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# Activation of additively manufactured electrodes using methanol and ethanol solutions

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## Abstract

The use of polymer additive manufacturing to produce electrodes is an increasingly popular area of electrochemical research. However, one downside of additively manufactured electrodes is the frequent need to remove polymer from the electrode surface to reveal a triple-phase boundary in order for improved electrode performance to be realized. A common way to achieve this, is surface activation via chronoamperometry within an aqueous sodium hydroxide solution. However, it has not been investigated whether the same activation can be carried out effectively in solutions of sodium hydroxide in simple alcohols. Therefore, in this work, we study the effect of performing common chronoamperometric additive manufacturing electrode activation methodologies in methanolic and ethanolic solutions of 0.05 M sodium hydroxide and compare these to activation carried out in standard aqueous solutions at concentrations of both 0.05 M and 0.5 M. We show that the alcoholic solutions are more effective in removing polymer from the additive manufacturing electrode surface, but that this does not lead to any improvement in electrode currents, and furthermore appears to hinder electron transfer kinetics at the additive manufacturing electrode surface, with the latter effect shown to be related to differences in the surface functionality of the exposed carbon black filler particles. As well as being interesting chemical experiments in their own right, these results may well be of interest to electrochemists who intend for their additive manufactured electrodes to be applied in these alcohols or indeed other non-aqueous solvents.

## KEYWORDS

activation, additive manufactured electrodes, ethanol activation, methanol activation, sodium hydroxide activation

## 1 | INTRODUCTION

Additive manufacturing, also commonly known as 3D printing, refers to a manufacturing approach in which objects are made by the incremental addition of thin,

pseudo-2D layers of material until the desired 3D whole has been produced. This contrasts with better-established subtractive and formative approaches, which rely on removing material from or shaping an existing object, respectively [1].

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Typically, additive manufacturing workflows start with the generation of a 3D computer aided design (CAD) file, which is then processed into a series of 2D “slices” and a set of digital instructions which an additive manufacturing printer can use to produce parts. The layer-by-layer assembly approach inherently allows for complex designs, for example nested structures and overhangs, which are often not easily accessible by traditional manufacturing techniques. Additionally, since CAD files can be easily modified, the use of additive manufacturing inherently affords a high degree of customizability, and because additive manufacturing printers are relatively small, and becoming increasingly affordable, additive manufacturing printed parts are becoming increasingly easy to print locally and on demand. This can lead to significant reductions in lead time and carbon footprint, since parts need not be shipped, and reductions in cost and material waste, as there is reduced need to rely on specialist manufacturers or estimate the number of parts required [2]. Overall, these advantages of additive manufacturing has increased uptake in both industry and scientific research over the last couple of decades.

One research area in particular in which the benefits of additive manufacturing are being increasingly recognized is the field of electrochemistry, where the ability to produce complex, bespoke devices quickly and at low cost is especially appealing [3]. Examples of additively manufactured printed objects reported by electrochemists include, not only the types of fixtures and sample holders typical of laboratory settings [1b], but also additively manufactured used as direct replacements for traditional electrodes [4]. Typically, these consist of a conductive polymer composite filament which can be printed into the desired shape using a relatively cheap, and readily available Fused Filament Fabrication (FFF) printer. The polymer component is already widely used in FFF printers, using commercially conductive filaments are available comprising carbon black within PLA (Polylactic acid) filament [3]. A major disadvantage of additive manufactured electrodes is the frequent need to remove polymer material from the surface of the electrode before use, which exposes more of the conductive filler particles to the solution and improves additive manufactured electrode performance. This is known as “activation”, and a number of different additive manufactured electrode activation methods have been reported in the literature, including: solvent activation, where the surface layer of polymer is removed through exposure to a compatible solvent (*e.g.* PLA in DMF) [5]; mechanical activation, where surface polymer is physically removed, *e.g.* by polishing [6]; thermal activation, where surface polymer is removed by burning; ablative

activation, where the polymer is removed with high energy radiation, *e.g.* using plasma or a laser [7]; and electrochemical activation, where the additive manufactured electrode is placed in a solution which reacts with and removes polymer rapidly on application of electric potential [8]. The above list is not exhaustive; the topic of additive manufactured electrode activation has recently been discussed in more detail by Rocha *et al.* [9] While all of these methods successfully activate additive manufactured electrodes, they also have drawbacks, such as the use of expensive or complicated experimental equipment, the addition of significant time to the production process, inconsistent results, the use of hazardous solvents, or indeed a combination of all of the above.

One of the activation methods with the fewest drawbacks is electrochemical activation, which is typically carried out by chronoamperometry using PLA additive manufactured electrodes in a solution of hydroxide. The activation process is thought to occur by hydrolysis of the PLA polymer, a process also referred to as saponification, and has the advantage that the extent of the reaction can be relatively precisely controlled by experimental parameters such as applied potential, sodium hydroxide concentration, and time [8b,9]. This method also allows controlled activation of individual components of a single unit, since only the part to which potential is applied will be completely activated. Overall, it is clear that electrochemical activation is currently one of the best techniques for improving additive manufactured electrode performance.

To date, the only sodium hydroxide/solvent systems reported for electrochemical activation of additive manufactured electrodes have been aqueous. However, hydrolysis of PLA should also be accessible using sodium hydroxide in other protic but non-aqueous solvents, such as ethanol and methanol, which are both easily accessible for electrochemists. While interesting chemical studies in their own right, performing activation in these solvents might also be more appropriate for hypothetical future cases where the subsequent electrochemical procedures are being performed using additive manufactured electrodes in the solvent in question, for example in the field of electrosynthesis, where reactions are often carried out in alcohols such as methanol and ethanol [10]. This could be especially useful considering the fact that Williams *et al.* noted absorption of water by additive manufactured electrodes activated in NaOH (aq), subsequent desorption of which into solution might prove problematic in some cases [11]. Consequently, in this paper, we present the report of the activation of carbon black within composite additive manufactured electrodes using ethanolic and methanolic sodium hydroxide

solutions and comparison to standard aqueous activation solutions.

## 2 | MATERIALS AND METHODS

All chemicals were used as provided without further purification. Commercial conductive PLA/carbon black filament (1.75 mm, ProtoPasta, Vancouver, Canada) was purchased from Farnell (Leeds, UK). Sodium hydroxide pellets (>97%), potassium ferricyanide (99%), and potassium ferrocyanide (98.5–102.0%) were obtained from Sigma-Aldrich. Ethanol (99%+) and methanol ( $\geq 99\%$ ) were obtained from Fisher Scientific and deionized water was generated by a Millipore Milli-Q Integral 3 water purification unit, which dispensed water with a resistivity greater than or equal to 18 M $\Omega$ cm at 25 °C.

All computer designs and .3MF files seen throughout this manuscript were produced using Fusion 360<sup>®</sup> (Autodesk<sup>®</sup>, CA, United States). These files were sliced and converted to.GCODE files ready for printing by the open-source software, PrusaSlicer (Prusa Research, Prague, Czech Republic). The additively manufactured electrodes (AMEs) were 3D-printed using fused filament fabrication (FFF) technology on a Prusa i3 MK3S+ (Prusa Research, Prague, Czech Republic). The additive manufactured electrodes were printed with a rectilinear infill [12] using a 0.4 mm nozzle diameter, a nozzle temperature of 215 °C, and bed temperature of 60 °C. They were printed in standard “lollipop” shapes with lengths, thicknesses and head diameters of 25 mm, 2 mm, and 5 mm, respectively, as described in our previous work [11].

Contact angles were assessed using a bespoke additive manufactured printed measurement set-up consisting of a additive manufactured stage, a Hamilton syringe, and a generic USB digital microscope connected to a computer. This equipment allowed consistent delivery of droplets to part surfaces which could be recorded as video and/or photographs using the microscope. Where possible, contact angles were analyzed using ImageJ and the DropSnake plug-in [13], with reported values being the average and standard deviation of three repeat measurements. Solvent ingress measurements were made according to our previously reported method [11], but with samples being studied in ethanol and methanol in addition to deionized water.

The activation of the additive manufactured electrodes was performed using chronoamperometry in solutions of sodium hydroxide in ethanol, methanol, and water at an approximate concentration of 0.05 M. Activation was also conducted in an aqueous solution of sodium hydroxide at a concentration of approximately

0.5 M. In each case, a potential of +1.4 V was applied for 200 s, followed by application of a potential of -1.0 V for 200 s, which are established activation parameters. An Ag|AgCl electrode was used as a reference for all activation solutions; while it is acknowledged that this type of electrode is not intended for non-aqueous solvents, it can be repeatable and stable in protic non-aqueous solvents like simple alcohols [14]. In this case, it also appeared to give stable results over the course of the experiments (*i.e.* activation profiles did not seem to change significantly), and was certainly the most straightforward reference electrode available.

X-ray Photoelectron Spectroscopy (XPS) data were acquired using an AXIS Supra (Kratos, UK), equipped with a monochromated Al X-ray source (1486.6 eV) operating at 225 W and a hemispherical sector analyzer. The analyzer was operated in fixed analyzer transmission mode with a pass energy of 160 eV for survey scans and 20 eV for region scans with the collimator operating in slot mode for an analysis area of approximately 700×300  $\mu$ m, the FWHM of the Ag 3d5/2 peak using a pass energy of 20 eV was 0.613 eV. Before measurement, each AME was briefly dipped in 2-propanol to remove contaminants and dried in air. If there was not a graphitic sp<sup>2</sup> peak present in the C 1s region of the spectra, the binding energy scale was calibrated by setting the sp<sup>3</sup> C 1s peak to 285.0 eV; this calibration is acknowledged to be flawed [15], but was nonetheless used in the absence of reasonable alternatives, and because only limited information was to be inferred from absolute peak positions. If there was a graphitic sp<sup>2</sup> peak present, the binding energy scale was calibrated by setting this peak's maximum to 284.3 eV [16]. Calibration and fitting was carried out in CasaXPS, with default peak shapes used for all peaks, apart from the graphitic sp<sup>2</sup> which was fitted with an asymmetric peak for reasons described elsewhere [17].

Cyclic voltammetry experiments were made using a Metrohm AG Autolab PGSTAT128 N (Utrecht, The Netherlands) controlled by NOVA 2.1.5. An Ag|AgCl electrode was used as a reference (note that the reference used for this experiment was a fresh reference electrode that had not been placed within any alcoholic solutions). A coil of nichrome wire was used as a counter electrode. For the purposes of the measurements, care was taken to submerge in solution only the head of the additive manufactured electrode, with the remaining length from the shoulder onwards not immersed. This was to make sure a repeatable-as-possible area of the additive manufactured electrode was measured.

Note that solution composition and their labelling is as follows: 1) 0.05 M solutions of NaOH in ethanol (0.05 M\_EA); 2) 0.05 M solutions of NaOH in methanol

(0.05 M\_MA); 3) 0.05 M aqueous solutions of NaOH (0.05 M\_WA); iv) 0.5 M aqueous solutions of NaOH (0.5 M\_WA). The conductivity was measured which provided the following: 0.05 M\_EA ( $0.99 \pm 0.01$  mS); 0.05 M\_MA ( $3.84 \pm 0.01$  mS); 0.05 M\_WA ( $11.19 \pm 0.01$  mS) and 0.5 M\_WA ( $96 \pm 1$  mS).

### 3 | RESULTS AND DISCUSSIONS

We first explore the additive manufactured electrodes (see Materials and Methods section) in wetting behavior of water, methanol and ethanol. As shown within Figure S11, the contact angle of water can be measured to be  $88 (\pm 3)^\circ$ , both methanol and ethanol rapidly wetted the electrode surface with a contact angle too low to be measurable. While the macroscopic surface roughness of the additive manufactured electrode indicates means that the contact angle measured for water is unlikely to be a true reflection of the contact angle of water [18], the results clearly indicate that ethanol and methanol have significantly more favorable energetic interactions with the material than water, and these solvents would be expected to wet the additive manufactured surface to a greater extent during the activation process. However, contact angle measurements cannot be used in this case to infer any differences in interaction between methanol or ethanol with the additive manufactured electrodes. Next, the ease of ingress of water, methanol, and ethanol into the additive manufactured electrodes was investigated by measuring the mass of solvent immersed in each type of liquid. The method used was the same as previously reported [11], and mass uptake against time is shown in Figure 1.

While both the extent and rate of solvent absorption by the additive manufactured electrodes was similar in both methanol and ethanol, the samples absorbed significantly lower amounts of water and at a significantly slower rate of uptake. Therefore, during the activation reaction, methanol and ethanol solutions would be expected to penetrate a similar volume of the additive manufactured electrodes, which would be expected to be a much greater volume than the aqueous solutions are able to penetrate.

Once interactions with the pure solvents had been characterized, samples of additive manufactured electrodes were activated by chronoamperometry within solution composition and their labelling: 1) 0.05 M solutions of NaOH in ethanol (0.05 M\_EA); 2) 0.05 M solutions of NaOH in methanol (0.05 M\_MA); 3) 0.05 M aqueous solutions of NaOH (0.05 M\_WA); iv) 0.5 M aqueous solutions of NaOH (0.5 M\_WA). Note these concentrations were chosen as 0.05 M since this is the limit of solubility of standard NaOH pellets in ethanol and methanol; higher concentrations of NaOH in these solvents can be achieved by reacting the solvent with sodium metal, or purchased from chemical suppliers, but it was felt that dissolving pellets in pure solvent reflected the practice most likely to be followed by working electrochemists. A solution of 0.5 M aqueous NaOH was tested in addition to one of 0.05 M as this is a commonly used solution for chronoamperometric activation [8b]. As shown in Figure 1B, currents are recorded when additive manufactured electrodes are subjected to an applied potential of +1.4 V for 30 min (1800 s), which allows the maximum activation current in each solution to be recorded; a summary is presented within Table 1.

As can be seen by reference to Figure 1B and Table 1, activation in 0.05 M\_MA led to the highest maximum

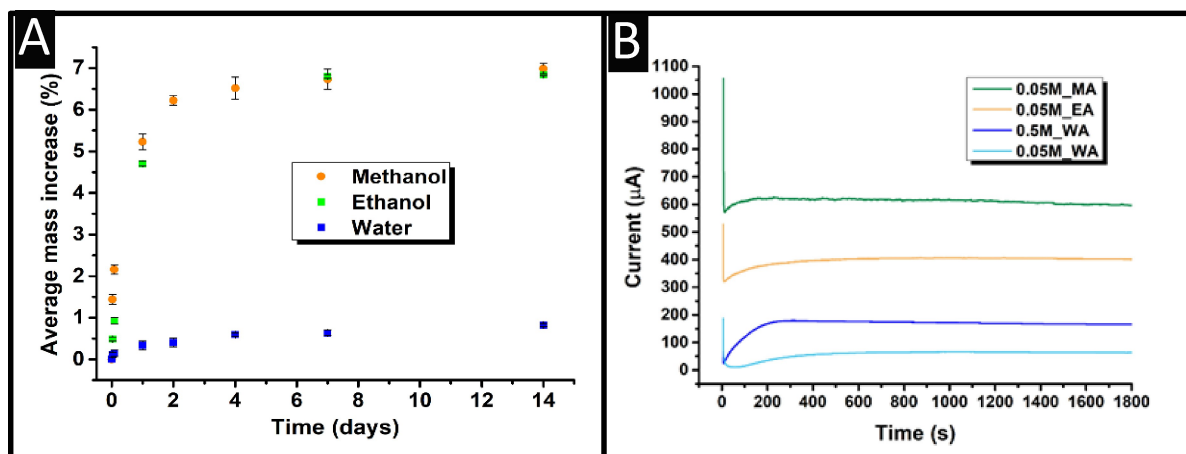


FIGURE 1 A: plot of mass against immersion time for unmodified additive manufactured electrodes kept in methanol, ethanol, or water. B: Plot of current versus time for the application of +1.4 V in each solvent, where the concentration of sodium hydroxide was either 0.5 M or 0.05 M. MA = methanol activation, EA = ethanol activation, and WA = water activation.

**TABLE 1** The extreme values of current and the current changes recorded when a potential of +1.4 V was applied to additive manufactured electrodes over 30 min.

Solution	Minimum current/ $\mu\text{A}$ (+1.4 V, 1800 s)	Peak current/ $\mu\text{A}$ (+1.4 V, 1800 s)	Current increase/ $\mu\text{A}$ (+1.4 V, 1800 s)
0.05 M_MA	572 $\pm$ 19	627 $\pm$ 25	54.6 $\pm$ 6.7
0.05 M_EA	321 $\pm$ 15	407 $\pm$ 33	86 $\pm$ 6
0.5 M_WA	24.5 $\pm$ 5.4	180 $\pm$ 12	155.5 $\pm$ 7.6
0.05 M_WA	10.4 $\pm$ 4.3	65.6 $\pm$ 9.7	55.2 $\pm$ 3.2

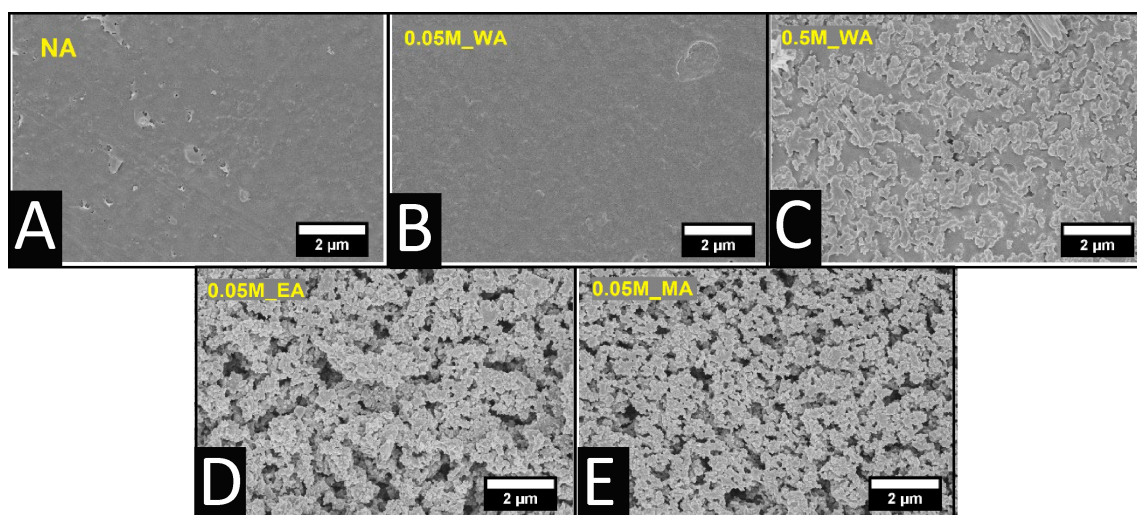
current, followed by 0.05 M\_EA, then by 0.5 M\_WA and finally 0.05 M\_WA. This suggests that the trend in the extent of the activation reaction, and, subsequently, amount of PLA removed from the surface in each solution is: methanol (0.05\_MA), ethanol (0.05\_EA), water (0.5 M\_WA), and water (0.05 M\_WA). In the case of methanol (0.05\_MA), specifically, the recorded current signal is noisy, which could be due to relatively large local changes in structure occurring at once, *i.e.* carbon black falling off the surface. By contrast, the differences in current increase *i.e.* maximum minus minimum current over 30 min at +1.4 V in each solution follow the trend: water (0.5 M\_WA), ethanol (0.05 M\_EA), methanol (0.05 M\_MA)  $\approx$  water (0.05 M\_WA).

The different activation currents for 0.5 M NaOH (0.5 M\_WA) and 0.05 M NaOH (0.05 M\_WA) are relatively easy to explain since higher concentrations of NaOH in the same solvent would be expected to lead to higher solution conductivities and greater rates of reaction. However, the differences between the aqueous solutions and other samples are more complicated to explain since the trends in activation currents correlate neither to the trends in solvent/solid interactions observed nor to differences in solution conductivity (see Materials and Methods section). While chronoamperometric removal of PLA in solutions of sodium hydroxide is assumed to occur due to saponification, *i.e.* hydrolysis of the polymer's ester group, as far as we aware, the exact nature of the mechanism occurring when a potential is being applied to the polymer is yet to be determined. It is hence difficult to assign a cause to the trends in peak activation currents observed when using alcoholic solutions of sodium hydroxide versus aqueous solutions. Similarly, the reasons for the trend in current increases are unclear but are speculated to be due to each solution changing the surface chemistry of the conductive filler to a different extent. For example, activation in 0.5 M NaOH (0.5 WA), which saw the highest current increase, might cause both removal of the polymer by saponification and changes to the carbon black surface chemistry which make subsequent removal of PLA occur significantly more readily. However, this is again speculation made without a full understanding of the

chemical processes occurring when a potential is applied to these composite materials while in sodium hydroxide solutions; more work is clearly needed to understand this topic.

Next, physicochemical characterization is performed. As shown within Figure 2, through comparison of the unmodified additive manufactured electrode surface it can be seen that activation using 0.05 M methanolic or ethanolic solutions of sodium hydroxide caused extensive damage to the surface part, with a highly rough and porous surface visible after treatment. By contrast, treating the additive manufactured electrodes with a 0.05 M aqueous solution of sodium hydroxide led to few discernible changes to the surface in comparison to the unmodified additive manufactured electrode surface. Treatment with a 0.5 M aqueous solution of sodium hydroxide caused some visible damage to the additive manufactured electrodes, but this was clearly not the same extent as caused by the 0.05 M alcoholic sodium hydroxide solutions. Overall, it can be concluded that alcoholic solutions of sodium hydroxide remove polymer more readily from the surface of additive manufactured electrodes than aqueous solutions, even at substantially lower concentrations.

XPS was used to further investigate the surface properties of the additive manufactured electrodes treated using the different sodium hydroxide solutions. As can be seen in Figure 3, the C 1s region of the unmodified additive manufactured electrodes sample could be fitted with three symmetric peaks at 289.3 eV, 287.2 eV, and 285.0 eV, which are assigned to the O–C=O, O–C–O, and CH<sub>3</sub> groups of the PLA polymer, respectively (with contributions to the lowest binding energy peak from alkyl impurities on the polymer surface). These results are consistent with previously-reported XPS spectra for the same material [11]. The 0.05 M\_WA sample showed little change in the C 1s region, which supports the observation made from SEM images that treatment in this solution leads to insignificant changes to the additive manufactured electrodes surface. Contrast, the lowest binding energy peak in the C 1s spectrum for the 0.5 M\_WA was significantly more intense than in the unmodified additive manufactured electrodes, and an



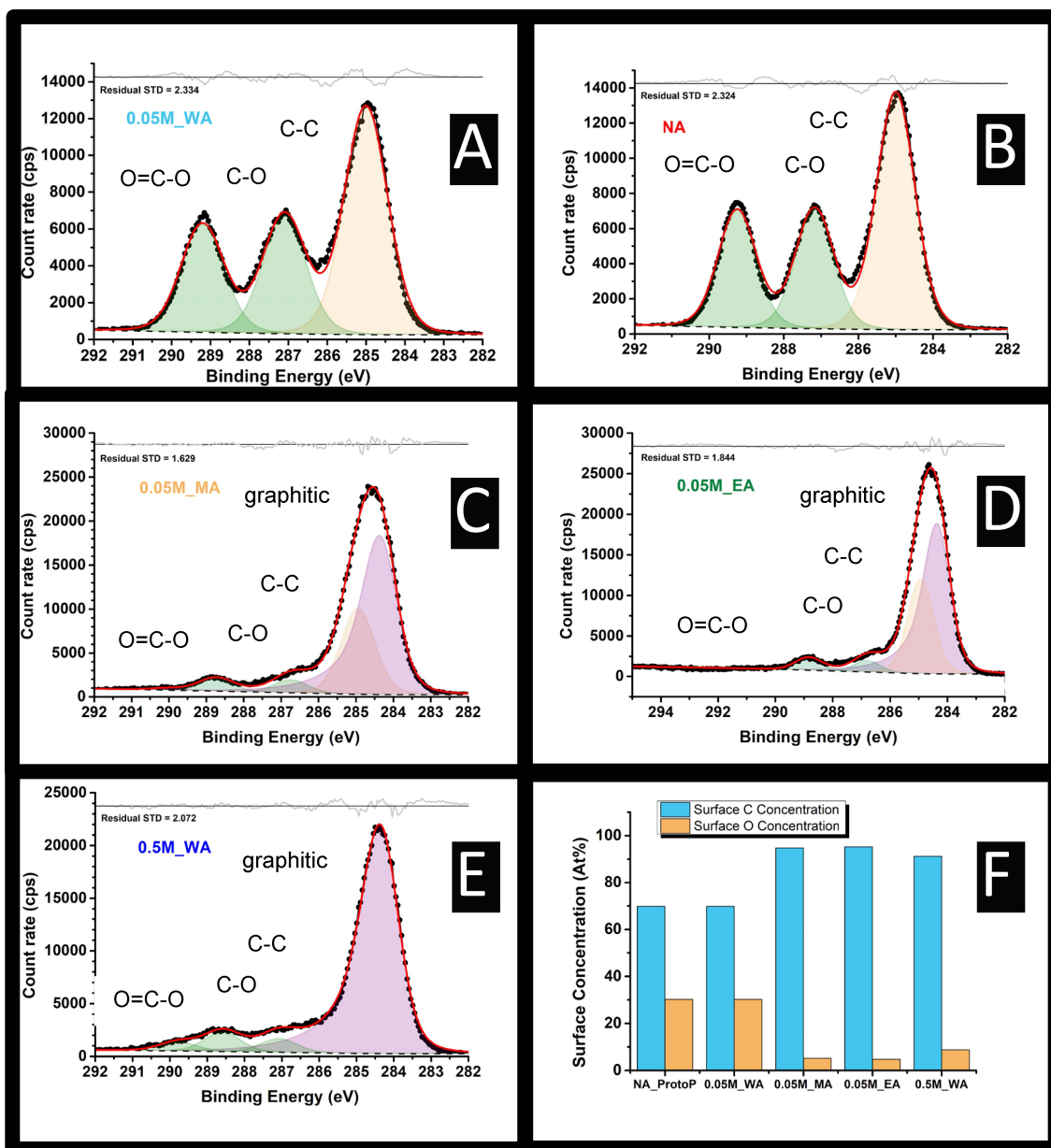
**FIGURE 2** SEM images of additive manufactured electrodes: (A) Prior to any electrochemical experiments; (B) after activation in 0.05 M NaOH within water; (C) after activation in 0.5 M NaOH within water; (D) after activation in 0.05 M NaOH within ethanol; (E) after activation in 0.05 M NaOH within methanol.

asymmetric peak was required for an adequate fit. Asymmetry is indicative of  $sp^2$  carbon [16], and in this case indicates that the activation process has exposed carbon black on the sample surface, which is consistent with the SEM result and confirms the saponification of the polymer. Three other peaks are required to fit this spectrum, although they are quite shifted in binding energy compared to the additive manufactured electrode and 0.05 M\_WA. This is speculated to be an artifact of calibrating the binding energy scale for these samples to the  $sp^3$  C 1s environment at 285.0 eV, which is known to be variable [15], and may well produce a different result to calibrating against the  $sp^2$  C 1s environment at 284.3 eV. The C 1s spectra of the 0.05 M\_EA and 0.05 M\_MA samples were similar, and also required the fitting of an asymmetric, relatively intense, low binding energy peak; this again supports SEM images showing that carbon black was revealed on the surfaces of these additive manufactured electrodes by the activation processes. In contrast to the 0.5 M WA sample, the alcoholic-activated additive manufactured electrodes required a relatively large peak fitted to the shoulder of the asymmetric  $sp^2$  peak. This shoulder is thought to arise from ethoxide or methoxide groups from solution undergoing addition to oxygen-bearing groups on the carbon black surface (e.g., carboxyl) during the activation process. Overall, the XPS spectra in the C 1s region again demonstrate the successful removal of polymer from the additive manufactured electrode surface when 0.05 M alcoholic sodium hydroxide solutions are used, and when 0.5 M aqueous solutions are used, but unsuccessful removal of polymer when 0.05 M aqueous solutions are used. Furthermore, differences in the peak shapes in this

region reveal that using alcoholic sodium hydroxide solutions leads to formation of additional organic groups on the carbon black surface in comparison to activation in aqueous solution.

A comparison of the area of the O 1s region of the XPS spectra to the C 1s region is shown in Figure 3F in terms of surface atom concentration (the spectra for the O 1s region of each sample are shown in Figure SI2). Compared to the additive manufactured electrodes or 0.05 M\_WA samples, it can be observed that the surface oxygen concentration is around 25 At% lower for the 0.05 M\_EA and 0.05 M\_MA samples than additive manufactured electrodes or the 0.05 M\_WA sample, and around 21 At% lower for the 0.5 M\_WA sample. This decrease in surface oxygen content can be attributed to removal from the surface of the relatively oxygen rich PLA and exposure of the relatively oxygen poor carbon black. The slightly raised surface oxygen content of the 0.5 M\_WA sample relative to the alcohol activated samples is probably largely due to the lower extent of PLA removal apparent from the SEM images, but it is speculated to also be due in some part to the aqueous solution creating a greater number of oxygen bearing surface groups on the CB; as can be seen in Figure SI2, the O 1s spectrum for the 0.5 M\_WA sample shows a high-binding energy shoulder on the main peaks which is significantly larger than in the other samples. This could correspond to an increased number of  $-OH$  or  $O=C-O$  groups on the carbon black surface in the 0.5 M\_WA.

The differently activated additive manufactured electrodes were explored through cyclic voltammetry in a solution of 1 mM ferrocyanide in 0.1 M aqueous KCl, which is a well-known inner-sphere redox probe, and



**FIGURE 3** XPS spectra showing the C 1s environment for Additive manufactured electrodes before and after electrochemical activation in different sodium hydroxide solutions. It can be seen that the 0.05 M WA sample (B) is not distinguishable from the non-activated AME (A), while the 0.05 M MA (C), 0.05 M EA (D), and 0.5 M WA (E) samples show a large peak corresponding to the  $sp^2$  environment of graphitic carbon. These samples also show a significant increase in the surface C concentration relative to O, as can be seen in (F). This is further evidence of the success of the electrochemical activation procedure for revealing carbon black.

hence should be sensitive to differences in surface chemistry caused by using different activation solutions; typical voltammograms are presented in Figure 4, with peak current values evaluated in Table 2.

The heterogeneous rate constant,  $k_{obs}^0$  is determined from the peak-to-peak separations ( $\Delta E_p$ ) which is applicable for quasi-reversible electrochemical processes where  $\Delta E_p > \sim 150$  mV [19] using:

$$k_{obs}^0 = 2.18 \left( \frac{\alpha D n \nu F}{RT} \right)^{\frac{1}{2}} \exp \left( - \frac{\alpha^2 n F}{RT} \Delta E_p \right) \text{ where } \alpha \text{ is the transfer}$$

**TABLE 2** A table comparing the peak current values obtained by electrodes activated using the different activation solutions for cyclic voltammograms of  $[\text{Fe}(\text{CN})_6]$  and acetaminophen.

Activation	IP $[\text{Fe}(\text{CN})_6]/\mu\text{A}$	IP acetaminophen/ $\mu\text{A}$
0.5 M WA	$138 \pm 7$	–
0.05 M WA	$89 \pm 9$	$7.76 \pm 1$
0.05 M EA	$126 \pm 6$	$11.3 \pm 1$
0.05 M MA	$148 \pm 7$	$10.5 \pm 1$



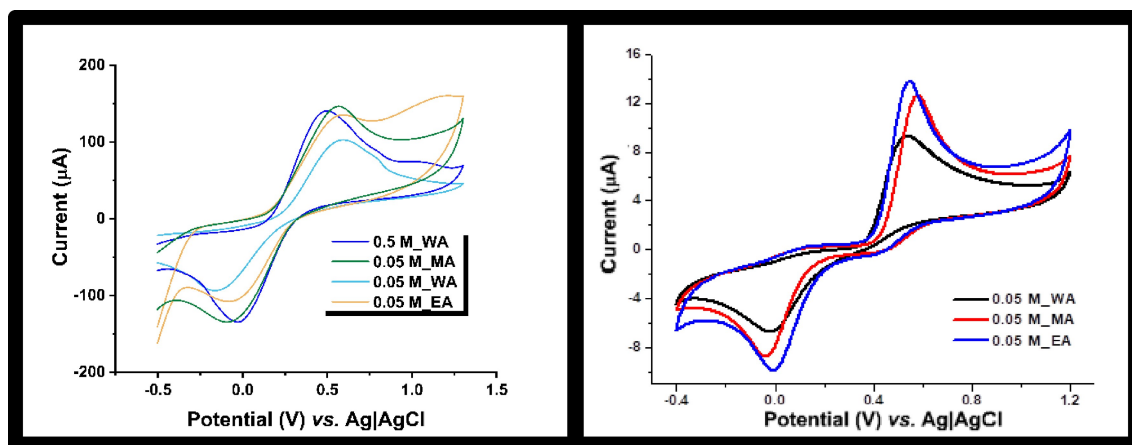


FIGURE 4 A) Cyclic voltammograms of  $[\text{Fe}(\text{CN})_6]/0.1 \text{ M KCl}$ . Scan rate:  $50 \text{ mVs}^{-1}$ . B) Cyclic voltammograms of acetaminophen ( $100 \mu\text{M}$ ) within PBS ( $\text{pH}=7.4$ ). Scan rate:  $50 \text{ mVs}^{-1}$ .

coefficient (usually assumed to be close to 0.5). The  $k_{\text{obs}}^0$  is found to correspond to ethanol (0.05 M\_EA):  $2.39 \times 10^{-5} \text{ cm s}^{-1}$ ; methanol (0.05 M\_MA):  $1.85 \times 10^{-5} \text{ cm s}^{-1}$ ; 0.5 M NaOH (0.5 M\_WA):  $4.45 \times 10^{-5} \text{ cm s}^{-1}$ ; 0.05 M NaOH (0.05 M\_WA):  $7.19 \times 10^{-6} \text{ cm s}^{-1}$ . The magnitude of the  $k_{\text{obs}}^0$  is in-line with other reports [20].

It can be observed that the additive manufactured electrodes, apart from the 0.05 M\_WA sample show similar current magnitudes under the same applied potential, but the current magnitudes seen for the 0.05 M\_WA sample are consistently approximately 50% smaller. From SEM images of the samples (Figure 2), it might be expected that the 0.05 M\_EA and 0.05 M\_MA samples would display a significantly greater current magnitude than the 0.5 M\_WA sample since a significantly larger area of carbon black appears to be exposed at the additive manufactured electrode surface after activation in either of the alcoholic solutions. The fact that this is the case might suggest that there is an upper limit to benefits of polymer removal by electrochemical activation of additive manufactured electrodes, i.e., once a certain amount of polymer has been etched away, there are no further gains in electrochemical performance even if polymer can continuously be removed. The additionally exposed carbon black seen in the SEM images is speculated to be loosely bound to the surface and hence not contributing useful electrochemical area to the electrode.

This trend implies that activating the additive manufactured electrodes in alcoholic sodium hydroxide solutions changes the surface chemistry of the carbon black in a manner that hinders electron transfer compared to activation in aqueous solutions. This can be linked back to the XPS results, where R–O groups were identified on the surface of the 0.05 M\_EA and 0.05 M\_MA additive manufactured electrodes, but not the 0.5 M\_WA AME,

which in turn had a greater concentration in surface oxygen groups. These differences in carbon black surface functionality clearly affect the rate of electron transfer in the additive manufactured electrodes. This work is consistent by the work Ji *et al* who show that the ferri-/ferrocyanide couple is an inner sphere redox probe, differences can indicate different surface chemistries where are indirectly responsible upon heterogeneous charge transfer which arises because the oxygenated moieties must “block” the edge plane sites [21].

## 4 | CONCLUSIONS

This work demonstrates that the use of solutions of sodium hydroxide in methanol or ethanol for chronoamperometric activation of CB/PLA additive manufactured electrodes produces significantly larger extents of polymer removal than the aqueous sodium hydroxide solutions typically used for the process. This was evidenced by SEM, which showed a rougher, more porous surface for additive manufactured electrodes activated in alcohol, and increased activation currents were also seen in alcoholic solutions. We show that the use of alcoholic solutions hinders electron transfer kinetics at the additive manufacturing electrode surface, with the latter effect shown to be related to differences in the surface functionality of the exposed carbon black filler particles. The above results indicate that the use of solutions of sodium hydroxide in ethanol or methanol for chronoamperometric activation of additive manufactured electrodes does not offer any advantage for electrochemical analysis in absolute terms. Nonetheless, the work is expected to be informative for researchers who might be required to use non-aqueous activation solvents for electrochemical activation, for example those

intending to use activated additive manufactured electrodes to carry out electrosynthesis in dry and/or alcoholic solutions.

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### CONFLICT OF INTEREST STATEMENT

The authors declare no conflicts of interest.

### DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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### REFERENCES

1. a) H. Agrawaal, J. E. Thompson, *Talanta Open* **2021**, *3*, 100036; b) M. J. Whittingham, R. D. Crapnell, E. J. Rothwell, N. J. Hurst, C. E. Banks, *Talanta Open* **2021**, *4*, 100051.
2. M. Attaran, *Bus. Horiz.* **2017**, *60*, 677–688.
3. R. D. Crapnell, C. Kalinke, L. R. G. Silva, J. S. Stefano, R. J. Williams, R. A. Abarza Munoz, J. A. Bonacin, B. C. Janegitz, C. E. Banks, *Mater. Today* **2023**, *71*, 73–90.
4. a) R. M. Cardoso, C. Kalinke, R. G. Rocha, P. L. Dos Santos, D. P. Rocha, P. R. Oliveira, B. C. Janegitz, J. A. Bonacin, E. M. Richter, R. A. Munoz, *Analytica chimica acta* **2020**, *1118*, 73–91; b) M. H. Omar, K. A. Razak, M. N. Ab Wahab, H. H. Hamzah, *RSC Adv.* **2021**, *11*, 16557–16571.
5. R. Gusmão, M. P. Browne, Z. Sofer, M. Pumera, *Electrochem. Commun.* **2019**, *102*, 83–88.
6. C. Kalinke, N. V. Neumsteir, G. de Oliveira Aparecido, T. V. de Barros Ferraz, P. L. Dos Santos, B. C. Janegitz, J. A. Bonacin, *Analyst* **2020**, *145*, 1207–1218.
7. M. J. Glowacki, M. Cieslik, M. Sawczak, A. Koterwa, I. Kaczmarzyk, R. Jendrzewski, L. Szykiewicz, T. Ossowski, R. Bogdanowicz, P. Niedzialkowski, *Appl. Surf. Sci.* **2021**, *556*, 149788.
8. a) E. Sigley, C. Kalinke, R. D. Crapnell, M. J. Whittingham, R. J. Williams, E. M. Keefe, B. C. Janegitz, J. A. Bonacin, C. E. Banks, *ACS Sustain. Chem. Eng.* **2023**, *11*, 2978–2988; b) E. M. Richter, D. P. Rocha, R. M. Cardoso, E. M. Keefe, C. W. Foster, R. A. Munoz, C. E. Banks, *Anal. Chem.* **2019**, *91*, 12844–12851; c) M. Schneider, N. Fritzsche, A. Puciul-Malinowska, A. Bališ, A. Mostafa, I. Bald, S. Zapotoczny, A. Taubert, *Polymers* **2020**, *12*, 1711.
9. D. P. Rocha, R. G. Rocha, S. V. Castro, M. A. Trindade, R. A. Munoz, E. M. Richter, L. Angnes, *Electrochem. Sci. Adv.* **2022**, *2*, e2100136.
10. a) C. Kiaku, J. M. Walsh, M. C. Leech, D. L. Poole, J. Mason, I. C. Goodall, P. Devo, K. Lam, *Org. Lett.* **2023**, *25*, 1147–1150; b) M. C. Leech, K. Lam, *Nat. Rev. Chem.* **2022**, *6*, 275–286.
11. R. J. Williams, T. Brine, R. D. Crapnell, A. G.-M. Ferrari, C. E. Banks, *Mater. Adv.* **2022**, *3*, 7632–7639.
12. E. Bernalte, R. D. Crapnell, O. M. Messai, C. E. Banks, *Chem-ElectroChem* **2024**, *11*, e202300576.
13. A. F. Stalder, G. Kulik, D. Sage, L. Barbieri, P. Hoffmann, *Colloids Surf. A* **2006**, *286*, 92–103.
14. G. Inzelt, A. Lewenstam, F. Scholz, *Handbook of Reference Electrodes, Vol. 541*, Springer Berlin, Heidelberg, **2013**.
15. G. Greczynski, L. Hultman, *Sci. Rep.* **2021**, *11*, 11195.
16. R. Blume, D. Rosenthal, J. P. Tessonnier, H. Li, A. Knop-Gericke, R. Schlögl, *ChemCatChem* **2015**, *7*, 2871–2881.
17. T. R. Gengenbach, G. H. Major, M. R. Linford, C. D. Easton, *J. Vac. Sci. Technol. A* **2021**, *39*, 013204.
18. A. Marmur, *Soft Matter* **2006**, *2*, 12–17.
19. M. Velicky, D. F. Bradley, A. J. Cooper, E. W. Hill, I. A. Kinloch, A. Mishchenko, K. S. Novoselov, H. V. Patten, P. S. Toth, A. T. Valota, *ACS Nano* **2014**, *8*, 10089–10100.
20. R. S. Shergill, C. L. Miller, B. A. Patel, *Sci. Rep.* **2023**, *13*, 339.
21. X. Ji, C. E. Banks, A. Crossley, R. G. Compton, *ChemPhysChem* **2006**, *7*, 1337–1344.

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