Effect of degassing electrolyte on polarisation curve shape with the aim to apply knowledge to electrochemical machining

Rebecca Leese[1], Dr. Atanas Ivanov

Brunel University, Kingston Lane, Uxbridge, UB8 3PH
[1]rebecca.leese@brunel.ac.uk

Abstract

Electrochemical machining is a manufacturing process which relies on the anodic dissolution of the work piece. The accuracy of the hole created is dependent on a number of factors including the applied potential. A higher applied potential creates a larger overcut and therefore decreased accuracy. Early indications from polarisation curves suggest that removing dissolved oxygen from the solution can somewhat prevent passivation of the work piece surface allowing a lower machining potential to be used which should improve machining accuracy.

1. Introduction

Electrochemical machining is a non-conventional manufacturing process which relies on duplicating the shape of a tool electrode into a work piece via the anodic dissolution of the work piece [1]. In electrochemical machining, both the tool electrode and the work piece are submerged in a conducting electrolyte, usually an aqueous salt solution such as sodium chloride or sodium nitrate [2]. A potential is applied between the two electrodes ensuring the work piece becomes the anode. The applied potential causes a DC current to flow between the electrodes, dissolving the anode material in the process. The reaction at the cathode is usually hydrogen gas generation. Usually a complex shaped tool electrode is used for a sinking operation.

There have been recent developments which aim to use much smaller electrodes to machine complex shapes by moving the smaller tool electrode along a designated route [1]. This however requires higher resolution of the dissolution process to achieve the required accuracy. As a result a new ECM technique was developed by Kock et. al [3], known as pulsed electrochemical machining (PECM). PECM uses high frequency voltage pulses to confine the machining to the areas of the work piece polarised by the tool electrode [4]. Using a pulsed voltage to machine the work piece allows the inter-electrode gap (IEG) to be reduced, with the IEG being proportional to the pulse width [3].

Zhang et al observed that the machining overcut was reduced when a lower machining potential was used [4]. This improves the machining accuracy, enabling smaller features to be produced using electrochemical machining. Machining overcut is the effect observed due to current extending beyond the tool edge so a hole is created that is wider than the tool used. It was hoped that displacing dissolved oxygen from the electrolyte would enable a lower machining potential to be employed which would improve machining accuracy because using a lower

machining potential also decreases the chances of sparking occurring during machining. Sparking causes defects on the tool electrode and the work piece. [5]
Some metal-electrolyte systems encounter problems with passivation which makes machining the material more difficult or impossible. Passive layers are formed from metal salts and oxides (FeO, $FeCl_2$, $Fe(OH)_2$). The passive film can be electrically insulating but in other cases the passive film is added material which needs removing before dissolution of the pure metal can be commenced. It is preferable to prevent or minimise a passive film forming. The aim of this research is to investigate the effect of displacing dissolved oxygen in the electrolyte by degassing the electrolyte before commencing a polarisation curve experiment in order to improve the quality of the ECM process. Polarisation curves are used in electrochemical machining research to determine whether an electrolyte-metal system is suitable and which potential will enable anodic dissolution of the work piece [6]. Polarisation curves also reveal the machinability characteristic of the material.

2. Method

An electrochemical cell was set up using a double junction Ag/AgCl reference electrode, a homemade platinum (Pt) flag counter electrode and iron (Fe) metal wire of 1 mm diameter immersed approximately 1 cm into the solution as the working electrode. The electrolyte was degassed for ten minutes by bubbling oxygen free nitrogen through the solution for ten minutes. The nitrogen bubbling through the solution displaces the dissolved oxygen in the solution. Three different electrolytes were used which were sodium chloride, sodium nitrate and sodium chlorate at concentrations of 0.1 M, 0.5 M and 1.0 M. The temperature of the electrochemical cell was controlled using a water bath at temperatures of 20 ºC, 40 ºC and 60 ºC. The experimental set up is show in figure 1.
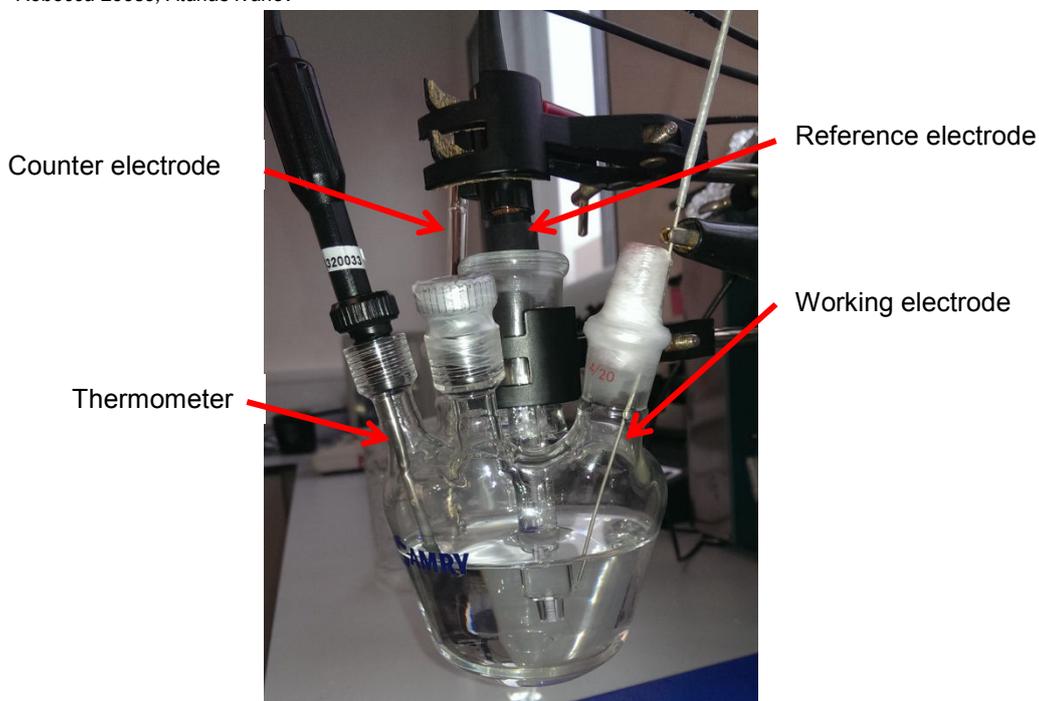
Figure 1: Experimental set up for polarisation experiments excluding the water bath

A potentiostat (IviumStat, Ivium Technologies), shown in figure 2 was used to scan the potential from -0.5 V to 10.0 V at a scan rate of 20 mV s^{-1}. IviumSoft was used to record the data and Microsoft Excel was used to do some data analysis.
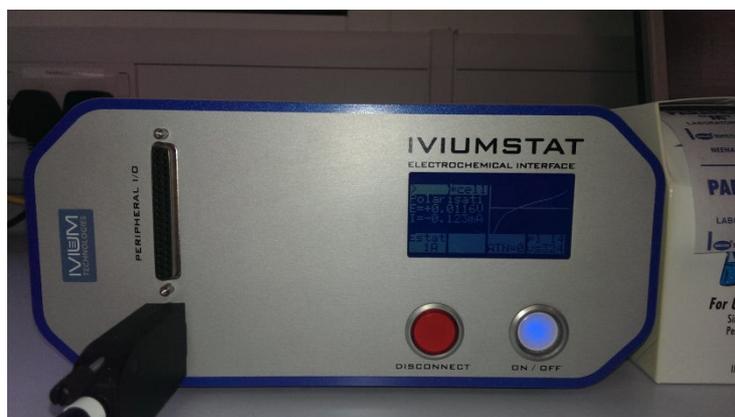

Figure 2: IviumStat potentiostat used in the experiments

All solutions were made with salts from Sigma Aldrich with purity > 99.9 % and using 18.2 MΩ purified water from an Elga PureLab water purifier system.

The experiments were designed using the Taguchi method. The effect of removing dissolved oxygen from the solution is only considered for experiments conducted at the same pH for ease of analysis. The experimental design table is discussed later.

3. Results & Discussion

Polarisation curves, which observe the current response to an applied potential field, were carried out using the method described in the method section.

The effects of degassing the solution to displace the dissolved oxygen are observed in the lower potential region where passivation would usually occur.
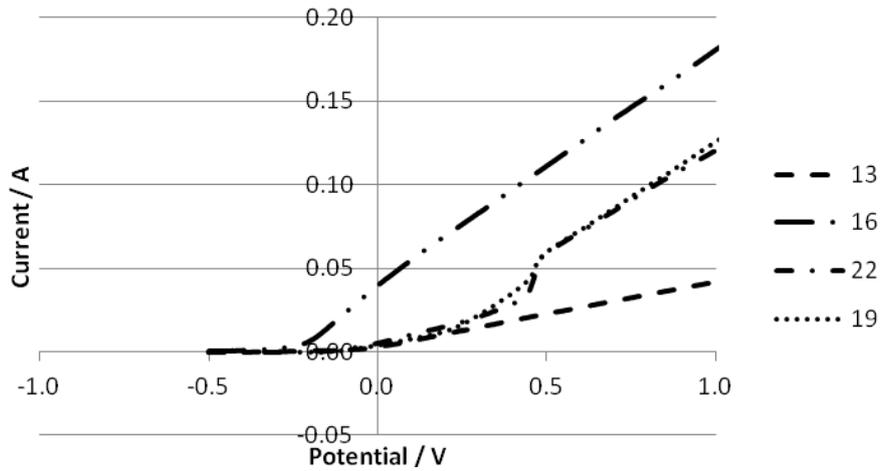
For iron there are small changes in the polarisation curve shape for electrolytes containing aggressive chlorine ions. Figure 3 shows the polarisation curves for iron in NaCl and $NaClO_3$. Looking at the polarisation curves conducted in NaCl it is possible to see a slight peak at around 0.45 V for experiments numbered 19 and 22 but this is absent for experiments numbered 13 and 16; table 1 gives details of the experimental conditions for each experiment number. Experiments 13 and 16 were degassed using oxygen-free nitrogen gas for ten minutes before the experiment was started. This slight peak is potentially due to the presence of dissolved oxygen in the solution which may react at the surface of the working electrode. There is also a slight peak at around 0.45 V for experiment number 24 in the sodium chlorate electrolyte. This solution was not degassed and so this peak which is not present in experiments 15 or 18 could be attributed to the presence of dissolved oxygen in the solution. Table 1 shows the experiment conditions for the polarisation curves depicted in figure 3.

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Table 1: Experimental conditions for polarisation curves in NaCl and NaClO₃.

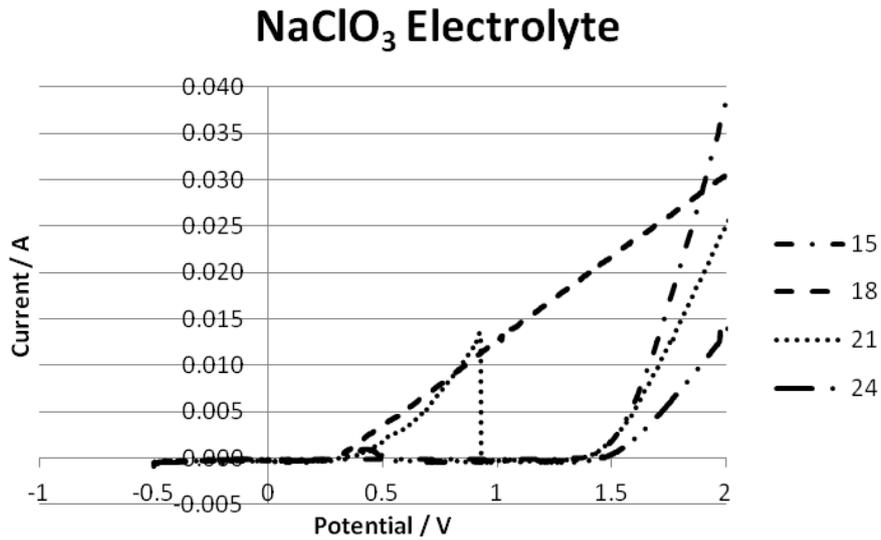| Experiment No.	Electrolyte	Concentration / M	pH	Temperature / °C	Degassed?
13	NaCl	0.1	7	60	Y
16	NaCl	0.5	7	60	Y
19	NaCl	1.0	7	20	N
22	NaCl	1.0	7	40	N
15	NaClO₃	1.0	3	40	Y
18	NaClO₃	0.1	3	40	Y
21	NaClO₃	0.5	3	60	N
24	NaClO₃	0.5	3	20	N

Figure 3: Polarisation curves for an iron working electrode in NaCl and $NaClO_3$.

Looking at the polarisation curves for iron in sodium nitrate electrolyte there is no clear differences in curve shape between the experiments which have been degassed and those which have not been degassed, shown in figure 4. Table 2 shows the experimental conditions for the polarisation curves shown in figure 2.

Table 2: Experimental conditions for polarisation curves in $NaNO_3$ electrolyte.

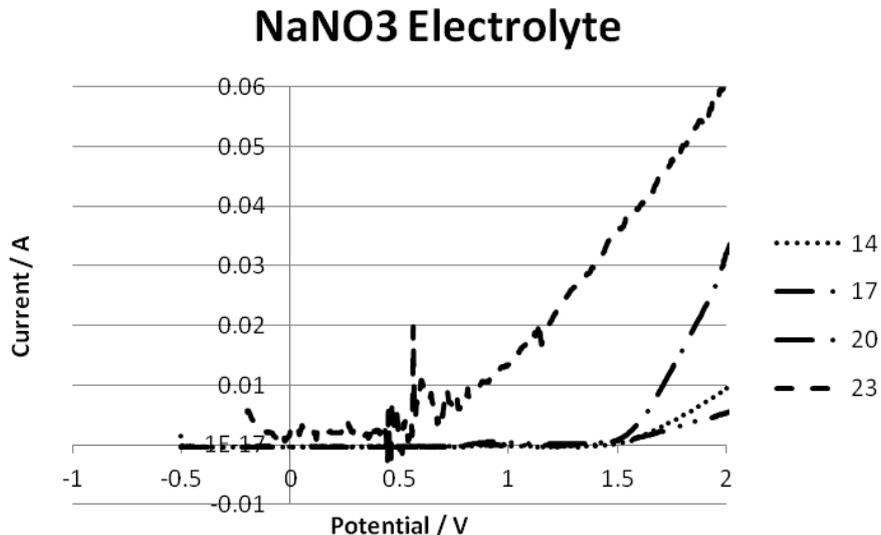| Experiment No.	Electrolyte	Concentration / M	pH	Temperature / °C	Degassed?
14	NaNO3	0.5	12	20	Y
17	NaNO3	1.0	12	20	Y
20	NaNO3	0.1	12	40	N
23	NaNO3	0.1	12	60	N

NaNO3 Electrolyte

Figure 4: Polarisation curve for iron in $NaNO_3$

For all experiments, only the curve shape is important. The chosen electrolyte affects the shape of the curve, all shown curves are conducted at the same pH so peak position is not affected by the pH. Temperature and concentration do not affect the peak positions but they do affect the current maximum.

From the results shown above it appears as though displacing dissolved oxygen could affect the machining and hopefully a lower potential can be used to machine the work piece, improving accuracy and decreasing the energy cost. To the author's knowledge, this is new novel research which has not been applied to ECM.

More work needs to be carried out to determine the extent to which displacing the oxygen from the solution does affect machining, ideally conducting comparison experiments using electrochemical machining rather than polarisation curves.

4. Conclusion

ECM is very promising process for zero defect manufacturing it is a stress-free metal processing technique and in theory can be used to remove one atom of material at a time provided conditions are optimised. It can be seen from the iron polarisation curves conducted in sodium chloride and sodium chlorate that displacing dissolved oxygen from the electrolyte affects the shape of the curve at low potentials where passivation would normally occur. This same effect is not observed in sodium nitrate solution with iron.

Further testing needs to be done to confirm whether this affects the quality of electrochemical machining with respect to the surface finish by allowing a lower machining potential to be utilised lowering the possibility of sparking occurring during machining and lowering the overcut of the machining process.

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