohm, 6.1006.520) and an 863 Compact IC Autosampler (Metrohm, 2.863.0010).

A calibrated pH meter (Metrohm 913 pH meter and 827 micro pH meter) was used to track the pH values in real time, while only the final stable pH was considered for calculation and evaluation of the PANI-SS mesh proton delivery ability. Following each acidification phase, an equilibration time of 5–10 min was used to ensure measurement precision and to account for any lag due to incomplete proton diffusion. Only until the measurement had stabilized was the final pH measured. Measurements were carried out at least in triplicate under

Table 1. Experimental Conditions for PANI Electropolymerization on the SS Mesh^a

PANI type	initiation	up to the 50th cycle	from the 50th cycle
50 scans	1.1 V for 10 s	from −0.35 to 0.85 V	
75 scans	1.1 V for 10 s	from −0.35 to 0.85 V	from −0.60 to 1.00 V 25 cycles
100 scans	1.1 V for 10 s	from −0.35 to 0.85 V	from −0.60 to 1.00 V 50 cycles

^a0.1 M aniline and 0.5 M H₂SO₄ solution. Scan rate: 50 mV s^{−1}.

similar conditions for every experiment (except for the bioreactor sample acidification, where a single sample was separated into six identical portions for individual processing).

The samples originated from the Baltic Sea presented a salinity of approximately 0.1 M, which is similar as the control experiments performed with the 0.1 M NaCl sample solutions. Accordingly, initial systematic studies to ensure the model system mimicked the real-sample ionic strength. Then, the alkalinity of the seawater was considered when calculating the number of protons delivered. Detailed titration protocols and alkalinity results are provided in the [Supporting Information](#). By measuring the direct pH change without complex pre-treatment, we accurately captured the real proton delivered, considering both pH changing and overcoming the alkalinity within the complex matrix. To prevent suspended particles from covering active sites, our cell design included active stirring. Postexperimental energy dispersive spectroscopy (EDS) analysis of the meshes used in the bioreactor samples showed no significant accumulation of silicon (Si), confirming that site-blocking was minimal. This is further supported by the consistent proton transfer amounts observed across different samples. Also, a 5–10-min equilibration period was strictly followed to ensure that the pH readings reflected the stable bulk equilibrium of the complex matrix rather than localized fluctuations.

RESULTS AND DISCUSSION

Optimization of PANI Synthesis on SS Meshes

Table 1 presents the three conditions investigated to integrate PANI on SS meshes. A strategy of increasing the number of CV cycles was followed to obtain thicker PANI films. In principle, this is convenient toward enhanced proton storage and release performance.^{8,31,32} While experimental potential windows were selected based on our previous research on PANI film deposition on traditional substrates (e.g., glassy carbon or indium tin oxide),⁸ the total number of cycles was selected based on the observed CVs. In detail, a preliminary experiment considered electropolymerization from -0.35 to 0.85 V with 100 cycles.

The generated PANI film was rather thick but fragile, showing it breaks easily. However, applying the option of two subsequent, different potential windows, from -0.35 to 0.85 V during the first 50 scans and then from -0.60 to 1.00 V for an increasing number of scans (25 and 50), was found to produce more robust films. In addition, this protocol ensures sufficient overpotential for monomer oxidation and reprotonation as the film thickened. This sort of potential adjustment is known to effectively compensate for the iR drop, enabling thicker and more uniform coatings within practical deposition times. In the CVs registered during the three established synthesis (Figure 2), it was observed that, as the PANI film grew, the redox peak positions gradually shifted, which can be attributed to an increase in the iR drop across the resistive film because of the resistance increasing with film thickness ($R \propto L/\sigma A$).^{8,33}

Upon closer inspection on the synthesis CVs (Figure 2), pairs of anodic and cathodic peaks typically observed in PANI electropolymerization appeared, thus confirming successful deposition onto the SS-mesh electrodes.³⁴ Considering the anodic scan, the first peak at 0.2 V involved the redox process from entirely neutral (leucoemeraldine) to partially oxidized PANI (emeraldine).³⁵ The less intensive peak at the anodic limit (~ 0.85 V) was assigned to the redox process between the partially and fully oxidized PANI state (pernigraniline). These transitions involve the proton-coupled oxidation of amine to imine functionalities within the polymer backbone, a

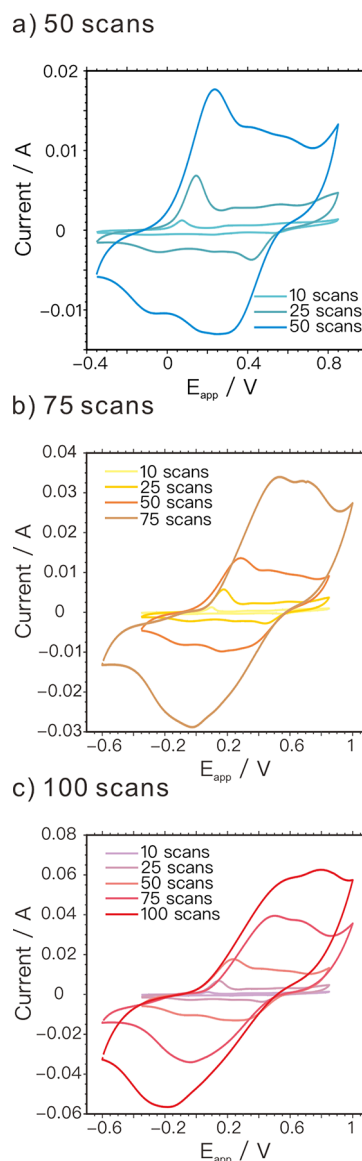


Figure 2. Cyclic voltammograms recorded during the electropolymerization of PANI onto SS mesh electrodes under different synthesis conditions. (a) 50 scans: 50 successive scans from -0.35 to 0.85 V. (b) 75 scans: 50 successive scans from -0.35 to 0.85 V followed by 25 successive scans from -0.60 to 1.00 V. (c) 100 scans: 50 successive scans from -0.35 to 0.85 V followed by 50 successive scans from -0.60 to 1.00 V. All polymerizations were conducted in a solution of 0.1 M aniline and 0.5 M H_2SO_4 with a scan rate of 50 mV s^{-1} .

hallmark of PANI electroactivity.^{8,35,36} Additional peaks between 0.2 and 0.8 V, particularly the second oxidation peak that becomes more prominent after 50 scans, was ascribed to the oxidation of degradation products formed from polymer hydrolysis during the electropolymerization process.^{34,37}

In the case of just applying 50 scans from -0.35 to 0.85 V (Figure 2a), the increased peak current and a polymerization peak at ~ 0.20 V were observed, confirming active PANI growth. For 75 scans (extra 25 scans from -0.60 to 1.00 V, Figure 2b), the polymerization peak currents kept increasing, suggesting that the growth was not yet completed at this point. Notably, a peak at ~ 0.55 V became more prominent compared to the prior film (50 scans), indicating the development of

secondary oxidation processes. Upon reaching 100 scans (extra 50 scans from -0.60 to 1.00 V, Figure 2c), the growth rate was found to slow down, as evidenced by a minor increase in peak current. This was likely due to transport limitations within the thicker polymer layer that is getting formed compared to the two previous films (50 and 75 scans).

Morphology Study of the PANI-SS Meshes through Scanning Electron Microscopy (SEM)

The SEM images of the three PANI films (Figure 3a–c) revealed the progressive evolution of PANI morphology with the increasing number of CV scans, with distinct structural transitions in polymer growth, branching, and porosity. At the 50 CV scans stage (Figure 3a), the PANI layer exhibited a fiber-like structure composed of compact and short fibrils that bridged adjacent mesh wires. This morphology reflected an early stage of PANI polymerization, where the film growth was relatively dense and uniform, with minimal voids and negligible evidence of degradation features.^{8,38} Prolonged deposition to 75 cycles (Figure 3b) resulted in a more porous and elongated fibrillar scaffold with well-interconnected strands. Interestingly, SEM images obtained in higher magnification showed that the intersections of the mesh wires (Figure 3d) possessed a slightly thicker PANI layer than the single wires, which can be attributed to the structural influence of the substrate. The reduction in fibril diameter is likely due to an increase in film resistance and the associated iR-drop. Namely, with the continuous PANI deposition, the film thickness increased while the interfacial overpotential decreased according to Butler–Volmer kinetics ($\text{growth rate} \propto e^{\eta}$), slowing the local deposition rate and thus favouring the formation of thinner fibrils.

In addition, as shown in Figure S1, the crossing SS wires were more pronounced with the PANI film following the shape of the mesh substrate. PANI deposition with 100 scans (Figure 3c and e) resulted in a PANI film near to completely covering the SS mesh substrate, forming a continuous solid layer rather than following the shape of the mesh electrode. Although offering an enlarged surface area, the thinner fibrils and reduced cross-linking were found to compromise mechanical cohesion: the layer was found to be physically unstable, exhibiting signs of fraying and delamination during rinsing. In contrast, the optimized 75-scan meshes maintained structural integrity without observable delamination for over 50 acidification use (one week), justifying their selection for consistent acidification performance. The protective function of the PANI coating, which passivates the underlying SS and successfully stops possible substrate corrosion during the acidification process, is also considered throughout this one-week operating window.

Because the PANI film with 50 CV scans did not provide sufficient film coverage, we further examined the stability and porosity of PANI films synthesized with 75 and 100 CV scans. From a macroscopic perspective, the mesh synthesized with 75 scans maintained visible openings and good permeability, with water readily passing through it (Figure S2). In contrast, in the PANI film with 100 scans, the permeability was significantly reduced due to low film porosity. To further assess mechanical stability, the synthesized PANI-SS meshes were subjected to moderate stirring at 500 rpm in distilled water. While PANI films synthesized using 75 scans remained intact, the loosely packed structure at 100 scans was easily abraded off

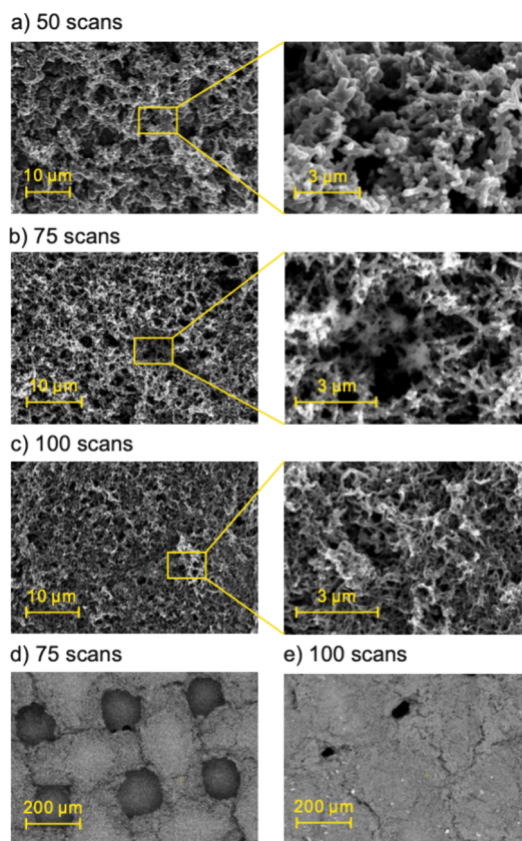


Figure 3. SEM images for PANI-SS meshes synthesis with (a) 50 scans, (b) 75 scans, and (c) 100 scans in micro view. Macro views of the 75 and 100 scans are provided in (d) and (e).

the mesh, particularly in such regions where the PANI film was unsupported on the mesh pore base. This result highlighted a critical trade-off between porosity, mechanical stability, and adhesion to select the optimal PANI film on SS meshes. While increased CV scans promoted polymer growth, excessive deposition on the SS meshes led to a fragile structure with poor mechanical endurance. Overall, we identified 75 scans as optimal for the polymerization process, using this film for further studies.

Scanning Electrochemical Microscopy (SECM) Study of the PANI-SS Meshes

SECM was utilized to investigate the electrochemical activity and structural characteristics of the PANI-SS meshes which were synthesized with 75 CV scans. The SECM investigation provided better understanding of the mesh morphology and material contrast between PANI-modified part and pure SS mesh. SECM imaging was performed at constant height feedback mode with a tip-to-substrate distance of ~ 17 μm and using a 25 μm diameter Pt ultramicroelectrode (UME) as the tip; more information is provided in Supporting Information and Figure S3. The 3D surface map of local conductivity, top-down 2D projection, and line-scan current profile along the path were used for the analysis. Figure 4a and b show a 2000 μm × 2000 μm SECM map, revealing material contrast between bare SS and PANI-coated regions. The left portion of the image (from $x = 0$ to 1000 μm) corresponds to uncoated SS, while the right portion $x > 1000$ μm represents the PANI-

coated area. This transition was confirmed by the line scan in Figure 4c, which traversed diagonally across both regions.

The measured current response at the UME was influenced by both the intrinsic conductivity of the substrate and the tip-to-substrate distance variations caused by sample roughness and topographical differences. While SS inherently exhibited high conductivity, the PANI-coated regions display an enhanced current response. Notably, the PANI layer was locally thicker at the intersections of the meshes, further influencing the tip-to-substrate distance and local electrochemical performance. Thus, the SECM micrograph reflected the material contrast between the PANI-covered areas and the pure SS mesh region. Because the PANI-SS mesh was placed on an insulating double-sided tape, the mesh holes produced substantially lower current magnitudes due to the negative current feedback of the tape. Besides, the estimation of the sample thickness based on the SEM and SECM characterization (from the results shown in Figures S1 and S3, respectively) was accomplished. The analysis revealed that the width of interconnected SS single wires was 127 μm , while it was ca. 173 μm , once the PANI film was applied yet providing pores of ca. 158 μm .

The Influence of Electrochemical Parameters in Acidification from PANI-SS Meshes

To understand the oxidation conditions (and related parameters) needed to observe an effective sample acidification process from PANI-SS meshes, a systematic study was conducted to evaluate the effects of different oxidation potentials and times. After identifying the most suitable conditions for the single PANI-SS mesh, the optimized parameters were further applied to the system with an increased number of meshes^{1–5} to maximize the acidification capability in the bulk 0.1 M NaCl solution.

Regarding the applied potential, the 75-scan PANI-SS mesh was used to acidify 40 mL of 0.1 M NaCl solution (initial pH of 5.33 ± 0.06) under oxidation potentials of 0.1, 0.2, 0.3, and 0.4 V for 200 s. Figure 5a displays the dynamic charge and Figure 5b displays the amount of delivered protons calculated from the difference in pH observed before and after acidification at the increasing potentials. For simplicity, such a delivered number of protons is called from now on as “capacity”. As observed, the increase in oxidation potential from 0.1 to 0.4 V resulted in an increase in the total charge registered within 200 s, which directly correlated with an increase in the capacity.

The rapid release of charge at the beginning of each potential step was followed by a gradual current decline, indicating a decrease in the charge transfer rate (calculated as the slope of the charge-time profile) over time (see Figure S5 and Table S2). Furthermore, most of the charge release occurred within the first 100 s, particularly at higher oxidation potentials (e.g., 0.4 V).

Continuous pH monitoring during the experiment showed that at lower oxidation potentials (0.1 and 0.2 V), the pH change was minimal, indicating insufficient proton release. This was likely due to insufficient PANI oxidation (i.e., converting amines into imines), resulting in inadequate proton transfer into the solution to be manifested in a pH change in its bulk. In contrast, with oxidation potentials above 0.3 V, PANI can be adequately oxidized, releasing enough protons to lower the pH by half a unit or more. Applying 0.4 V, a single PANI-SS mesh resulted in a significant increase in capacity, reducing the pH down to 4.3. Notably, previous studies showed that PANI-mediated acidification exhibits a potential-dependent behavior, with higher oxidation potentials accelerating material degradation and decreasing its lifetime.⁸ Accordingly, applying PANI under certain acidification levels involves balancing pH requirements and the level of degradation of the utilized film.

Next, three PANI-SS meshes were repeatedly used to acidify a 0.1 M NaCl solution five times consecutively. After each acidification cycle, the electrode was regenerated in 10 mM H_2SO_4 with an applied potential of 0 V for 600 s. Excellent repeatability was demonstrated, with no significant variation in the acidification performance: final pH stabilized at 4.24 ± 0.04 . After the last regeneration, the PANI-SS mesh was stored for a week and then used for an extra acidification, resulting in a final pH of 4.27 ± 0.05 . The results pointed out a stable, consistent PANI-SS mesh acidification performance at an oxidation potential of 0.4 V, with high repeatability and a functional lifespan exceeding one week.

To investigate the influence of oxidation time on the proton delivery process, the 0.1 M NaCl solution was acidified using one PANI-SS mesh electrode activated at 0.4 V for 50, 100, 200, and 300 s. The results are shown in Figure 5c and d, with the dynamic current profiles being shown in Figure S5b. Within the same time interval, the charge-time curves showed a generally consistent trend. As time increases, the slope of the dynamic charge curve decreases, indicating that the charge transfer rate decreases over time. The current gradually

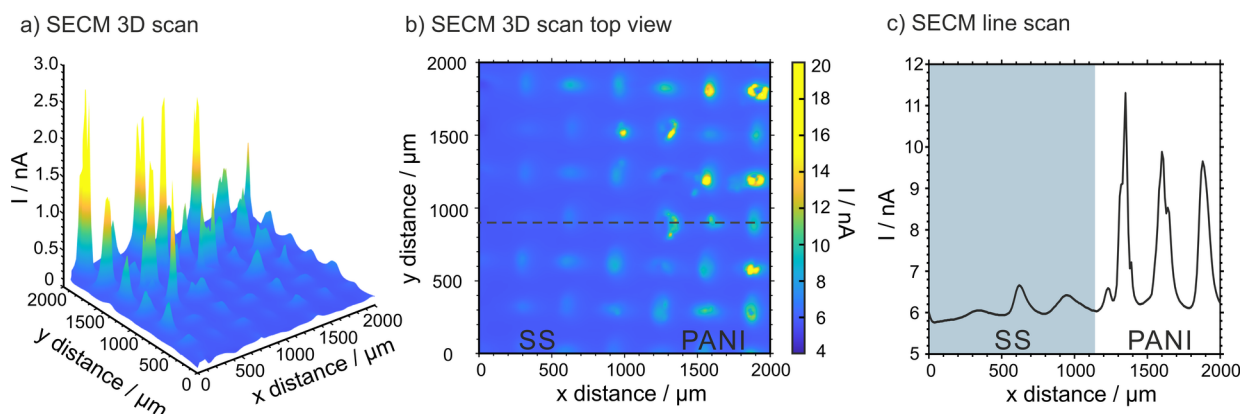


Figure 4. SECM images for a SS / PANI-SS mesh sample prepared with the 75-scan procedure. (a) 3D surface characterization. (b) Top view of the 3D surface characterization. (c) Line-scan profile corresponding to the probe's path in (b).

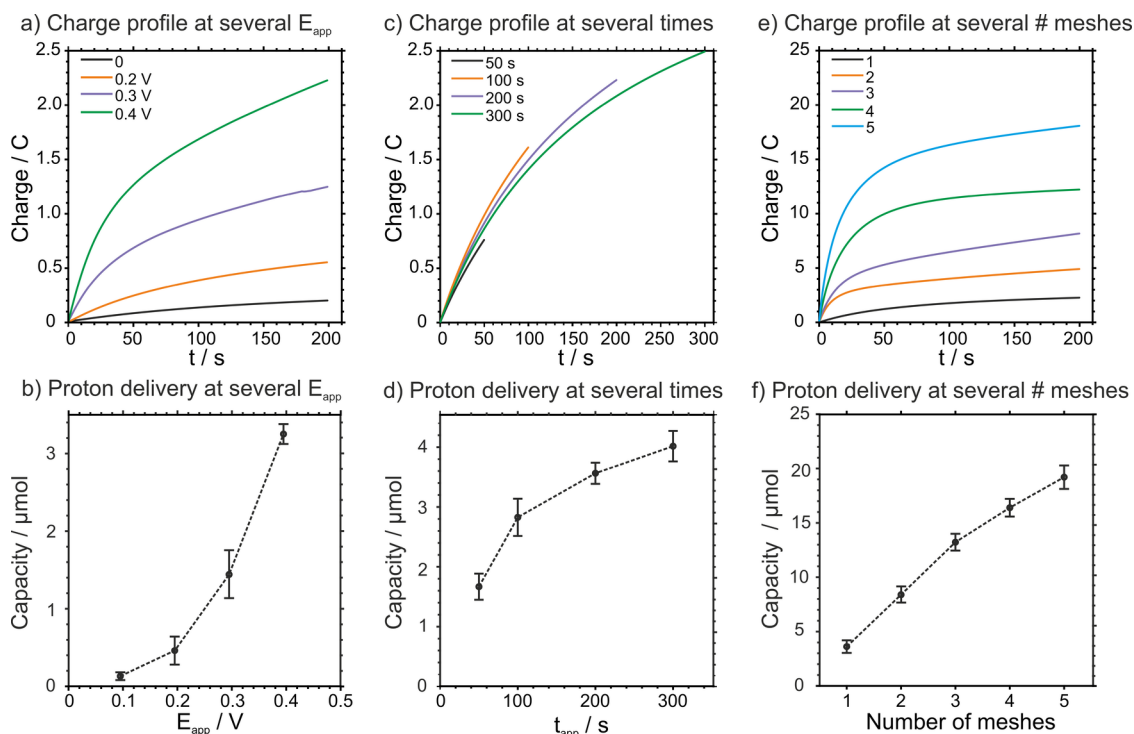


Figure 5. Charge profiles (a, c, and e) and the capacity (b, d, and f) observed at different oxidation potentials (a and b), oxidation times (c and d), and number of meshes (e and f). The error bars represent the standard deviation of $n = 3$ similar experiments.

decreases and flattens out, further supporting the conclusion that the charge transfer rate is not constant and is faster in the early stages, especially within the first 100 s. Extending the oxidation time to 300 s (green line in Figure 5c) increases the accumulated charge by only 9% relative to 200 s (yellow line in Figure 5c), indicating that most of the total charge is transferred within the first 200 s.

Table S3 contains a comparison of the pH variation achieved after each time, considering the solution's initial pH of 5.46 ± 0.10 . After 200 s, the pH decreased down to 4.21 ± 0.02 , while extending oxidation to 300 s resulted in a slightly lower pH of 4.15 ± 0.03 , reflecting a $\sim 13\%$ of increase in the total amount of protons that were delivered from the mesh to the solution (from 3.53 ± 0.17 to 3.98 ± 0.25 μmol , considering the initial and final pH of the sample). Even though the amount of integrated charge did not increase significantly over 200 s, a long oxidation period might be required to achieve more pronounced pH shifts in samples with significant buffer capacity, e.g., environmental waters. In practice, 200 s offered a balanced trade-off between charge utilization for proton delivery and minimal energy input for rapid pH adjustment. Effectively, if a lower final pH is required or the sample presents a high buffer concentration, extending the oxidation time can facilitate proton release. This flexibility allows tailoring the acidification procedure to specific application requirements.

Acidification Based on Increasing Number of PANI-SS Meshes

To further enhance proton delivery, the effect of increasing the number of PANI-SS meshes (ranging from one to five) was systematically investigated using the optimized parameters (0.4 V potential and 200 s duration). The results shown in Figure 5e and f as well as Table S4 demonstrated that the accumulated

charge and capacity increased with the number of meshes involved in the setup. The acidified solution exhibited a step-wise decrease in pH, reaching a value below 4 when two or more meshes were used. Under identical experimental conditions, employing five PANI-SS meshes, the pH of the sample solution reached a minimum of 3.36. However, as the number of meshes increased beyond three, the PANI-SS meshes became closer together, and the initial current during oxidation rapidly increased (Figure S5c), which manifested in the charge transfer rate not changing linearly with the number of meshes.

Importantly, varying the number of PANI-SS meshes in the system was found to affect the proton delivery per mesh during acidification, calculated considering the initial and final pH of the sample (Table S4). It remained consistent at approximately 3.62 $\mu\text{mol}/\text{mesh}$ when one mesh was used and increased slightly to 4.20 $\mu\text{mol}/\text{mesh}$ in the case of two meshes. It seemed to be maximized at 4.41 $\mu\text{mol}/\text{mesh}$ with three meshes but decreased down to 4.10 $\mu\text{mol}/\text{mesh}$ with four. Introducing a fifth mesh in the system further reduced the capacity per mesh to 3.84 $\mu\text{mol}/\text{mesh}$, despite a further increase in the corresponding charge.

Regeneration of PANI with Mining Leachates

The regeneration of PANI films under acidic conditions has been extensively demonstrated in previous studies.^{8,39} To investigate a more sustainable alternative, acidic mining leachates were tested as regeneration media. In this context, the leachates served as proton sources to restore the PANI film to its original, protonated state. For such a purpose, three samples were investigated, and the performance was compared to 10 mM H_2SO_4 : leachates dominated by HCl, H_2SO_4 , or HNO_3 . Because the raw leachates were highly acidic (concentration in acids around 6 M), they were diluted with distilled water until a pH of 1.6,

ensuring that the proton concentration was comparable to that of the 10 mM H_2SO_4 solution. In any case, the regeneration procedure involved applying a constant potential of 0 V for 600 s to facilitate the electrochemical reduction of PANI.

After regeneration in each sample, the meshes were oxidized in 0.1 M NaCl at 0.4 V for 200 s, and the proton release was quantified by both the capacity (considering the initial pH) and the resulting pH decrease. The results are summarized in Table 2. Regardless of the regeneration sample, the regenerated meshes consistently lowered the pH of the solution from ~ 5.6 to ~ 4.3 . The resulting capacity was around $3.07 - 3.55 \mu\text{mol}$, values essentially close to those obtained after regeneration in standard 10 mM H_2SO_4 (final pH: 4.33 ± 0.06 ; capacity: $3.47 \pm 0.07 \mu\text{mol}$). These findings confirmed that diluted mining leachates were fully compatible with PANI regeneration, providing reproducible performance comparable to that of laboratory-prepared acids.

Beyond their acidic nature, mining leachate samples contained various (metal) ions, primarily Fe, Al, Na, and Si (see Table S5). Assessing whether the regenerated PANI-SS meshes maintained their purity after rinsing or were contaminated by these external elements was crucial. The SEM-EDS analysis was conducted on seven PANI-SS mesh samples in total, as follows: (i) newly synthesized PANI-SS mesh, (ii) PANI-SS mesh regenerated in the three different leachates as well as 10 mM H_2SO_4 , and (iii) PANI-SS mesh subjected to acidification in NaCl solution and sediment-containing sample (freshly used after the synthesis). Targeted elemental analysis was performed for ions potentially present in the leachate (Fe, Al, Na, Si) as well as elements inherent to the PANI-SS mesh structure (C, Fe, S).

The results presented in Figure 6 showed that the dilution of the acidic leachates (60-time dilution for H_2SO_4 -based samples and 30-time dilution for HCl- and HNO_3 -based samples) reduced metal ion concentrations, as expected. EDS results revealed the presence of a small amount of Si and Na, with a trace amount of Al (less than 1%). A consistent presence of Fe and S was detected by EDS in all regenerated PANI-SS meshes. According to the initial compositional data of each leachate sample (Table S5), the Fe content was relatively low compared to other metals. Therefore, given the low likelihood of Fe contamination from the leachates, our observations were attributed to some parts of the SS substrate underlying the PANI film. With the SS being susceptible to oxidation, it may release Fe ions that subsequently contaminated the outer PANI layer and cause the increasing Fe detected through EDS. The presence of S was likely due to the use of H_2SO_4 as the electrolyte for both synthesis and regeneration of the PANI films, as residual sulfate may appear within the porous PANI structure, even after copious rinsing. Another noteworthy observation was the presence of Si, particularly in the meshes regenerated with HCl (0.2 atom %) and H_2SO_4 (0.1 atom %) leachate samples.

It is important to note that SEM-EDS analysis provides information on surface composition and potential adsorption or incorporation of elements within the PANI matrix but does not directly quantify metal ion release into the solution. Overall, the results suggested that PANI meshes regenerated using mining leachate wastes were generally resistant to metal ion contamination and hence, no subcontamination of the sample to be acidified is expected. Specifically, the low levels of detected foreign elements indicate minimal surface retention

Table 2. Investigation of the Acidification of 0.1 M NaCl Solution Using a PANI-SS Mesh Regenerated with Different Mining-Based Samples (MS)

regeneration solution	pH		amount of H^+ (μmol)
	start	final	average
H_2SO_4 MS	5.59 ± 0.12	4.37 ± 0.05	3.07 ± 0.06
HCl MS	5.60 ± 0.06	4.32 ± 0.05	3.28 ± 0.02
HNO_3 MS	5.61 ± 0.08	4.28 ± 0.08	3.55 ± 0.07
10 mM H_2SO_4	5.66 ± 0.13	4.33 ± 0.06	3.47 ± 0.07

after rinsing, although no direct quantification of metal leaching into solution was performed. Notably, in the control experiment where acidification was performed in 0.1 M NaCl, the elemental composition of the mesh remained consistent with that of the pristine PANI mesh, showing negligible variation; in contrast, significantly higher Si accumulation (1.2 atom %) was detected in the PANI-SS meshes utilized in the acidification of bioreactor sediment-containing samples. Given that these samples inherently contained high Si concentrations (primarily in the form of SiO_2), the porous nature of PANI facilitated Si adsorption and retention. Thus, the minor Si contamination observed after the regeneration was unlikely to impact samples acidification process, as the samples themselves contained substantial amounts of Si. These findings validated the use of mining leachates for PANI regeneration, offering a sustainable approach that not only recovered waste protons from mining byproducts but also aligned with green chemistry principles by minimizing reagent consumption and waste generation.

Acidification of Brackish Water Samples

Following, the feasibility of using PANI-SS meshes for brackish water acidification was investigated. Each experiment involved acidifying 40 mL of the sample under a constant oxidation potential of +0.40 V. Since the brackish samples had high alkalinity, a prolonged oxidation for 300 s was selected. Increasing the number of meshes was considered (from 1 to 5). After each acidification, all the meshes used for acidification of the sample were individually regenerated in the diluted H_2SO_4 -based mining leachate. The relationship between the number of meshes and proton delivery exhibited a trend like that observed in the unbuffered 0.1 M NaCl system (see Table 3 versus Table S4).

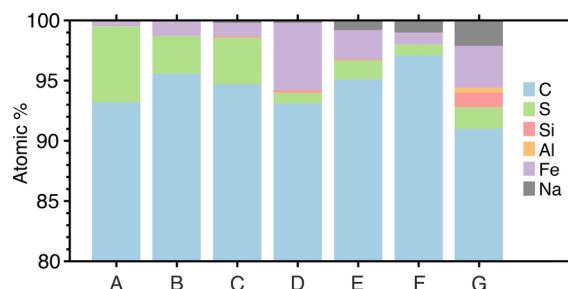


Figure 6. Atomic % of C, S, Si, Al, Fe, and Na detected with EDS in various PANI-SS meshes: (A) a raw PANI-SS mesh before any use, PANI-SS meshes regenerated in different acid solutions: 10 mM H_2SO_4 (B) as well as diluted HCl (C), H_2SO_4 (D) or HNO_3 -based mining leachates (E), and PANI-SS meshes used for acidification in 0.1 M NaCl (F) and a bioreactor sample containing 5% sediments (G).

Each number of meshes involved in acidification was tested in triplicate, consecutively using the same regenerated electrodes.

The initial pH of brackish water was 7.33 ± 0.08 and, as the number of meshes increased from one to five, both the transferred charge and the final pH achieved after acidification progressively improved. With the five PANI-SS meshes, the pH reached a minimum of approximately 3.89 (Table 3). Considering the solution's inherent alkalinity, the calculation of total proton delivery must account for two components: the protons consumed to overcome the initial alkalinity, and the protons used to achieve the observed pH reduction. Therefore, instead of focusing solely on pH reduction as previously for the NaCl sample, the proton delivery was calculated based on the pH shift and solution alkalinity of 0.7 mM, as shown in the Supporting Information (Section 2). Using three meshes, the capacity per mesh reached a maximum of $5.08 \mu\text{mol}/\text{mesh}$, after which the capacity per mesh decreased slightly, mirroring the trend observed in the 0.1 M NaCl solution. The overall capacity per mesh in the buffered brackish water was found to be greater compared to the (unbuffered) NaCl sample.

To determine the lowest achievable pH using the PANI-SS mesh system, experiments were conducted with five meshes under extended acidification durations, applying not only the standard oxidation potential of 0.4 V, but also elevated potentials of 0.5 and 0.6 V to evaluate their impact on proton transfer and pH reduction (Table 4). Notably, the current profile in Figure S5a indicated that the system did not reach a steady state after 300 s. Because this may suggest that the PANI film possessed residual ability for further oxidation, the duration for acidification was extended to 600 s. At an applied potential of 0.4 V, the resulting pH decreased to 3.73 ± 0.05 , correlating with a measurable release of $25.18 \pm 0.52 \mu\text{mol}$ of protons. Increasing the potential to 0.5 V resulted in a further pH reduction to 3.57 ± 0.03 , corresponding to $29.11 \pm 1.16 \mu\text{mol}$ of released protons.

Unlike the stable repeatability observed at 0.4 V, applying 0.5 V led to a significant worsening in cyclability. Consecutive acidification cycles showed diminishing proton release, with

final pH values increasing from 3.54 to 3.56, and even reaching pH of only 3.61 after the third round. This performance loss proved to be irreversible since the meshes failed to recover their initial performance even after an extended relaxation period overnight. This confirmed that while higher potentials might offer an increased proton release feature, they could induce permanent structural damage that simple regeneration cannot repair. The irreversible acidification process became particularly pronounced at an oxidation potential of 0.6 V: although the sample was acidified to a pH of 3.51, the PANI-SS mesh suffered severe degradation, and the regeneration was proven to be ineffective. Accordingly, subsequent acidifications with the same (regenerated) mesh revealed pH values shifting substantially (only reaching a final pH of around 3.8 or higher), rendering it unsuitable for reliable long-term reuse under these experimental conditions. Notably, conclusions regarding electrode degradation are based on the observed loss of regeneration capability, the electrochemical response, and irreproducible final pH values rather than on a statistical evaluation of repeated measurements with the same mesh.

These findings are strongly supported by existing literature, which links excessively high oxidation potentials to PANI over-oxidation, a process known to reduce electrochemical stability and cause polymer degradation via side process other than proton delivery.^{8,32,37} In conclusion, the oxidation time should be the primary tunable parameter to accommodate different sample conditions and target pH levels. While the acidification potential can also be adjusted, it is less recommended; applying potentials exceeding 0.5 V may compromise the lifetime and reversibility of the PANI-SS meshes.

One of the meshes used in this study was considered only in experiments involving an applied potential of 0.4 V, both in artificial and seawater samples, to evaluate its lifetime. This PANI mesh was reused as needed in a set of experiments lasting 18 days, demonstrating no operational change in this period after proper regeneration. Within this time frame, the mesh was used for a number of 16 acidification processes. Regarding biofouling in seawater samples, accumulation of organic matter or microorganisms on the mesh could

Table 3. Influence of the Number of PANI-SS Meshes on the Acidification of the Brackish Water Sample^a

mesh number	pH		ΔpH	amount of H^+ (μmol)	H^+ (μmol) per mesh
	start	final		average	
1	7.17 ± 0.07	6.41 ± 0.04	0.77 ± 0.10	3.76 ± 0.05	3.76 ± 0.05
2	7.26 ± 0.05	5.97 ± 0.04	1.28 ± 0.09	9.27 ± 0.94	4.64 ± 0.47
3	7.18 ± 0.07	4.76 ± 0.05	2.42 ± 0.13	15.24 ± 0.40	5.08 ± 0.13
4	7.25 ± 0.02	4.05 ± 0.06	3.20 ± 0.03	19.14 ± 0.17	4.78 ± 0.04
5	7.24 ± 0.05	3.89 ± 0.05	3.35 ± 0.03	23.08 ± 0.66	4.62 ± 0.13

^aApplied potential of 0.4 V for 300 s.

Table 4. Acidification of Brackish Water Samples with 5 Meshes at Different Applied Potentials for 600 s

E_{app}/V	pH		ΔpH	amount of H^+ (μmol)	H^+ (μmol) per mesh
	start	final		average	
0.4	7.41 ± 0.06	3.73 ± 0.05	3.67 ± 0.04	25.18 ± 0.52	5.03 ± 0.11
0.5	7.34 ± 0.05	3.57 ± 0.03	3.77 ± 0.15	29.11 ± 1.16	5.82 ± 0.23
0.6 ^a	7.38	3.51	3.87	33.94	6.79

^a $n = 1$, after 0.6V oxidation, the PANI could not be effectively regenerated.

potentially occur, depending on the specific organic load of the matrix. However, no visual degradation or loss of proton delivery efficiency was observed in our experiments. This suggests that under the evaluated conditions, biofouling did not compromise the system's performance in seawater.

Acidification of Sediment-Seawater Samples to an Aimed pH Range of 4–5

The PANI-SS mesh system was evaluated to achieve a specific pH reduction in sediment-based samples. Representative sediment samples were employed: each of them contained 5% (w/w) of various Baltic Sea sediment dispersed in a 0.1 M NaCl medium (characterized by an alkalinity of approximately 0.65 mM). The pH desired for this sample when a bioremediation process occurs is between 4 and 5, since the initial pH of the sediment has a strong impact on bioleaching efficiency.¹ For example, it was shown that when the initial pH was set to 5 for the sediment, the bioleaching acidification and oxidation effects were the highest when compared to other initial pH values.^{3,7,9,11} Previous findings in this work showed that three PANI-SS meshes were sufficient to lower the pH of brackish water to ~ 4.7 . Accordingly, 40 mL of each sample was acidified in an electrochemical cell using three PANI-SS meshes operated in parallel at +0.40 V for 600 s. The six independent sediment samples (S1–S6) were divided into two groups for acidification. Two sets of meshes with three meshes in each set were employed for each sample. After each acidification cycle, the meshes were rinsed with deionized water and regenerated in diluted H₂SO₄-based mining leachate before a new usage.

As presented in Figure 7 (data in Table S7), the results across all six samples were highly consistent. The average initial pH was 7.52 ± 0.05 , which dropped to a final pH of 4.54 ± 0.06 after treatment. The corresponding average capacity was 8.38 ± 0.24 μmol , confirming that the target pH range was reliably reached. The similarity in results between the two mesh sets confirmed the system's excellent reproducibility and the meshes' effective reusability after regeneration. Notably, the same meshes were used in the entire set of experiments, with all of them working properly and on demand during the approximately 1-month duration of the experiment.

Figure S6a depicts pH concentrations during the programmed bioleaching experiments. Among control samples (without sulfur addition), PANI-acidified samples reached a lower pH value (pH = 2.60) than the HCl-acidified samples (pH = 3.02). In terms of sulfur-added samples, both PANI-acidified and HCl-acidified samples had the similar final pH values (range of 1.39–1.42). However, HCl-acidified samples showed a slightly lower pH trend in the initial days. Figure S6b shows SO₄^{2−} production during experiments, since SO₄^{2−} is another indicator for sulfur oxidation and microbial activity during bioleaching. Control samples presented lower SO₄^{2−} concentrations when compared to the sulfur-added samples.

Although control samples had sulfur source originated from the sediment, a lower bioavailability for microorganisms showed the need for external sulfur addition. As observed in Figure S6b, SO₄^{2−} concentrations reached to 6099 and 6899 mg/L at the end of the experiments for PANI-acidified and HCl-acidified sediment samples, respectively, providing rather similar levels. Another observation was that HCl-acidified sediment samples provided higher SO₄^{2−} concentrations during the experiments. Although PANI-assisted sediment samples showed slightly

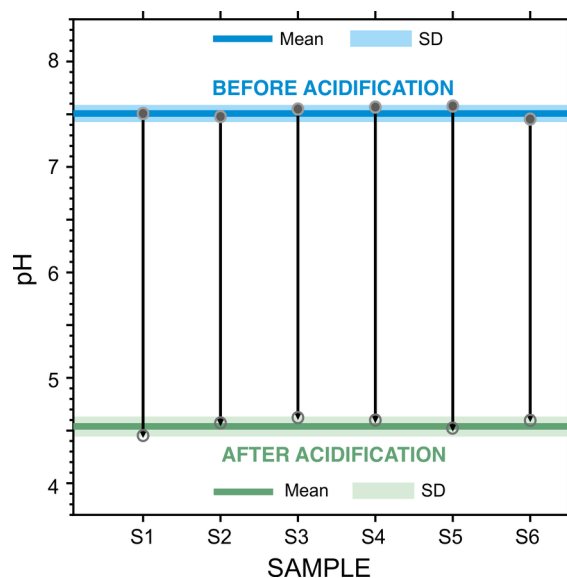


Figure 7. Initial and final pH of six Baltic Sea sediment samples (S1–S6) acidified using a system based on three PANI-SS meshes. Gray circles indicate pH values before and after acidification. Dark (blue and green) and light (blue and green) lines show the mean and standard deviation of 6 consecutive acidifications.

higher pH and lower SO₄^{2−}, they also promoted bioleaching efficiency and did not negatively affect the microbial activity. Notably, chemical costs related to the acid addition are one of the challenges for establishment and scaling-up the bioleaching systems, and PANI-SS meshes can provide chemical-free and nontoxic bioleaching operation instead.

Overall, this study showed a promising application of PANI-SS meshes for bioleaching operation for resource recovery. Compared to conventional acidification processes based on chemical addition, this strategy can enable controlled pH adjustment without introducing counter ions to the system and lower chemical consumption and secondary contamination in resource recovery and remediation processes. Importantly, this strategy can also be implemented to other resource recovery applications such as volatile fatty acids production in anaerobic fermentation and in situ remediation of metal-contaminated environments, which generally require acidic environment. While scaling up this concept is, in principle, feasible, it will require addressing key challenges related to mass transport limitations, electrode spacing, and ohmic losses. In larger systems, reduced diffusion rates and nonuniform proton distribution may limit efficiency, while increased interelectrode distances can lead to significant potential drops. These limitations could be mitigated through the development of advanced electrode architectures, such as segmented mesh arrays with independent current control, combined with optimized cell design and fluid dynamic modeling to ensure homogeneous proton delivery and efficient operation at scale.

CONCLUSIONS

This study demonstrates that PANI-SS meshes enable reagent-free electrochemical acidification. An electrochemical process based on an applied potential of 0.4 V for 200 s is identified as the optimal operating condition, providing efficient proton

release while maintaining material stability for various usage cycles. A key advantage of the system here developed is its regeneration using acidic mining leachates, which preserves the functionality of PANI and significantly reduces the need for synthetic chemicals. Notably, SEM-EDS analysis confirmed that this regeneration approach does not result in notable contamination or structural alteration of the PANI material. The PANI-SS meshes proved effective in complex environmental matrices, where the degree of acidification could be readily tuned by adjusting the number of meshes employed. Specifically, the pH of brackish water was reduced to 3.73 using five meshes, while sediment-based samples reached a pH of 4.5 with three meshes. Also, this approach showed feasibility in terms of bioleaching applications without disrupting traditionally obtained efficiency. Although further studies are required to fully assess scale-up possibilities (including long-term durability, matrix impact, and energy cost), the outcomes underscore the potential of the herein-presented strategy for pH adjustment in bulk samples, supporting circular acidification workflows and enabling closed-loop or automated operation in real-world environmental and biogeochemical applications.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acselectrochem.6c00085>.

Additional experimental details, calculations, experimental results (Tables S1–S7), and Figures S1–S5 (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The research is funded by the European Union's Horizon Europe (SYMBIOREM Grant agreement ID: 101060361) funded by the European Union. Views and opinions expressed are, however, those of the author(s) only and do not necessarily reflect those of the European Union or the European Research Executive Agency (REA). Neither the European Union nor the granting authority can be held responsible for them. M.C. acknowledges the support of the Swedish Research Council (Project Grant VR-2023-04808).

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