

Article

Improved Capacitance of Electropolymerized Aniline Using Magnetic Fields

William T. McLeod, Anjaiah Sheelam, Aspen K. Kroiss and Jeffrey G. Bell * 

Department of Chemistry, Washington State University, Pullman, WA 99164, USA;
william.t.mcleod@wsu.edu (W.T.M.)

* Correspondence: jeffrey.g.bell@wsu.edu

Abstract: With the rise in intermittent energy production methods and portable electronics, energy storage devices must continue to improve. Supercapacitors are promising energy storage devices that are known for their rapid charging and discharging, but poor energy density. Experimentally, one can improve the energy density by improving the operating cell voltage and/or improving the overall capacitance, which have traditionally been achieved using difficult, complicated, or expensive syntheses involving additional chemicals or many steps. In this work, we demonstrate a method to improve the capacitance of electropolymerized polyaniline (PANI, a conductive polymer common in supercapacitor applications) with zero additional energy input or chemical additives: the use of a permanent magnet. Using a pulsed-potential polymerization method, we show that the inclusion of a 530 mT magnetic field, placed directly under the surface of the working electrode during electropolymerization, can result in a PANI film with a capacitance of 190.6 mF; compare this to the same polymerization performed in the absence of a magnetic field, which has a significantly lower capacitance of 109.7 mF. Electrochemical impedance spectroscopy indicates that PANIs formed in the presence of magnetic fields demonstrate improved capacitor behavior, as well as lower internal resistance, when compared to PANIs formed in the absence of magnetic fields. To probe the performance and stability of PANI films synthesized in the presence and absence of magnetic fields, galvanostatic charge–discharge was completed for symmetric capacitor configurations. Interestingly, the PANI films formed in the presence of 530 mT magnetic fields maintained their capacitance for over 75,000 cycles, whereas the PANI films formed in the absence of magnet fields suffered serious capacitance losses after only 29,000 cycles. Furthermore, it is shown that performing the polymerization in magnetic fields results in a higher-capacitance polymer film than what is achieved using other methods of forced convection (i.e., mechanical stirring) and outperforms the expected capacitance (based on yield) by 13%, suggesting an influence beyond the magnetohydrodynamic effect.

Keywords: magnetoelectrochemistry; supercapacitor; conductive polymer; electropolymerization; polyaniline



Citation: McLeod, W.T.; Sheelam, A.; Kroiss, A.K.; Bell, J.G. Improved Capacitance of Electropolymerized Aniline Using Magnetic Fields. *Sustainability* **2023**, *15*, 15419. <https://doi.org/10.3390/su152115419>

Academic Editors: Kaan Kalkan and Antonio Caggiano

Received: 1 September 2023

Revised: 17 October 2023

Accepted: 26 October 2023

Published: 30 October 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Energy storage devices must improve in order to support the integration of intermittent power sources, like wind and solar, into the energy grid, as well as to keep up with the increasing demand for portable electronics and electric vehicles. Supercapacitors are promising energy storage devices that can work in place of, or alongside, batteries [1,2]. While useful for their quick charging and discharging, which provides high power density, they are limited by their low energy density [3–7]. Whether for use as primary or auxiliary energy storage applications, the increase in the energy density of supercapacitors would lead to cheaper and more effective systems. This poor energy density is often improved by electrode modification for increased conductivity or active surface area.

Supercapacitors are generally divided into three categories based on their type of electrodes: electrical double-layer capacitors (EDLCs), which store charge purely in the

structure of the electrical double layer; pseudocapacitors, which store energy in fast redox, intercalative, or underpotential processes; and hybrid capacitors, which have a mix of different capacitor-type storage mechanisms or a mix of capacitor-type and battery-type storage mechanisms [3,4,6,8,9]. A common form of redox pseudocapacitance is the use of redox-active polymers, such as polyaniline (PANI), polypyrrole (PPY), polythiophene (PTH), and others as electrodes [10–14]. These polymers are convenient for the ease with which they can be deposited onto conductive surfaces via electrochemical deposition, improving both the conductivity and active surface area of electrodes. Herein, we propose a method to synthesize PANI via electrochemical deposition under a constant magnetic field to improve the capacitance of the resultant film. Other surface modification techniques for improved energy storage applications require complicated, multi-step processes [15]; additional energy input from sources, such as heating [16–19]; or additional chemical input, in the form of catalysts or dopants [20–22]. The use of permanent magnets offers a simple approach for improving polymer properties with zero additional energy input, such as from heating, higher overpotentials, or electromagnetism; zero additional chemical input, such as catalysts or dopants; and zero additional fabrication steps, such as pre- or post-treatments.

Although it has been known since the 1970s that magnetic fields can influence electrode processes [23–25], further research remains necessary to fully characterize their alteration of more complex processes, such as polymerization and other electrode modifications. The utility of magnetic fields and their effects has become of great interest for electrochemical energy storage applications, due to the versatility of their applications. Recently, magnetic fields have been employed for energy storage to fabricate nanomaterial-based supercapacitors by altering the morphology of nanomaterial deposits on electrodes [26–28], to improve the specific capacitance of metal oxide supercapacitors [29–31], to improve zinc–bromide static batteries by inhibiting dendrite growth and increasing diffusion [32], to fabricate improved cathode [33,34] and anode [35] materials for Li-ion batteries, and to enhance the cycling performance of Li-ion [36,37], Li-S [38], and Li-metal anode batteries [39]. (For further reading about current research on the applications of magnetic fields in energy storage, the reader is directed to reviews by Shen et al. [40] and Raj et al. [41]). Polyaniline [42–44] and other electroactive polymers [45–49] have been synthesized in magnetic fields, although those studies primarily focused on the fundamental characterization of the magnetic field's influence instead of the enhancement of their energy-storing properties. Previous work has shown that magnetic fields can influence the rates of radical-based reactions [50], suggesting that they should alter the yield of aniline electropolymerization. Furthermore, magnetic fields have been shown to induce convection in aqueous systems via the magnetohydrodynamic (MHD) effect [23,32,51,52], in which charged species moving through a magnetic field are caused to move in a spiral path via the Lorentz force, defined in Equation (1):

$$\mathbf{F}_L = q(\mathbf{E} + \mathbf{v} \times \mathbf{B}) \quad (1)$$

where $\mathbf{F}_L$ represents the Lorentz force vector on a moving charged particle, q represents the charge on that particle, $\mathbf{E}$ represents the electric field vector, $\mathbf{v}$ represents the velocity of the particle, and $\mathbf{B}$ represents the magnetic field vector.

In this study, an external magnetic field is applied in order to yield a PANI film with improved capacitance. When aniline is dissolved in an acidic solution, the aniline monomer becomes charged by adopting a proton to the amine. As the aniline monomer is consumed by the polymerization reaction, a net movement of charged aniline monomers occurs toward the electrode surface. This net movement is induced to rotate via the MHD effect, creating convection. This convection is herein exploited to yield higher-capacitance PANI films. To the best of our knowledge, this is the first report on employing external magnetic fields to affect the capacitance of polymeric materials. We investigate the effect of a magnetic field on the resulting capacitance of the PANI obtained using three different polymerization protocols: constant-potential, swept-potential, and pulsed-potential. Constant- and swept-potential polymerizations are commonly employed in the

literature for growing PANI films on electrodes, while pulsed-potential techniques are less common but are still employed [53,54]. The PANI films obtained in the presence and absence of magnetic fields were characterized using a combination of scanning electron microscopy and electrochemical techniques. The electrochemical characterization reveals that the optimized pulsed-polymerization protocol yielded a PANI film with a capacitance of 190.6 mF when polymerized in a magnetic field, whereas the PANI film formed in the absence of a magnetic field had a capacitance of 109.7 mF. The results indicate that the application of a magnetic field via a permanent magnet is a viable strategy for improving the capacitance of an electropolymerized product without adding any additional chemicals or energy into the system.

2. Materials and Methods

2.1. Materials and Equipment

Aniline (C_6H_7N) was purchased domestically from BeanTown Chemical (99%) and Sigma Aldrich ($\geq 99.5\%$), and both were used as described in Section 2.2 without further refinement. Hydrochloric acid (HCl, 12.1 N) was purchased from Fischer Scientific. Sulfuric Acid (H_2SO_4 , 5 N) was purchased from Sigma Aldrich. All electrodes were purchased from CH Instruments. The working electrode was cleaned by polishing successively in 0.3 and 0.05 μm alumina slurries before rinsing with distilled water, sonicating, rinsing again, and drying with a Kimwipe. All experiments, except galvanostatic charging and discharging and those described in Section 3.3, were performed on a PalmSens4 potentiostat. The galvanostatic charging and discharging experiments were performed on a BioLogic BCS-805 battery cycler, and the experiments in Section 3.3 were performed on a CH Instruments 760E electrochemical workstation. The block magnet used was a 2-inch neodymium, nickel-coated magnet purchased from K&J Magnetics, Inc., and the strength of its magnetic field at the surface of the electrode was determined with an MF-30K Gaussmeter from Latnex.

2.2. Aniline Polymerization

Solutions of aniline were prepared in deionized water with acid and left in the dark for 24 h before use. For the electrochemical polymerizations, a 2 mm platinum disk electrode served as the working electrode, a platinum wire served as the counter electrode, and a saturated Ag/AgCl electrode served as the reference (all reported potentials are versus sat. Ag/AgCl). The working electrode was modified in solutions of 1 M aniline and 2 M HCl. Three types of polymerization procedures were carried out: a potentiostatic polymerization for 30 s, a cycled potential polymerization for 10 scans, and pulsed-potential polymerizations with periodic interruptions. All pulsed-potential procedures with different pulse and downtime combinations were normalized in order to spend a total of 30 s in the high potential region.

2.3. Modified Electrode Characterization

Capacitance of the modified electrodes was determined using cyclic voltammetry in 1 M H_2SO_4 solutions from 0 V to 1 V, and the resultant area under the curve (AUC) was compared to the AUCs for the control to determine the increase in capacitance. The capacitance of an electrode can be determined using the equation

$$C = \frac{1}{\left(\frac{dV}{dt}\right) \Delta V} \int i(t) dV \quad (2)$$

in which C is the capacitance of the electrode, $\frac{dV}{dt}$ is the scan rate of the cyclic voltammogram, ΔV is the voltage window, and $i(t)$ is the current. It is shown in Equation (2) that the capacitance of the working electrode is proportional to the area of the CV and, thus, the increase in capacitance between two electrodes is found by the proportion of the areas of their CVs in sulfuric acid.

The absolute capacitance was measured by performing cyclic voltammetry in 1 M H_2SO_4 solutions from 0 V to 1 V at scan rates from 0.025 to 0.1 V/s and plotting the peak current versus the scan rate. The capacitance could then be determined from the following equation

$$i(t) = C \frac{dV}{dt} \quad (3)$$

in which $i(t)$ is the peak current during the scan, C is the capacitance of the electrode, and $\frac{dV}{dt}$ is the rate of the scan. From this equation, the capacitance can be taken as the slope of the peak current as a function of the scan rate.

The electrodes were further characterized using electrochemical impedance spectroscopy (EIS) in 1 M H_2SO_4 at an the open circuit potential from 100 kHz to 100 mHz.

Galvanostatic charging and discharging tests were performed on a BioLogic BCS-805 battery cycler. Cells were constructed by modifying two platinum disk electrodes as previously described and placing them in a solution of 1 M H_2SO_4 to simulate a symmetric capacitor. Cells were made using either two electrodes that were modified with no magnetic field or two electrodes that were both modified in the presence of a magnetic field.

The magnet was never applied to the system during characterization. All references to the effect of the magnetic field refer to its application during electropolymerization.

2.4. Experimental Setup

For the electropolymerizations in a magnetic field, the cell was placed on top of a block magnet such that the working electrode was suspended over the center of the top face of the magnet, as shown in Figure 1A. The electrode was brought as close as possible to the bottom of the cell to ensure maximum field strength, and the cell could be moved up or down with 1 mm spacers to control the strength of the field. The electrode was placed at the same depth for the control polymerizations. The magnet was oriented such that the field lines were normal to the plane of the electrode surface, and the position and size of the working electrode permits the assumption that the magnetic field lines were parallel at the electrode surface, as shown in Figure 1B. For the experiments in which the magnetic field was oriented parallel to the plane of the electrode surface, the magnet was placed on its side and the cell was raised such that the surface of the electrode was in line with the pole of the magnet.

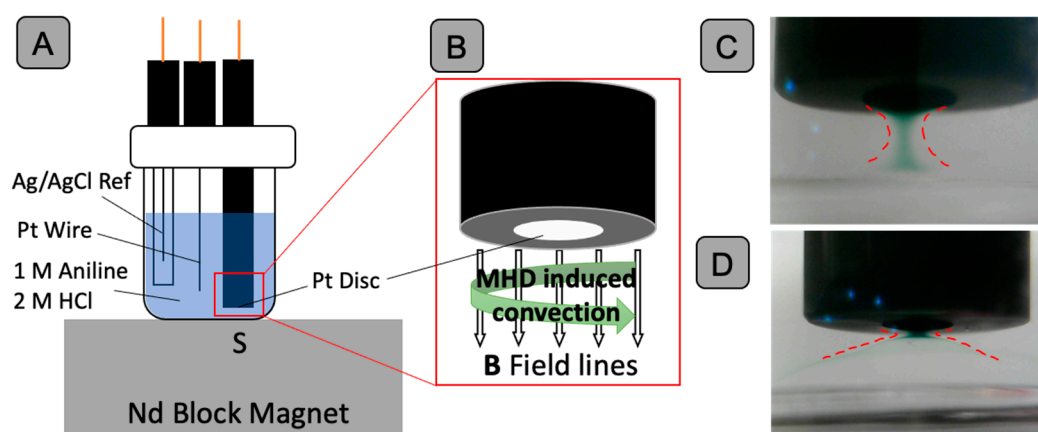


Figure 1. (A) Schematic of experimental setup for a magnetic field oriented perpendicular to the surface of the Pt disc working electrode; (B) Schematic of magnetic field lines and MHD at the working electrode surface; (C) Image of electrode surface during polymerization under no magnetic field, in which the polyaniline can be seen to drift down off the electrode surface in a column due to gravity; (D) Image of electrode surface during polymerization under 530 mT, in which the MHD effect creates a cone around which the polyaniline rotates as it drifts away from the electrode surface.

2.5. Scanning Electron Microscopy Images

The SEM images were taken on an FEI Apreo VolumeScope SEM scanning electron microscope after affixing an adhesive carbon tab to the working electrode, growing the polymer on the tab, allowing the tab to dry, and then transferring the tab to an SEM stub.

3. Results

3.1. Traditional Polymerization Techniques

In order to show that the magnetic field would affect the electropolymerization of aniline, the electrode was first modified using the potentiostatic method, holding it at 1.1 V for 30 s in a solution of 1 M aniline and 2 M HCl. The potential of 1.1 V was selected after determining, using cyclic voltammetry (CV), that it was appropriately high enough to oxidize aniline but not so high as to promote the oxygen evolution reaction (OER) on the working electrode. The modified electrode was then characterized using CV in 1 M sulfuric acid, and the peaks matched the expected peaks for polyaniline [55,56]. When the procedure was repeated under the influence of a 530 mT magnetic field, it was found that the average capacitance of the resultant PANI film was improved over that of the control by $+28\% \pm 6\%$. Figure 1C,D shows the effect that the magnet has on the solution dynamics. When no magnetic field is applied, the polyaniline that does not deposit on the electrode surface drifts to the bottom of the cell in a column, but when a 530 mT field is applied, convection is induced via the MHD effect, causing the polyaniline to rotate in a wide cone as it descends. This forced convection decreases the size of the diffusion zone, which increases the yield of the electropolymerization. The electrode was then modified using the swept-potential, or cyclic voltammetry, method. The electrode was swept from -0.1 to 1.1 to -0.1 V for 10 cycles at a scan rate of 100 mV/s. When the procedure was repeated under the influence of a 530 mT magnetic field, the capacitance of the PANI film was found to have improved by $+19\% \pm 9\%$.

3.2. Optimization of Polymerization Technique

In order to maximize the effect of the Lorentz force, a pulsed-potential method was employed to increase the average current during polymerization. The waveform employed is shown in Figure 2A, and the parameters are defined as follows: the pulse time, t_p , is the length of time each individual pulse lasts; the downtime, t_d , is the length of time between each pulse, during which the electrode is charged to some potential below the polymerizing region; the pulse potential, E_p , is the potential at which the electrode is charged during each pulse (maintained at 1.1 V for all the experiments); and the downtime potential, E_d , is the potential to which the electrode was set in between pulses.

A variety of pulse times and downtime combinations were tried to find the optimal combination. All the combinations used a pulse potential of 1.1 V and a downtime potential of -0.1 V, and the runtime was normalized such that the total amount of time spent in the polymerizing region ($t_p \times n$, where n = the number of cycles) was 30 s. The various times and their resulting changes in capacitance when polymerized under a magnetic field are shown in Table 1. The change in capacitance was determined by comparing the areas of the CVs of the modified electrodes, measured in 1 M H_2SO_4 , to the same polymerization protocol performed in the absence of a magnetic field, as shown in Figure 2C.

The effect of the magnet began to decrease as the pulse time approached zero, likely because the shorter pulses did not induce a meaningful level of convection. When employing longer pulse times, the average current density decreases as the pulse current is given longer to decay, minimizing the influence of the Lorentz force on the polymerization. Multiple cycles are necessary to maintain a high average current density, while too many cycles (i.e., shorter pulse times) prevent convection from causing significantly increased mass transport.

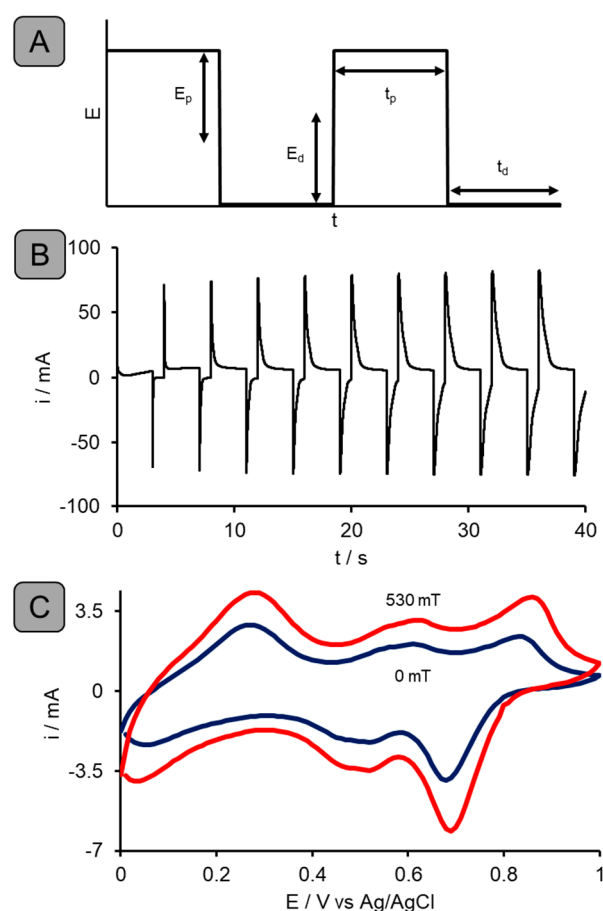


Figure 2. (A) General applied potential waveform; (B) i vs. t curve of pulsed-potential polymerization; (C) an example of a comparison of two characterization CVs.

Table 1. The change in capacitance when polymerized under a magnetic field with the following pulse time and downtime combinations.

Pulse Time (s)	Downtime (s)	% Change in C
0.1	0.1	-3 ± 3
0.1	1	-1 ± 12
1	0.1	$+34 \pm 15$
1	1	$+30 \pm 29$
2	0.1	$+39 \pm 12$
2	1	$+47 \pm 10$
2	5	$+35 \pm 6$
3	0.5	$+46 \pm 4$
3	1	$+48 \pm 7$
3	5	$+46 \pm 7$
3.75	1	$+45 \pm 8$
4.29	1	$+47 \pm 7$
5	1	$+42 \pm 9$
15	1	$+35 \pm 9$
30	0	$+28 \pm 6$

Interestingly, the influence of the magnetic field strength, shown in Figure 3A, is asymptotic within the range obtainable with the permanent magnet used. Within this range of field strengths, it is not believed that the magnet has a significant influence on the formation of aniline radicals [57]. Instead, the dominant influence of the magnet is believed to be convection induced by the MHD effect. Increasing the strength of the magnetic field

increases the rate of rotation. However, in a highly concentrated solution, such as described in Section 2.2, the diffusion zone is already very small. Induced convection may further reduce its size, but the difference between two very high rotation speeds is negligible, as evidenced by the asymptotic trend of the data shown in Figure 3A. Further increases in the magnetic field strength within the same order of magnitude are not expected to produce significant improvements beyond what is achieved at 530 mT.

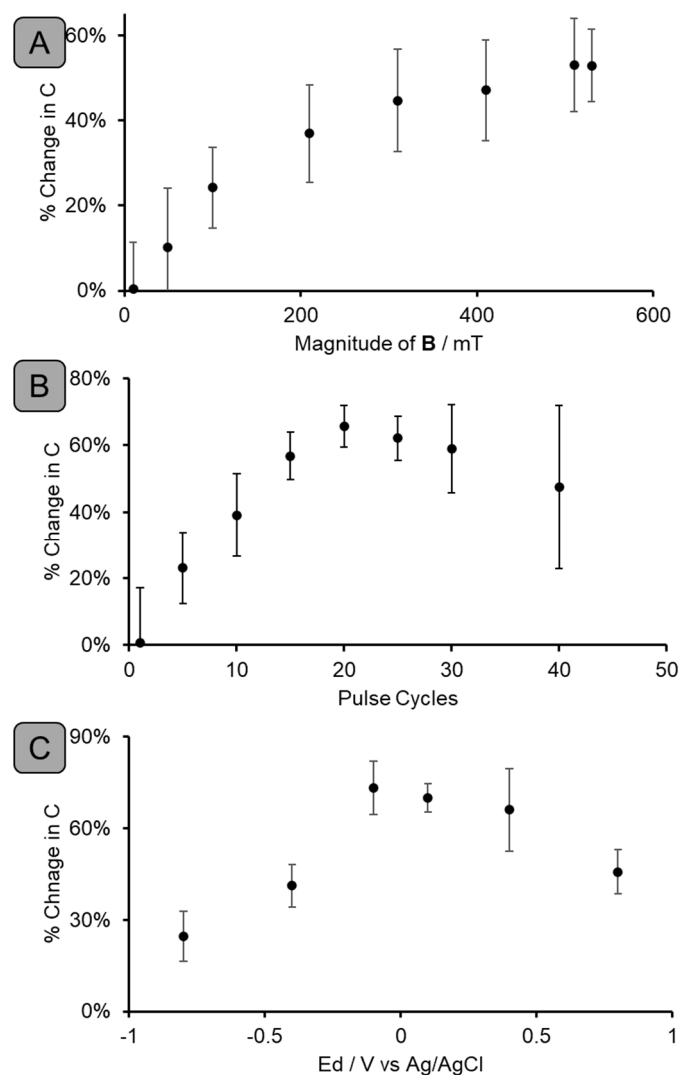


Figure 3. (A) The effect of the magnet at various magnetic field strengths versus the control. The electrode was modified with a pulse of 1.1 V for 3 s and a downtime of -0.1 V for 1 s for 10 cycles in 1 M aniline and 2 M HCl. (B) The effect of a 530 mT magnetic field on the resulting capacitance of the polymer versus the control when running the polymerization for different lengths of time. The electrode was modified with a pulse of 1.1 V for 3 s and a downtime of -0.1 V for 1 s in 1 M aniline and 2 M HCl. (C) The effect of 530 mT on the capacitance of the polymer versus the control at various downtime potentials. The electrode was modified with a pulse of 1.1 V for 3 s and a downtime of 1 s for 20 cycles in 1 M aniline and 2 M HCl.

During aniline electropolymerization, some of the polymer formed is deposited on the counter electrode rather than on the working electrode. Some of this deposit consists of material formed at the working electrode that does not deposit there and instead travels to and deposits on the counter. In order to investigate the effect that the magnetic field might have on this or other interactions with the electric field, experiments were conducted in which the magnet was placed on its side next to the cell, such that the magnetic field

lines ran horizontal and parallel to the plane of the working electrode surface, rather than perpendicular as shown earlier. The cell was raised such that the surface of the working electrode was even with the pole of the magnet and was placed as close as possible to ensure the maximum possible field strength. In this configuration, the strength of the magnetic field at the center of the working electrode was 390 mT. Two orientations of the cell were used: one in which the counter electrode was placed in line with the pole of the magnet and the working electrode, such that the magnetic field lines and electric field lines were parallel, and one in which the counter was placed at a right angle to the line from the pole of the magnet to the working electrode, such that the magnetic field lines were perpendicular to the electric field, as shown in Figure 4.

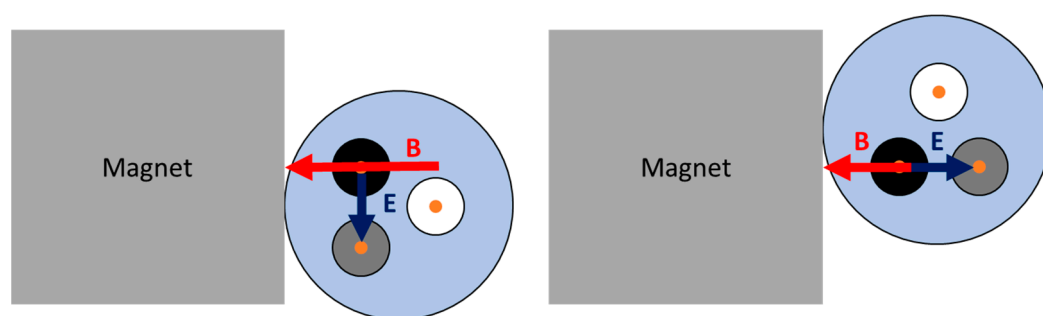


Figure 4. A top-down view of the experimental set-up, showing the relative orientations of the magnetic field lines (B) and electric field lines (E). The black circle represents the working electrode, the grey circle represents the counter electrode, and the white circle represents the reference electrode. The face of the magnet is oriented towards the electrochemical cell and is centered at the face of the working electrode.

When the magnetic field was oriented parallel to the electrode surface, its effect on the product was slightly reduced at that field strength when compared to the previous perpendicular orientation. There was not a significant difference between whether the magnetic field was oriented parallel to or perpendicular to the electric field, indicating that the dominant influence of the magnet is over processes at the working electrode surface and not processes involving the counter. When the magnetic field was oriented perpendicular to the electric field, the capacitance was increased by $+39\% \pm 12\%$, and when it was oriented parallel to the electric field, the capacitance was increased by $37\% \pm 11\%$. This indicates no substantial difference between different orientations of the electric field. The effect of the magnetic field under these conditions is slightly decreased from those shown in Figure 3A, in which the magnetic field was oriented perpendicular to the electrode surface, and the trend indicates that a 390 mT field would induce an improvement in capacitance of over 45%. This value does, however, fall within the range of experimental error.

When investigating the impact of runtime, the improvement caused by the magnet was found to increase as the length of polymerization increased, until it reached an upper limit, after which it began to decrease, as shown in Figure 3B. This is attributed not to aspects of the magnetic field effects, but rather to the total loading capacity of the polyaniline on the platinum electrode. At longer runtimes, both with and without the magnet being present, visible amounts of polyaniline that had not adsorbed to either the working or counter electrodes were found in the solution, indicating that longer runtimes approached a finite loading capacity of the electrode for the polymer. This is further evidenced by the sharp drop in the reproducibility of polymerizations at long runtimes, where the total yield depends not on the current passed but on the mass retained.

The influence of the downtime potential was investigated over a voltage range between -800 mV and $+800$ mV, as shown in Figure 3C. At a high downtime potential ($+800$ mV), the reverse current that occurs during downtime was significantly diminished because aniline oxidation still occurred at the working electrode surface, albeit to a lesser degree. Thus, for nearly all of this high-potential downtime, a low-magnitude forward current

was flowing. Therefore, the effect of this high-potential downtime was simply to reduce the magnitude of the current, thereby reducing the effect of the Lorentz force and, in turn, reducing convection. In the middle region (+400 mV to −400 mV), the potential dropped low enough to cause reduction events inside the polymer, driving a reverse current, and aniline oxidation stopped at the working electrode. This generated a high reverse current (as seen in Figure 2B), which generated convection. If the downtime is extended to a long period of time (>60 s), the reverse current will decay to 0 at all middle potentials. At a large negative downtime potential (−800 mV), the effect was again reduced despite the reverse current during downtime being very high, as the potential was low enough to fully reduce the polymer. At this very negative potential, aniline oxidation began to occur on the counter electrode, which promoted hydrogen evolution on the working electrode, which could damage the polymer. It is necessary to create a large change in potential during downtime to generate a high reverse current but not to polarize so strongly as to generate hydrogen evolution.

The optimized procedure (a pulsed-potential deposition with a pulse of 1.1 V for 3 s and a downtime of −0.1 V for 1 s, running for 20 cycles, and applying a magnetic field of 530 mT) was characterized via CV and EIS in sulfuric acid. A series of CVs were performed at varying scan rates on electrodes modified with and without the presence of a magnetic field. As shown in Figure 5A, the slope of the peak current as a function of the scan rate represents the capacitance of the electrode. It is shown that the application of a magnetic field increased the capacitance of the modified electrodes by 74%. For further characterization, EIS was performed on the electrodes at the open circuit potential (Figure 5B). It is shown that for the electrodes modified in the presence of a magnetic field, the slope of the Warburg diffusion line was significantly increased, which also indicates improved capacitance, as the slope of the Warburg diffusion line tends to infinity for pure capacitors [58].

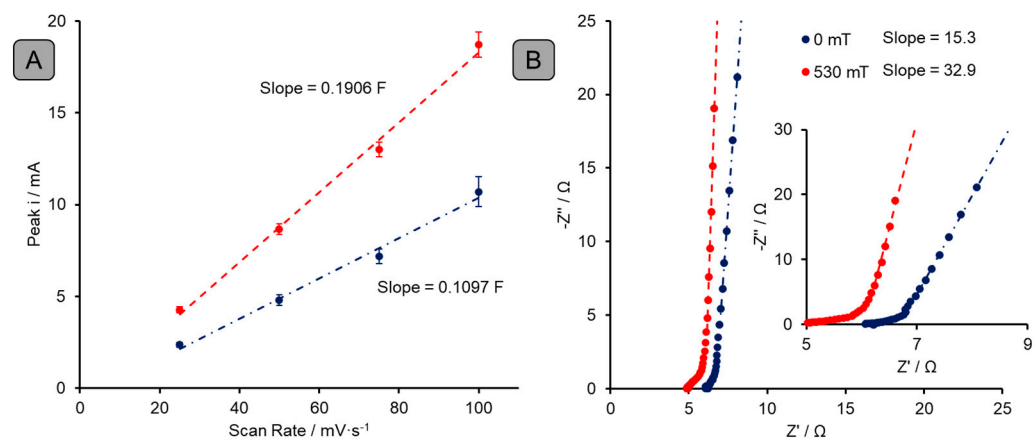


Figure 5. (A) Peak current vs. scan rate for a series of CVs of two modified electrodes in 1 M H₂SO₄: one modified under no magnetic field, the other modified under 530 mT. (B) EIS in 1 M H₂SO₄, from 100 kHz to 100 mHz, at the open circuit potential of an electrode modified under no magnetic field and an electrode modified under 530 mT. All electrodes were modified with a pulse time of 3 s, a downtime of 1 s, and a downtime potential of −0.1 V for 20 pulses in 1 M aniline and 2 M HCl.

Galvanostatic charge/discharge (GCD) is an ideal approach for investigating the electrochemical capacitance of materials. GCD was performed on symmetric capacitor configurations composed of PANI films synthesized in the absence (Figure 6A) and the presence (Figure 6B) of 530 mT magnetic fields. The cells were constructed by placing two platinum electrodes, both modified either with or without a magnetic field, into a 1 M H₂SO₄ solution to simulate the behavior of a symmetric supercapacitor. The cells were charged and discharged at currents ranging from 0.5 to 2 mA. The longer discharge times

of the cells composed of PANI synthesized in a magnetic field at the same applied currents confirms their improved capacitance.

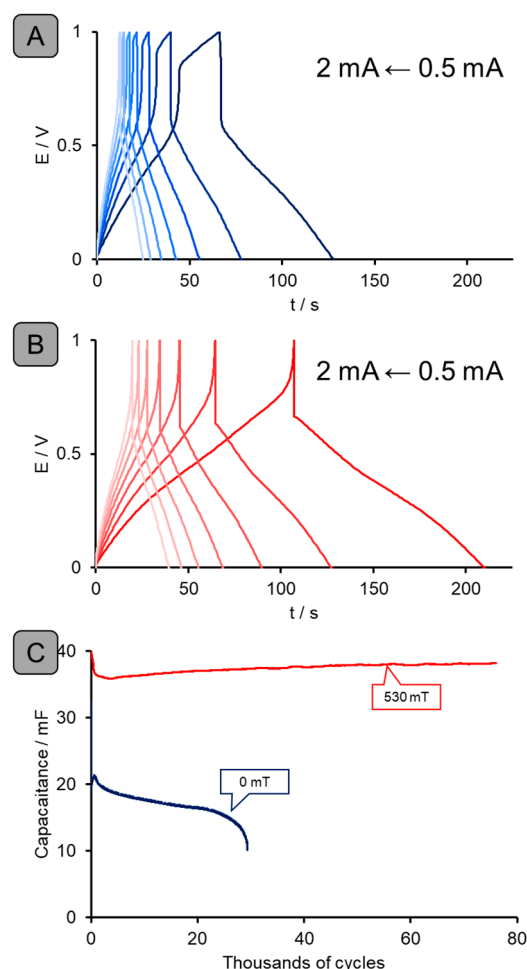


Figure 6. (A) Galvanostatic charging–discharging curves at 0.5, 0.75, 1, 1.25, 1.5, 1.75, and 2 mA for a cell constructed from electrodes modified with no magnetic field. (B) Galvanostatic charging–discharging curves at 0.5, 0.75, 1, 1.25, 1.5, 1.75, and 2 mA for a cell constructed from electrodes modified under 530 mT. (C) The capacitance per cycle of galvanostatic charging and discharging at 5 mA for two cells constructed with electrodes modified under no magnetic field and one cell constructed of electrodes modified under 530 mT.

The cells were then tested for their durability during cycling, as shown in Figure 6C. The cell made with the electrodes modified under no magnetic field showed significant losses in capacitance before failure at approximately 29,000 cycles. The cell constructed with electrodes modified under 530 mT showed a slight decrease in capacitance in the initial 100 cycles before stabilizing and showed no further loss in capacitance for up to 75,000 cycles, at which point the experiment was ended due to time constraints.

3.3. Role of Convection

To investigate the cause of the improvement, the morphology of the polymers formed with and without the presence of a magnetic field were investigated via scanning electron microscopy. To perform the analysis conductive, adhesive carbon tabs were affixed to the working electrode surface, and the PANI was deposited on the carbon. The carbon tabs were then transferred to SEM stubs for imaging. The PANI films exhibited an intertangled fibrous structure. The bulk of both PANI films were similar in fiber density and thickness (as shown in Figure 7A,B), however, the edge sites show different morphologies. At some edge sites, significantly thinner fibers were observed on the PANI film synthesized in the

presence of a 530 mT magnetic field. These thin fibrous structures were both more common and more pronounced in the polymer formed under 530 mT, suggesting that not only does forced convection, driven by the MHD effect, result in a larger PANI yield, but that the thickness of the PANI fibers can be influenced by these conditions.

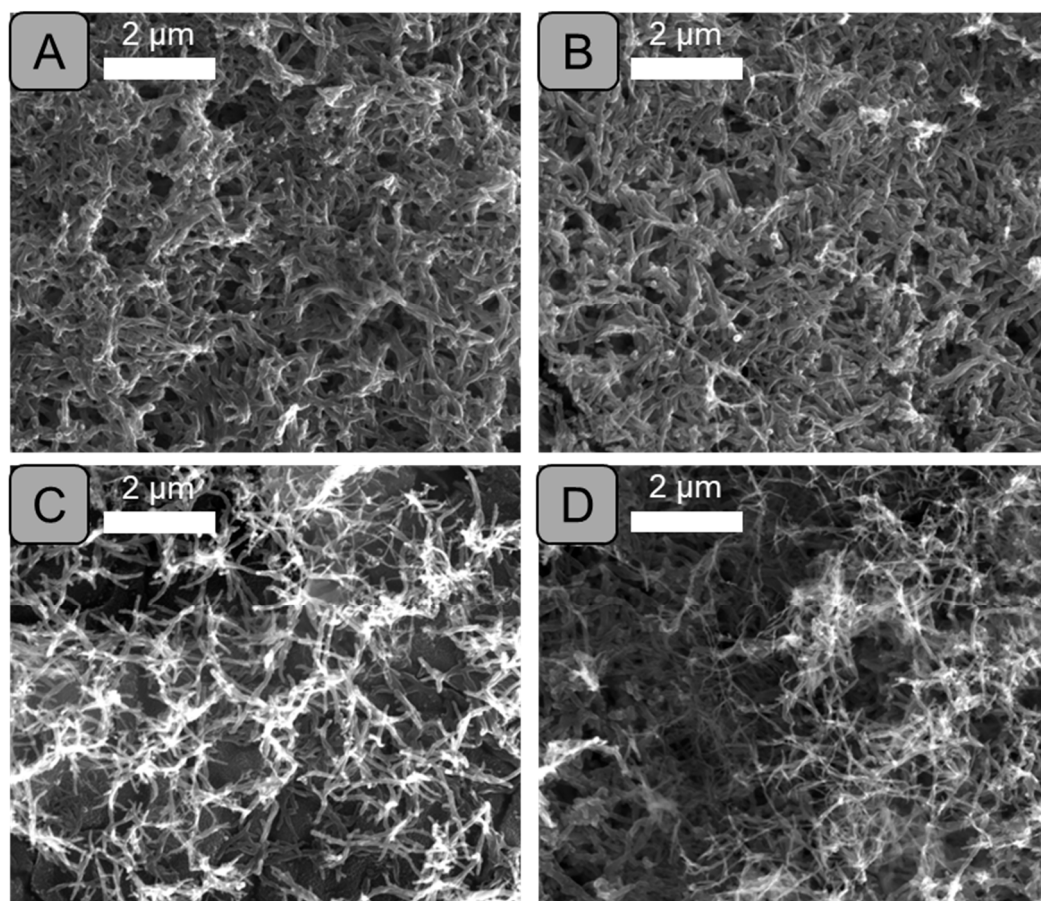


Figure 7. (A) Micrograph of bulk polymer formed under no magnetic field. (B) Micrograph of bulk polymer formed under 530 mT. (C) Micrograph of a thin-fiber edge site formed under no magnetic field. (D) Micrograph of a thin-fiber edge site formed under 530 mT.

In order to determine whether the observed capacitive differences were caused solely by the Lorentz force-induced convection, the polymerization protocol was applied to stirred systems under no magnetic field (i.e., forced convection). A 12.7 mm long magnetic stir bar was placed in the cell and rotated at a variety of rotation speeds using a magnetic stir plate. The strength of the magnetic field at the surface of the stir plate was approximately 10 mT, which was small enough to have no impact on the polymerization. It is shown in Figure 8A that the peak current during polymerization, when performed in the presence of a magnetic field, was less than when stirring the solution; however, the current decayed slower than what was observed using the stirred or unstirred (no magnetic field) polymerization protocols. Despite this decreased peak current, the total capacitance of the electrode modified in the magnetic field was higher than for any of those modified in the presence of forced convection (Figure 8B), having a 34% higher capacitance than that modified with the fastest stir rate of 1000 rpm.

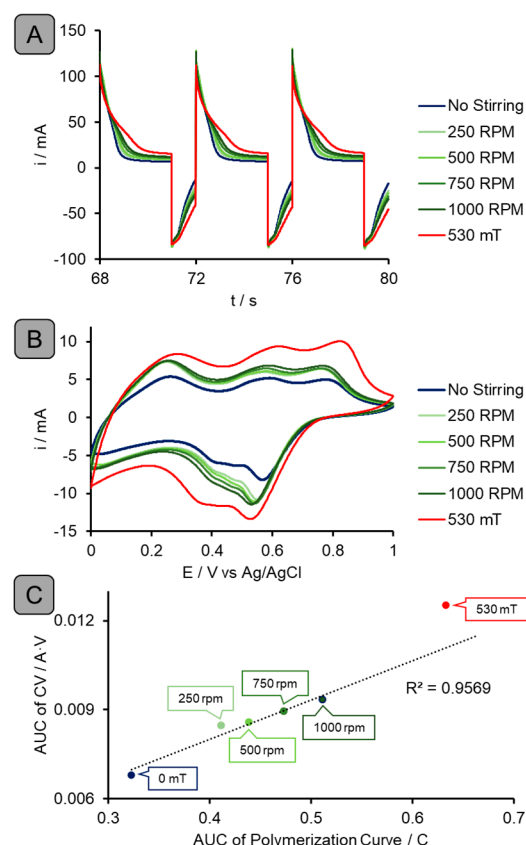


Figure 8. (A) The current response of the final three pulses of polymerization when stirring at various rates versus the control and when polymerizing in the presence of a magnetic field. (B) CVs in 1 M H_2SO_4 of the electrodes modified in (A). (C) The areas inside the characterization CVs in (B) plotted against the areas under the full polymerization curves in (A).

When the full polymerization curves are integrated, which represents the total charge passed in the forward current that is not returned in the reverse current, it is seen that the polymerization in the presence of the magnet passed the most total charge. It is shown in Figure 8C that there is a linear correlation between the total charge passed during polymerization and the area of the characterization CV (proportional to the total capacitance) for all the electrodes modified without the use of the magnet. Here, we also see that the electrode modified in the presence of the magnetic field lies above the trend, with a 13% higher capacitance than expected for that yield, indicating that the increase in capacitance of the polymer is a result of more than simply increased yield.

4. Conclusions

Herein we have shown that the application of a magnetic field during the electropolymerization of aniline in a strongly acidic environment can increase both the yield and capacitance, by upwards of 70%, of the resulting PANI films. The characterization of the PANI films using electrochemical impedance spectroscopy and galvanostatic charge/discharge experiments confirm the increased capacitance of the PANI films synthesized in the presence of 530 mT as compared to the PANI films formed in the absence of a magnetic field. Moreover, the PANI films formed in the presence of magnetic fields were able to retain their capacitance for over 75,000 cycles, indicating increased stability over the PANI formed in the absence of magnetic fields, which exhibited an extreme loss of capacitance after 29,000 cycles. This technique allows for an improved energy storage material without the use of any extra or expensive materials. Furthermore, the use of permanent magnets instead of electromagnets for this application allows this improvement to be achieved without the input of any additional energy. To the best of our knowledge, this is the first

example in the literature to explore the effect on capacitance of a magnetic field during an electropolymerization. This work also achieves a significant improvement in the polymer product with field strengths notably lower than many of those found in comparable studies of magnetoelectropolymerizations. The results suggest that this method could be applied to other electroactive polymers, provided their monomers are charged in solution and, thus, able to be influenced by the Lorentz force.

Although the primary influence of the magnet on the polymerization process is from forced convection via the MHD effect, it remains to be shown what effect the magnet has on the electropolymerization beyond increased yield from induced convection. Figure 8C suggests that the magnetic field creates an improvement in the capacitive behavior of the polymer beyond increased yield; however, the nature of this influence remains unidentified. While there does appear to be a slight difference in morphology, this does not appear to be significant enough to account for the improvement. Future work related to magnetically influenced electropolymerization will aim to investigate (i) whether intrinsic properties of the polymer, such as average molecular weight or branching, are altered when polymerized in the presence of magnetic fields, (ii) whether the magnetic field has a meaningful effect on the stability of the radical intermediates at various field strengths, and (iii) the effects of other field orientations, such as strongly diverging or converging field lines. Furthermore, for device applications, investigations using compatible substrates (e.g., carbon mesh, indium tin oxide (ITO), etc.) are necessary to determine if the influence of the magnet is equally advantageous to justify integration into supercapacitor applications.

Author Contributions: Conceptualization, J.G.B., A.S. and W.T.M.; methodology, W.T.M. and J.G.B.; validation, W.T.M., A.S. and A.K.K.; formal analysis, W.T.M.; investigation, W.T.M., A.S. and A.K.K.; resources, J.G.B.; data curation, W.T.M.; writing—original draft preparation, W.T.M.; writing—review and editing, J.G.B., A.S. and W.T.M.; visualization, W.T.M.; supervision, J.G.B.; project administration, J.G.B.; funding acquisition, J.G.B. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data in this article will be made available upon request.

Acknowledgments: The authors would like to acknowledge the Franceschi Microscopy and Imaging Center at Washington State University for the use of their scanning electron microscope.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Shah, N.; Czarkowski, D. Supercapacitors in Tandem with Batteries to Prolong the Range of UGV Systems. *Electronics* **2018**, *7*, 6. [\[CrossRef\]](#)
- Oubelaid, A.; Alharbi, H.; Humayd, A.S.B.; Taib, N.; Rekioua, T.; Ghoneim, S.S.M. Fuzzy-Energy-Management-Based Intelligent Direct Torque Control for a Battery—Supercapacitor Electric Vehicle. *Sustainability* **2022**, *14*, 8407. [\[CrossRef\]](#)
- Najib, S.; Erdem, E. Current progress achieved in novel materials for supercapacitor electrodes: Mini review. *Nanoscale Adv.* **2019**, *1*, 2817–2827. [\[CrossRef\]](#) [\[PubMed\]](#)
- Poonam; Sharma, K.; Arora, A.; Tripathi, S.K. Review of supercapacitors: Materials and devices. *J. Energy Storage* **2019**, *21*, 801–825. [\[CrossRef\]](#)
- Raza, W.; Ali, F.; Raza, N.; Luo, Y.; Kim, K.-H.; Yang, J.; Kumar, S.; Mehmood, A.; Kwon, E.E. Recent advancements in supercapacitor technology. *Nano Energy* **2018**, *52*, 441–473. [\[CrossRef\]](#)
- Sheelam, A.; McLeod, W.T.; Badam, R.; King, M.; Bell, J.G. Chapter 27—Comparison between supercapacitors and other energy storing electrochemical devices. In *Smart Supercapacitors*; Hussain, C.M., Ahamed, M.B., Eds.; Elsevier: Amsterdam, The Netherlands, 2022; pp. 673–712.
- Chakraborty, S.; Mary, N.L. Review—An Overview on Supercapacitors and Its Applications. *J. Electrochem. Soc.* **2022**, *169*, 020552. [\[CrossRef\]](#)
- Liu, Y.; Jiang, S.P.; Shao, Z. Intercalation pseudocapacitance in electrochemical energy storage: Recent advances in fundamental understanding and materials development. *Mater. Today Adv.* **2020**, *7*, 100072. [\[CrossRef\]](#)

9. Şahin, M.; Blaabjerg, F.; Sangwongwanich, A. A Comprehensive Review on Supercapacitor Applications and Developments. *Energies* **2022**, *15*, 674. [\[CrossRef\]](#)
10. Loganathan, N.N.; Perumal, V.; Pandian, B.R.; Atchudan, R.; Edison, T.N.J.I.; Ovinis, M. Recent studies on polymeric materials for supercapacitor development. *J. Energy Storage* **2022**, *49*, 104149. [\[CrossRef\]](#)
11. Meng, Q.; Cai, K.; Chen, Y.; Chen, L. Research progress on conducting polymer based supercapacitor electrode materials. *Nano Energy* **2017**, *36*, 268–285. [\[CrossRef\]](#)
12. Tai, Z.; Yan, X.; Xue, Q. Three-Dimensional Graphene/Polyaniline Composite Hydrogel as Supercapacitor Electrode. *J. Electrochem. Soc.* **2012**, *159*, A1702. [\[CrossRef\]](#)
13. Abu Hassan Shaari, H.; Ramli, M.M.; Abdullah, M.M.; Mohtar, M.N.; Abdul Rahman, N.; Ahmad, A.; Osman, N.H.; Rusydi, F. Effects of Polymerization Time towards Conductivity and Properties of Poly(methyl methacrylate)/Polyaniline (PMMA/PANi) Copolymer. *Sustainability* **2022**, *14*, 8940. [\[CrossRef\]](#)
14. Badawi, N.M.; Batoo, K.M.; Ramesh, S.; Ramesh, K.; Imran, A. SWCNTs/PEDOT: PSS Coated Cotton for Wearable Clothes and Supercapacitor Applications. *Sustainability* **2023**, *15*, 889. [\[CrossRef\]](#)
15. Cao, Q.; Hao, S.; Wu, Y.; Pei, K.; You, W.; Che, R. Interfacial charge redistribution in interconnected network of Ni₂P–Co₂P boosting electrocatalytic hydrogen evolution in both acidic and alkaline conditions. *Chem. Eng. J.* **2021**, *424*, 130444. [\[CrossRef\]](#)
16. Hong, R.; Liu, Q.; Cao, Q.; Xu, J.; Xiao, R.; Zhang, H. Catalytic upcycling of waste polypropylene for gram-scale production of FeCo@N-doped carbon nanotubes toward efficient oxygen reduction electrocatalysis. *J. Electroanal. Chem.* **2023**, *936*, 117394. [\[CrossRef\]](#)
17. Bai, J.; Feng, Z.; Huang, L.; Tang, J.; Wang, Y.; Wang, S. Hardwood Kraft lignin-derived carbon microfibers with enhanced electrochemical performance. *Int. J. Biol. Macromol.* **2022**, *220*, 733–742. [\[CrossRef\]](#)
18. Li, L.; Nam, J.S.; Kim, M.S.; Wang, Y.; Jiang, S.; Hou, H.; Kim, I.-D. Sulfur–Carbon Electrode with PEO–LiFSI–PVDF Composite Coating for High-Rate and Long-Life Lithium–Sulfur Batteries. *Adv. Energy Mat.* **2023**, *13*, 2302139. [\[CrossRef\]](#)
19. Deng, W.; Xu, Y.; Zhang, X.; Li, C.; Liu, Y.; Xiang, K.; Chen, H. (NH₄)₂Co₂V₁₀O₂₈·16H₂O/(NH₄)₂V₁₀O₂₅·8H₂O heterostructure as cathode for high-performance aqueous Zn-ion batteries. *J. Alloys Compd.* **2022**, *903*, 163824. [\[CrossRef\]](#)
20. Rahman, M.M.; Joy, P.M.; Uddin, M.N.; Mukhlsh, M.Z.B.; Khan, M.M.R. Improvement of capacitive performance of polyaniline based hybrid supercapacitor. *Heliyon* **2021**, *7*, e07407. [\[CrossRef\]](#)
21. Heme, H.N.; Alif, M.S.N.; Rahat, S.M.S.M.; Shuchi, S.B. Recent progress in polyaniline composites for high capacity energy storage: A review. *J. Energy Storage* **2021**, *42*, 103018. [\[CrossRef\]](#)
22. Deng, W.-N.; Li, Y.-H.; Xu, D.-F.; Zhou, W.; Xiang, K.-X.; Chen, H. Three-dimensional hierarchically porous nitrogen-doped carbon from water hyacinth as selenium host for high-performance lithium–selenium batteries. *Rare Met.* **2022**, *41*, 3432–3445. [\[CrossRef\]](#)
23. Aogaki, R.; Fueki, K.; Mukaibo, T. Application of Magnetohydrodynamic Effect to the Analysis of Electrochemical Reactions 1. MHD Flow of an Electrolyte Solution in an Electrode—Cell with a short Rectangular Channel. *Denki Kagaku* **1975**, *43*, 504–508. [\[CrossRef\]](#)
24. Fahidy, T.Z. Magneto-electrolysis. *J. Appl. Electrochem.* **1983**, *13*, 553–563. [\[CrossRef\]](#)
25. Tacken, R.A.; Janssen, L.J.J. Applications of magneto-electrolysis. *J. Appl. Electrochem.* **1995**, *25*, 1–5. [\[CrossRef\]](#)
26. Kawamori, M.; Asai, T.; Shirai, Y.; Yagi, S.; Oishi, M.; Ichitsubo, T.; Matsubara, E. Three-dimensional nanoelectrode by metal nanowire nonwoven clothes. *Nano Lett.* **2014**, *14*, 1932–1937. [\[CrossRef\]](#)
27. Shao, J.; Li, W.; Zhou, X.; Hu, J. Magnetic-field-assisted hydrothermal synthesis of 2 × 2 tunnels of MnO₂ nanostructures with enhanced supercapacitor performance. *CrystEngComm* **2014**, *16*, 9987–9991. [\[CrossRef\]](#)
28. Xu, C.; Li, Z.; Yang, C.; Zou, P.; Xie, B.; Lin, Z.; Zhang, Z.; Li, B.; Kang, F.; Wong, C.P. An Ultralong, Highly Oriented Nickel-Nanowire-Array Electrode Scaffold for High-Performance Compressible Pseudocapacitors. *Adv. Mater.* **2016**, *28*, 4105–4110. [\[CrossRef\]](#)
29. Singh, M.; Sahoo, A.; Yadav, K.L.; Sharma, Y. Toward the Origin of Magnetic Field-Dependent Storage Properties: A Case Study on the Supercapacitive Performance of FeCo(2)O(4) Nanofibers. *ACS Appl. Mater. Interfaces* **2020**, *12*, 49530–49540. [\[CrossRef\]](#)
30. Sharma, V.; Biswas, S.; Chandra, A. Need for Revisiting the Use of Magnetic Oxides as Electrode Materials in Supercapacitors: Unequivocal Evidence of Significant Variation in Specific Capacitance under Variable Magnetic Field. *Adv. Energy Mat.* **2018**, *8*, 1800573. [\[CrossRef\]](#)
31. Zeng, Z.; Liu, Y.; Zhang, W.; Chevva, H.; Wei, J. Improved supercapacitor performance of MnO₂-electrospun carbon nanofibers electrodes by mT magnetic field. *J. Power Sources* **2017**, *358*, 22–28. [\[CrossRef\]](#)
32. Sheelam, A.; Glasco, D.L.; Bell, J.G. Retaining the reversible capacity by Lorentz forces for enhanced cyclability of aqueous zinc-bromide batteries using internal magnets. *Chem. Eng. J.* **2023**, *461*, 141900. [\[CrossRef\]](#)
33. Kim, C.; Yang, Y.; Ha, D.; Kim, D.H.; Kim, H. Crystal alignment of a LiFePO₄ cathode material for lithium ion batteries using its magnetic properties. *RSC Adv.* **2019**, *9*, 31936–31942. [\[CrossRef\]](#) [\[PubMed\]](#)
34. Li, L.; Erb, R.M.; Wang, J.; Wang, J.; Chiang, Y.-M. Battery Electrodes: Fabrication of Low-Tortuosity Ultrahigh-Area-Capacity Battery Electrodes through Magnetic Alignment of Emulsion-Based Slurries (Adv. Energy Mater. 2/2019). *Adv. Energy Mat.* **2019**, *9*, 1970006. [\[CrossRef\]](#)
35. Zhang, L.; Zeng, M.; Wu, D.; Yan, X. Magnetic Field Regulating the Graphite Electrode for Excellent Lithium-Ion Batteries Performance. *ACS Sustain. Chem. Eng.* **2019**, *7*, 6152–6160. [\[CrossRef\]](#)

36. Ganguly, D.; Piriya, A.V.S.; Ghosh, A.; Ramaprabhu, S. Magnetic field assisted high capacity durable Li-ion battery using magnetic α -Fe₂O₃ nanoparticles decorated expired drug derived N-doped carbon anode. *Sci. Rep.* **2020**, *10*, 9945. [[CrossRef](#)]
37. Tang, X.; Chen, G.; Mo, Z.; Ma, D.; Wang, S.; Wen, J.; Gong, L.; Zhao, L.; Huang, J.; Huang, T.; et al. Controllable two-dimensional movement and redistribution of lithium ions in metal oxides. *Nat. Commun.* **2019**, *10*, 2888. [[CrossRef](#)]
38. Li, W.; Liang, Z.; Lu, Z.; Tao, X.; Liu, K.; Yao, H.; Cui, Y. Magnetic Field-Controlled Lithium Polysulfide Semiliquid Battery with Ferrofluidic Properties. *Nano Lett.* **2015**, *15*, 7394–7399. [[CrossRef](#)] [[PubMed](#)]
39. Chen, Y.; Dou, X.; Wang, K.; Han, Y. Magnetically enhancing diffusion for dendrite-free and long-term stable lithium metal anodes. *Green Energy Environ.* **2022**, *7*, 965–974. [[CrossRef](#)]
40. Shen, K.; Xu, X.; Tang, Y. Recent progress of magnetic field application in lithium-based batteries. *Nano Energy* **2022**, *92*, 106703. [[CrossRef](#)]
41. Raj, K.A.S.; Rout, C.S. Recent developments, challenges and future prospects of magnetic field effects in supercapacitors. *J. Mater. Chem. A* **2023**, *11*, 5495–5519. [[CrossRef](#)]
42. Mogi, I. Electrochemical Polymerization of Aniline in High Magnetic Fields. *Denki Kagaku* **1994**, *62*, 1287–1289. [[CrossRef](#)]
43. Nafdey, R.A.; Kelkar, D.S. Structure and electrical properties of polyaniline synthesized in presence of low magnetic field. *Curr. Appl. Phys.* **2009**, *9*, 289–295. [[CrossRef](#)]
44. Lv, R.; Zhang, S.; Shi, Q.; Kan, J. Electrochemical synthesis of polyaniline nanoparticles in the presence of magnetic field and erbium chloride. *Synth. Met.* **2005**, *150*, 115–122. [[CrossRef](#)]
45. Cho, M.S.; Yun, Y.Y.; Nam, J.D.; Son, Y.; Lee, Y. Effect of magnetic field on electrochemical polymerization of EDOT. *Synth. Met.* **2008**, *158*, 1043–1046. [[CrossRef](#)]
46. Kawabata, K.; Nimori, S.; Goto, H. Horizontal and Vertical Orientation of Polythiophenes by Electrochemical Polymerization in Magnetically Aligned Smectic Liquid Crystal. *ACS Macro Lett.* **2013**, *2*, 587–591. [[CrossRef](#)]
47. Mogi, I. Magneto-electropolymerized film formation of polypyrrole. *Microelectron. Eng.* **1998**, *43–44*, 739–744. [[CrossRef](#)]
48. Mogi, I.; Watanabe, K.; Motokawa, M. Magneto-electropolymerization of conducting polypyrrole. *Phys. B Condens.* **1998**, *246–247*, 412–415. [[CrossRef](#)]
49. Wang, F.; Mori, K.; Kang, Z.; Oishi, Y. Magnetic field effects on the polymerization of 6-N,N-diethylamino-1,3,5-triazine-2,4-dithiol. *Heteroat. Chem.* **2007**, *18*, 60–64. [[CrossRef](#)]
50. Steiner, U.E.; Ulrich, T. Magnetic field effects in chemical kinetics and related phenomena. *Chem. Rev.* **1989**, *89*, 51–147. [[CrossRef](#)]
51. Hinds, G.; Coey, J.M.D.; Lyons, M.E.G. Influence of magnetic forces on electrochemical mass transport. *Electrochem. Commun.* **2001**, *3*, 215–218. [[CrossRef](#)]
52. Monzon, L.M.A.; Coey, J.M.D. Magnetic fields in electrochemistry: The Lorentz force. A mini-review. *Electrochem. Commun.* **2014**, *42*, 38–41. [[CrossRef](#)]
53. Karami, H.; Asadi, M.G.; Mansoori, M. Pulse electropolymerization and the characterization of polyaniline nanofibers. *Electrochim. Acta* **2012**, *61*, 154–164. [[CrossRef](#)]
54. Zhou, H.; Wen, J.; Ning, X.; Fu, C.; Chen, J.; Kuang, Y. Electrosynthesis of polyaniline films on titanium by pulse potentiostatic method. *Synth. Met.* **2007**, *157*, 98–103. [[CrossRef](#)]
55. Song, E.; Choi, J.-W. Conducting Polyaniline Nanowire and Its Applications in Chemiresistive Sensing. *Nanomaterials* **2013**, *3*, 498–523. [[CrossRef](#)] [[PubMed](#)]
56. Geniès, E.M.; Lapkowski, M.; Penneau, J.F. Cyclic voltammetry of polyaniline: Interpretation of the middle peak. *J. Electroanal. Chem. Interfacial Electrochem.* **1988**, *249*, 97–107. [[CrossRef](#)]
57. Rintoul, I. Kinetic control of aqueous polymerization using radicals generated in different spin states. *Processes* **2017**, *5*, 15. [[CrossRef](#)]
58. Lazanas, A.C.; Prodromidis, M.I. Electrochemical Impedance Spectroscopy—A Tutorial. *ACS Meas. Sci. Au* **2023**, *3*, 162–193. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.