

Electrochemical Machining Process Using Different Electrolytes for Improved Process Efficiency

Gurwinder Singh^{1*}, P. Sudhakar Rao¹, Rupinder Singh¹

¹National Institute of Technical Teacher's Training and Research (NITTTR), Chandigarh 160019, India

Abstract. Electrochemical machining (ECM) was developed as a result of the manufacturing and production industry's need to cut extremely hard alloys without leaving a troublesome layer. Manufacturing industries involved in gas turbine blades and aerospace need intricate geometries that would be difficult to make using standard methods. Because of high tool wear (TW) and metal removal rate (MRR), traditional machining processes such as milling and other conventional machining are inefficient for extracting metal from hard materials. This study outlines, a comprehensive analysis of the ECM processes using different electrolytes for better process efficiency.

1 Introduction

ECM includes dissolving the workpiece anodically to replicate the geometry of the tool electrode [1]. Both the tool electrode (as a cathode) and the workpiece (as an anode) are engrossed in an electrically conductive electrolyte in ECM, which is often solvent salt solutions like NaNO_3 , NaCl , etc. for the machining process [2-4]. A constant voltage is kept between the two electrodes with a gap, ensuring that the workpiece becomes the anode. As a result of the applied voltage, a direct current flows between the tool and workpiece, resulting in the removal of anode material [4]. To produce topographies on such a small scale, new manufacturing procedures must be developed to achieve miniaturization [5]. Recent advances have suggested the use of customized electrodes of smaller sizes, such as discs, rods, shafts, or hollow tubes to create complex geometrical shapes by moving that small tool along a preset route. Therefore, a higher response is required for the dissolving process for ECM. An entirely new ECM technique called pulsed electrochemical machining (PECM) was developed as the outcome of this research [6]. This process uses pulsed voltage, and the inter-electrode space (IES) is proportional to the pulse width [6-7] as per reported literature. Fig. 1 shows a flow diagram of the ECM process.

* Corresponding author: gurwinder.mech20@nitttrchd.ac.in

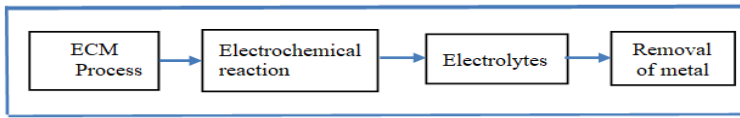
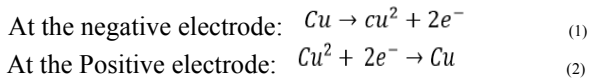


Fig. 1. Flow diagram of the ECM process.

1.1 Process Overview of ECM

A temperature-controlled, dormant copper sulfate (CuSO_4) solution is circulated between the two electrodes i.e., copper alloy (as an anode) and pure copper (as the cathode) through a constant current source. In the electrolyte, copper atoms dissolve and travel to the cathode, where they are eventually deposited. A variety of mechanisms were used to transport the copper ions through the solution. The passage of ions inside a solution that is affected by concentration gradients is referred to as diffusion. To accomplish attain concentration equality across the solution, ions flow from locations with greater concentrations to areas with lower concentrations [1, 8]. Due to the anode surface concentration of copper ions being much higher than the bulk solution concentration, ions of Cu diffuse away from the anode towards the bulk solution and the copper cathode in this ionic condition. Cathode surface concentration is fewer than bulk concentration as the Cu ions are expended on cathode surfaces. As Cu ions migrate across the solution due to a potential field, migration occurs during the process. Here, the positively charged Cu ions are electrostatically drawn to the cathode end by electrostatic attraction. In this electrochemical investigation evaluating electrode reactions, an upbringing electrolyte with a high concentration is frequently utilized to reduce the belongings of migration in the electrolyte solution. It's important to note that migration has little impact on species because it's carried by the background electrolyte. Flowing ions through a solution by convection would be a third option. As a result outside mechanical forces such as bubbling/ stirring helps the solution to move. Because copper electrolysis does not stir the solution, ions are not exposed to the effects of large convection (whether natural or forced) for example, agitating of solution [3].

During Copper electrolysis, the following reactions occur at the electrodes:



Both of these reactions arise simultaneously, which prevents any charge from collecting in that circuit. It is also uncharged because there are counter ions present.

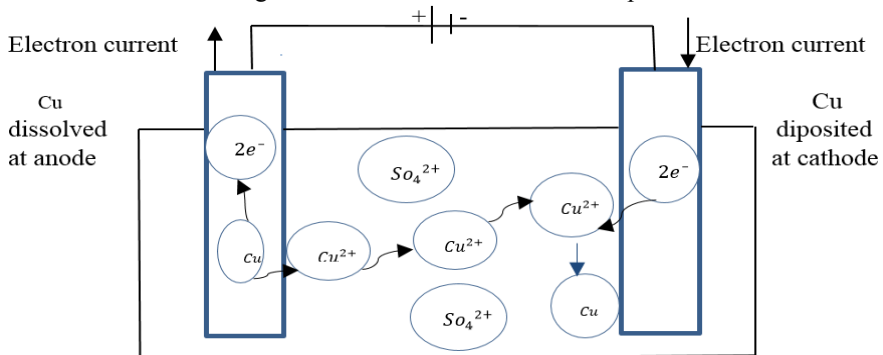
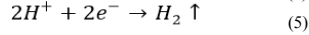
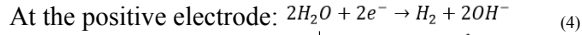
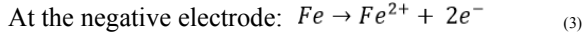


Fig. 2. Schematic illustration of the copper purification process.



Cu purification electrolyte processes are depicted as shown in Fig. 2. Anode impure copper is dissolved, thus reducing the bulk material removal. Under the anode, insoluble impurities are collected in the above process. Electrochemical sequences demonstrate that no additional reactions are occurring at either electrode due to less reactivity of Cu than Hydrogen [5]. A similar process to copper purification in ECM is the elimination of material. Another dissolution method is followed in ECM, but the current has been controlled in several ways to allow for a more exact and accurate dissolution process than copper electrolysis does in the electrolyte media. A variety of shapes and curves can be developed through this technique. The restrained anodic dissolution of Fe in $NaNO_3$ electrolytes demonstrates the distinctions between copper electrolysis and iron anodic dissolution. Tool and electrode spacing are condensed to micrometers to manage anodic dissolution-prone spots on the workpiece. This supports confining the current to the appropriate areas, allowing micromachining to occur. While both procedures involve dissolving metals, there are differences once the ions have been dispersed. Hydrogen evolution has been selected as a method. When the dissolution reaction occurs, a balancing current flows. Hydroxide ions are created by the electrolytic breakdown of water at the anode, which balances off the dissolution reaction current. Electrolysis of water produces iron ions that react with the hydroxides to yield insoluble metal hydroxides. In the process, the ions are eliminated and prevented from accumulating on the cathode as a result of their precipitation from the solution. A change in cathode geometry over time would be undesired in an ECM process. Instead, the cathode material allows for this. These reactions aren't electrochemical, but they happen regardless of whether or not there's current flowing, and they don't happen on the electrode surface [9-12]. It does not have any effect on the overall current flow as a result of this interaction. During the ECM of ferrous workpiece material in $NaNO_3$, the steps are shown in Fig. 3. This is what happens when electrodes are used, The creation takes place aside from the electrode surface moreover triggered by the electroless reaction that follows,

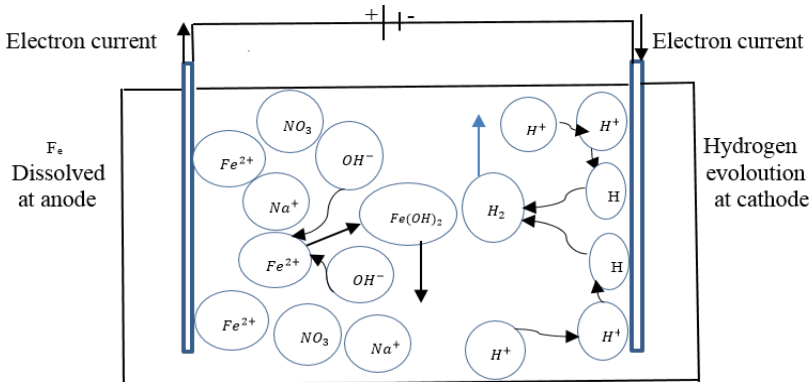
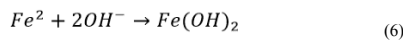
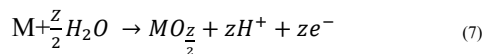


Fig. 3. A schematic of iron anodic dissolution.

2 Mechanism of layer formation in electrolysis

The chemical reaction between two terminals can be altered depending on the selection of the electrolyte based on its nature. The electrolytes are categorized as passivating and non-passivating [13]. To produce passive layers on the surface of the workpiece, passivating electrolytes are used. Hydroxides and oxides are formed when current is communicated between the workpiece and tool terminals. Sometimes the passive layer will form naturally and quickly, whereas in other cases it may only form due to the conduction of an anodic current through the passive layer. This relies both on the electrolyte used and the metal used to make the workpiece. Because a passive layer is used to increase the corrosion resistance, it reduces the material removal rate (MRR) and increases the possibility of machining the surface, which is unfavorable to ECM. Depending on the situation, the electrical isolation of passive films can prevent chemical compounds from being etched or dissolved. Because of this, the quality of manufacturing is improved [14-15]. As a result of the aggressive ions in non-passivating electrolytes, a coating cannot develop on the workpiece. Electrolytes that don't passivate have higher machining rates than passivating electrolytes, however, their surface finish quality can be degraded. The metal of the workpiece and the surroundings react to generate passive layers on the workpiece. A layer of oxide is formed on top of water molecules as they dissolve in the electrolytic solution, as seen below in equations [3, 16].



Passive films come in two varieties: insulators and non-insulators. The workpiece insulating film is self-contained. The result is a thick, dense, and uniformly distributed layer on the surface. The uneven electric field, on the other hand, might shatter and distort the passive film. The addition of certain functional ions can also affect the film [17]. So, it's crucial to choose the right electrolyte for the material you're going to the machine. The production of passive films must be avoided to attain the maximum MRR while utilizing the least amount of energy possible. Breaking sound or uneven current peaks may indicate that the passive film has broken down during the ECM process. It depends on the content and concentration of the electrolyte. It is important to note that a passive film's disintegration is almost independent of temperature and current density [18]. ECM researchers are well aware of this issue and have been working to develop strategies to eliminate the creation of passive films. The most typical strategy is to use an electrolyte that does not passivate, rather than removing the passive layer along with the underlying metal. The total charged passed is employed for metal removal since the anode is retained at a voltage where the formation of a passive layer is there, then consequently, the MRR increased.

2.1 Mechanism of Electrolytes

In the ECM process, the electrolyte is the predominant component. It plays a vital role in both material removal and tool wear. The ECM process primarily serves three purposes: transporting current between the tool and workpiece and eliminating reaction products from the IES [13]. The electrolyte used has an impact on the chemical machining process's performance. It must be non-corrosive and non-toxic, with good conductivity and electrochemical and chemical stability. The polarization curve can be used to identify the important properties of an electrolyte. The graphical depiction of voltage (power density) vs. current (current density) of an electrolyte cellular stack is known as a polarization curve [19, 20]. The electrolyte used in the ECM machining process is chosen so that no material deposition occurs on the cathode. If the deposition is present, it might distort the tool shape and affect the workpiece's surface finish. Furthermore, the electrolyte must be capable of

removing any excess heat generated during the ECM process. It eliminates the products of the reaction from the IES as well as the heat produced by the current's passage. To increase ECM's dimensional accuracy, localization effects can be forecast and controlled. The degree of localization is greater with low-concentration electrolytes, allowing for higher precision than with high concentrations [9, 21].

3 Choosing Electrolytes for ECM Process

Electrolytes are divided into four groups based on their chemical and physical properties. They are non-aqueous electrolytes, neutral aqueous salts, aqueous acids, and aqueous alkalis, respectively. The most commonly used electrolytes are neutral aqueous salts, which are relatively inexpensive and generally innocuous to working tools and machinery. Neutral electrolytes include metal chlorides and phosphates such as calcium, magnesium, sodium, potassium, and others. Acidic electrolytes are utilized when other electrolytes are not successful in dissolving the substance. Hydrochloric, sulfuric, nitric, and perchloric acids are examples of acidic electrolytes. The acidic electrolytes are utilized when other electrolytes are not successful in dissolving the substance. Sulfuric acid, hydrochloric acid, nitric acid, perchloric acid, and other acidic electrolytes are examples. Because the ions and additional reaction products are securely dissolved in electrolytic, the interelectrode gap can be greatly decreased. This also solves the issue of 'clogging'. This is why acidic electrolytes are preferred in electrochemical micromachining [22]. Ceramic electrolytes, dry polymer electrolytes, gel electrolytes, ionic plastic crystals, and other non-aqueous electrolytes are such examples. They can also operate at low IES because no gases or precipitation products are created. Metal workpieces are already machined with solid electrolytes. An ethylene glycol electrolyte to achieve quick micropatterning on Titanium [23, 24]. The electrolyte characteristics (concentration) can have an impact on the mechanism of ECM dissolution. The degree of localization is greater with low-concentration electrolytes, allowing for greater accuracy than with high concentrations. Although it has been reported that lower electron concentrations provide improved precision [25]. Concentrated sodium chloride is one of the most widely used electrolytes in the ECM process. It has also been noticed that there was no gas emission or precipitation. It is used for machining stainless steel surfaces when a gleaming finish is desired. Because sodium chloride is not suitable for coating on stainless steel metal, the workpiece can be machined swiftly and easily. If a very close duplicate of the tool is desired, another solution called sodium nitrate is typically utilized for machining the steel. Sodium nitrate avoids stray corrosion, which aids in the creation of a very accurate tool copy. The ECM process is also influenced by the current density. In the case of high current density-based anodic dissolution, for example, sodium nitrate electrolyte, where low current density causes electrolyte passivation [13]. The use of an electrolyte-rich in oxygen helps the ECM process. These consequences the cathode on temperature distribution in the ECM machining process. In conjunction with oxygen enrichment, sodium chloride is used. The involvement of oxygen in the mixture increased the rate of material removal [26]. A 0.05 M hydrochloric acid was used to discover submicron Nano resolution structures. It is obtained on the substrate of the nickel surface [27]. According to studies, a higher electrolyte concentration paired with a higher current density accelerates cutting and causes the tool to overcut the workpiece [28]. It was revealed that as the concentration of electrolytes grows, the resolution of the manufacturing process reduces. This was because as the electrolyte conductivity grew, so did the number of ions available for the process [29]. Mixing sodium chloride with HCl acid raised the electrolyte concentration, resulting in overcutting during machining. This implies that the optimistic relationship between the mixed electrolyte and

the electrolyte concentration contributes to boosting the machining rate. As a result, the benefits and drawbacks of various electrolyte concentrations are examined. Chemical etching is greatly reduced with the lower concentration electrolyte compared to the highly concentrated electrolyte. It comes in very handy while cutting micro-sized particles [30, 31]. Zohoor et al. investigated the role of electrolytes and the kind of electrolyte in the 304 Steel ECM process [30]. When potassium chloride, sodium chloride, and sodium nitrate were tested at different currents, it was discovered MRR of NaCl and KCl was higher than that of NaNO₃. The side gap for KCl was found to be the largest, while the side gap for NaNO₃ was found to be the smallest. Surface roughness rose with the current for sodium nitrate but decreased for sodium chloride and potassium chloride [32]. When a certain amount of acid comes in contact with natural salt electrolytes, research shows that it increases the side gap and MRR when compared to virgin natural electrolytes. Furthermore, it was observed that decrease in surface roughness with mixed electrolytes [33]. However, in the case of alkali or oxidant electrolytes like sodium bromate, the formation of an oxide passive layer reduces the machining rate as well as dimensional and geometrical precision [34]. Combining different alkaline-electrolyte solutions improves the accuracy of the electrochemical discharge machining (ECDM) process. Combining the two alkaline electrolytes showed the increased value of both electrical conductivity and microchannel depth of the workpiece and reduced value of accidental erosion [35]. The electrolyte is a substance that helps the body to stay hydrated. When the application of the complexing agent to an electrolytic solution happened, the ligand of the complexing agent reacts with the hydroxide ions along the oxygen molecule with the metal ion to form clathrate. Its result, clathrate, is water-soluble. The stability of the clathrate product is determined by the agent's capacity to compound. As a result, the insoluble products in the process are dissolved by complexing agents in this manner [36, 37]. Again, the complexing agents can considerably increase the MRR of the ECM process. Investigation of several compound electrolytes as well as usual electrolytes such as NaCl, NaNO₃, and NaClO₄. MRR of usual electrolytes such as NaNO₃ and NaClO₄ were demonstrated to be equal. Furthermore, adding complexing agents to the electrolytes, such as sodium gluconate, sodium citrate, and sodium tartrate, enhanced the MRR by 35%, 43%, and 34% respectively the elimination of extra heat from the reaction zone is also aided by electrolytes. The heat created during the process might be harmful to the tool and electrolyte. Unnecessary heat generated during the reaction causes bubbles to form across the IES, which might cause the electrolyte to boil. As a result, avoiding electrolyte boiling is crucial. To avoid boiling, the electrolyte temperature must be lower than the boiling point of the electrolyte. The temperature limitation of the electrolyte in the ECM equations [38-39].

$$T_b - T_{in} + \frac{1.0}{\alpha_k} \left[1.0 - \left(1.0 + \frac{s_k}{(1.0 - \alpha_{vo})^n} \frac{f^2}{U} \right)^{0.5} \right] \geq 0.0, \quad (8)$$

Where,

- T_b = the electrolyte's boiling temperature
- T_{in} = electrolyte's temperature at the intake
- α_k = electrolyte's temperature coefficient
- f = the tool feed rate
- U = the electrolyte flow velocity

4 Material Removal during ECM Process

When a stronger current is passed, the current density increases, meaning that more energy reaches the electrode surface in the same amount of time. As a result, the elimination of the material accelerates. This is advantageous due to the decreased machining times. Surface quality, on the other hand, can be affected if the current density is excessively high [39-41]. Sparks can arise between the workpiece and tool if the current is high enough or the IES is very small. This spark may damage the tool as well as the workpiece. The quantity of the substance that reacts in electrolysis is proportionate to the passing current and its period, i.e., the charge flow. That is also proportionate to the reactant's valency, or the number of electrons required in the reaction. The following equation is used to compute the amount of material eliminated.

Where,
$$m = \frac{i t A}{F v} \tag{9}$$

- A = atomic weight,
- F = Faraday constant,
- v = valency
- m = amount of material to remove,
- I = current passed, and
- t = time

If there is only a single reaction taking place at the workpiece side, the current efficiency would be close to or equal to 100%. The lower values of current efficiency can suggest that an alternative reaction is occurring at the same time or that the products have expected higher valency. That is, Fe₃⁺ is shaped rather than Fe₂⁺. The current efficiencies of more than 100% have been described in some circumstances [40-42]. This is conceivable because current efficiencies in ECM are well-defined as the ratio of the change in observed mass to the change in theoretical mass projected by Faraday's Ist law when the anodic dissolution is at 100% current efficiency [39-41].

$$\Delta m = k \Delta I + \Delta t \tag{10}$$

- where
- Δm = change in mass
 - Δt = change in time
 - ΔI = change in current

5 Conclusions

According to the review approach indicated above, many studies have successfully proved the implementation of ECM in producing micro topographies on surfaces by employing electrolytes in the machining process. However, because studies have only focused on a single metal/alloy to identify optimal machining settings, it is unknown what procedure or electrolyte to use for a specific metal option depending on the used electrolytes. For the machining of new material, wide research is needed to discover appropriate electrolytes as well as ideal machining parameters like useful voltage and pulse length, among other things. The importance of electrolyte mixing, as well as the electrolyte, which is the most important component of the ECM process, is also discussed in-depth for a better understanding. Currently, no scientifically supported approach is there to explain the usage of exact electrolyte solutions, IES distances, or machining settings, particularly for earlier research's

manufacturing uses of ECM technology. Electrochemical micromachining with alkaline electrolytes such as HCl and H₂SO₄ is favored due to the maximum efficiency of machining and surface finish precision. Solid electrolytes like ceramic, gel, polymer, and other electrolytes are implemented when the passive film is extremely undesirable and as IES is low.

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