Development of a Re-circulate Copper Etching System to Enhance the Precision of the HDI PCB Manufacturing

發展一個再循環蝕銅系統來增強HDI線路板生產過程的精密度

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1. Introduction

The Hong Kong printed circuit industry has played an important part in Hong Kong manufacturing industry, which supplies printed circuit boards (PCB) for various industries, from high tech electronics to domestic appliances. Currently, the PCB industry produces more than 26 million square meters of PCBs and generating estimated sales of US$1.1 billion per year. According to a recent PCB industry research report, it is forecasted that the HK/China PCB production will grow continually with an annual growth rate of 16.3% from the year 2003 to 2005 despite the global economic downturn. To cope with this increasing market demand, the Hong Kong PCB industry has to upgrade her manufacturing capability and simultaneously to tackle the generic manufacturing difficulties especially on the production efficiency and environmental issues.

Etching is an important process in the PCB manufacturing industry. Every year, approximately 7 million liter of etchant is being used by the PCB factories and generates a huge volume of waste. A total amount of HK$24 million is being spent for waste treatment on top of the HK$ 9 million chemical cost. Therefore, the regeneration of spent etchant and recovery of the copper is essential to minimize the operating cost of the etching process. Over years, in-situ method uses hazardous chemicals to oxidize the etchant. The etchant is treated through vigorous reactions for reuse; this requires high cost in chemical replenishment and safety measures. Due to the huge operating cost and enormous operating difficulties in maintaining the stable copper etching performance, PCB manufacturers are skeptical to incorporate their on-line etchant regeneration/recovery system with their etching line. We had investigated and established a new and innovative High Precision and Re-circulate Copper Etching System by employing the Hydroxyl Free Radical Oxidation techniques through the use of doped synthetic diamond electrodes. This system incorporates both the etching and regenerating processes in one unit and the etchant

1. 簡介

香港線路板工業，為各高新電子技術和家電等行業提供所必須的線路板，於香港製造業佔著舉足輕重的地位。香港的線路板生產商每天生產大約二千六百萬平方米線路板，總值約十億美元。據業內人仕透露，縱然世界經濟正濃罩著不明朗的因素，但香港和華南地區的生產商均估計2003至2005年度，線路板每年的生產量將續有16.3%的增長。隨著市場環境正慢慢好轉，各港商都積極地裝備自己，不單聚焦於技術水平，同時更針對效率的提升以及致力於環保生產以提高競爭能力。

在線路板的生產過程中，蝕銅是一個十分重要的流程。每年，香港線路板生產商大約消耗七百萬公升的蝕銅劑，同時製造出大量廢液。要有效地處理這大量廢液需動用約二千四百萬元、另再加九百萬元的蝕銅劑費用，這工序的成本絕不低廉。因此，循環再用飽和的蝕銅劑和回收有商業價值的金屬銅，是減低生產成本其中一個最有效的方法。

直至目前為止，線路板生產商對蝕銅劑的循環技術依然存疑，主因為一般蝕銅劑的循環技術少不了使用一些具危險性的化學物來氧化蝕銅劑，再經不同的化學流程，始能有效地轉化飽和的蝕銅劑、再生成為有用的化學物料。由於轉化過程耗資巨大且涉及安全問題，是故，泰半的線路板生產商均不願採用傳統的蝕銅劑循環技術。

有見及此，香港線路板協會聯同香港生產力促進局，在得到香港特區政府創新科技基金的資助下，研發出一個創新的、高精密的、採用了塗上人造鑽石的電極羥基氧化蝕銅循環系統技術。此創新系統揉合了蝕銅和循環再用兩個功能，並能更精密地控制整個蝕銅流程以及減少回收銅等問題。由於羥基自由基電解方法會把有用的銅回收，整個回收過程

performance is being precisely controlled with minimal fluctuation. Indeed, the key competitive edge with the named system would be its easy-to-manage and more precise controllable manner. Cuprous ions will be removed electrolytically by the hydroxyl free radical, which minimizes the uncertainties and the adverse effect of the chemical reaction. Therefore, the electrolytic regeneration of etchants and recovery of copper serves as a more economical alternative in saving replenishment chemicals. Besides, additional revenue comes from the by-product, the recovered copper.

亦不需再添加任何化學物料，故能有效地減低化學反應期間所帶來的不穩定因素。採用這項方法去回收有商業價值的銅將會是最具成本效益的方法，既能減少使用蝕銅劑，又能回收有商業價值的銅。

2. Experimental

The pilot scale continuous copper regeneration and recover system was built and tested.

The experimental setup of this continuous system is shown in Fig. 1. The total volume of the system is 550 liters (anode compartment = 240 L and cathode compartment = 310 L).

2. 實驗

實驗中設計了連續式蝕銅液再生裝置進行測定。裝置圖如圖1.所示，系統總容積550公升 (陽極間隔 = 240 L，陰極間隔 = 310 L)。

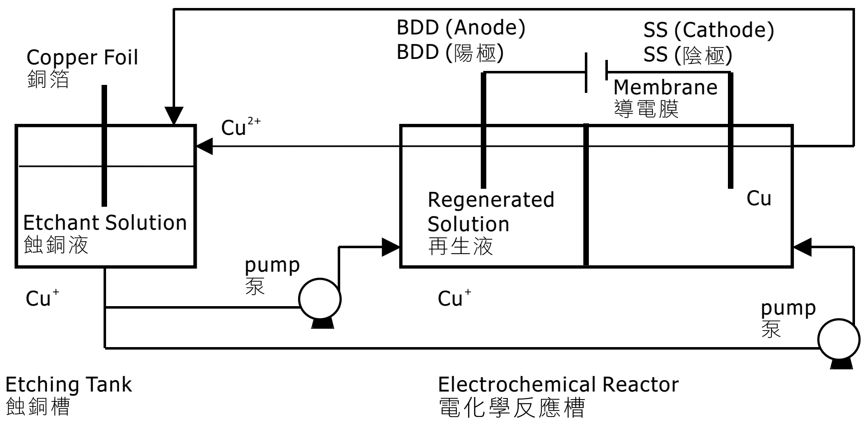

Fig.1(a) Schematic diagram
圖1(a). 連續式酸性蝕銅再生系統裝置圖

The fresh etchant solution was prepared by the following recipe: CuCl2 = 36.4 g/L, HCl = 0.01 M.

Copper coil was etched by the fresh etchant until the concentration reached to 1.52 g/L.

In this system, the spent copper etchant solution was continuously fed into the anode and cathode compartments by two metering pumps both at various flow rates. Boron doped diamond (BDD) and stainless steel (SS) served as the anode and cathode respectively. The effective areas of the two electrodes were both 4300 cm^2. After residing in the reactor for certain process time controlled by flow rate, the regenerated etchant solution exited from the reactor and flew back into the etching tank.

The regeneration test was conducted under constant voltage of 6.0V and current of 20A, corresponding to constant current density of 2.33 mA/cm^2.

新配製的蝕銅液按CuCl2 = 36.4 g/L、HCl = 0.01 M配方配製。銅箔被蝕銅液侵蝕直至達到1.52 g/L濃度。在此系統中，用過的蝕銅液通過泵、分別以不同的流量連續輸入配備了摻硼人造鑽石(BDD)的陽極區以及配備了不銹鋼(SS)的陰極區。陰陽二極有效面積均為4300 cm^2。以流量控制、經過一定的反應時間後，再生液由電化學反應槽回流至蝕銅槽。此再生實驗恒電壓6.0 V、恒電流20 A，相應電流密度為2.33 mA/cm^2。

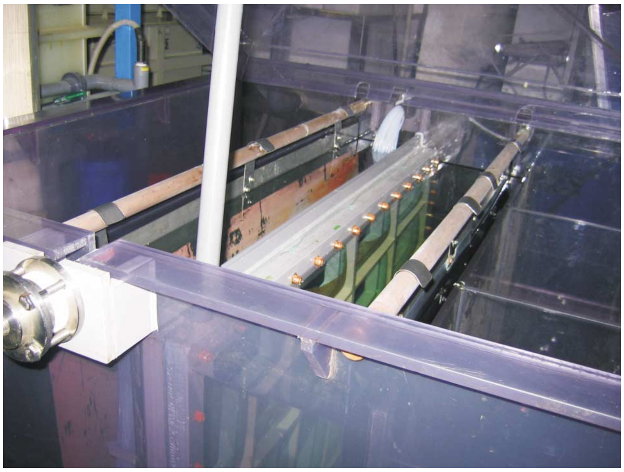

Fig.1(b) Photo of continuous acidic etchant regeneration system
圖1(b). 連續式酸性蝕銅再生系統實物照片

3. Results and Discussions

3.1. Dependence of cuprous ion concentration on ORP value

To measure the cuprous ion concentration in the solution containing both cupric (Cu^{2+}) and cuprous (Cu^{+}) ions, first we measured the dependence of cuprous ion concentration on the ORP value of the solution as below. From the curve (Fig.2) the concentration of cuprous ion during the regeneration process can then be obtained by measuring the ORP value of the regenerated solution.

3.2. Etchant regeneration and copper recovery

We measured the change of ORP value in the anolyte and catholyte at various process time. In addition, the change of specific gravity in the catholyte in terms of Baume degree was also measured. The results were shown in the below figures (Fig. 3).

From the above figure, the copper etchant regeneration and copper recovery can be calculated in Fig.4.

3. 實驗結果與討論

3.1. ORP值與一價銅離子濃度關係

測定溶液中銅離子的濃度，一價銅(Cu^{+}) 及二價銅(Cu^{2+})二者均需測定。如圖2.所示，首先，我們先找出溶液ORP值與一價銅離子濃度的關係。故當再生反應進行時，只需測定ORP值就可知道溶液中一價銅離子的濃度。

3.2. 蝕銅液再生與金屬銅回收

於不同的反應時間裡，我們先測定陽極區溶液與陰極區溶液ORP值的變化，此外，陰極區溶液的比重、波美度亦同時測定。有關結果見圖3.。

由圖3.的關係，蝕銅液再生與金屬銅的回收可計算如下：

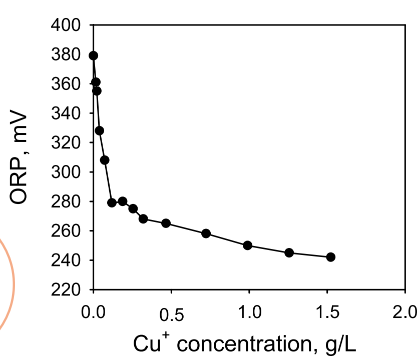

Fig. 2 Dependence of cuprous (Cu^{+}) concentration on ORP value
圖2. ORP值與一價銅離子濃度關係

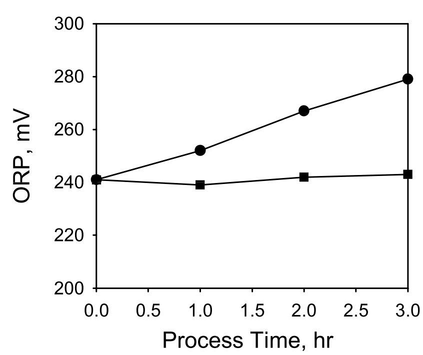

Fig. 3(a) The change of ORP value in the anolyte (●) and catholyte (■) against process time
圖3(a). 陽極區及陰極區溶液 ORP值變化與時間關係

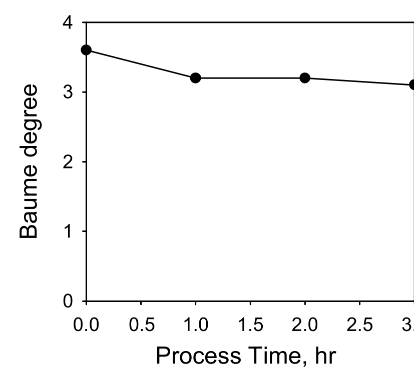

Fig. 3(a) The change of Baume degree in the catholyte against process time
圖3(b). 陰極區溶液波美度變化與時間關係

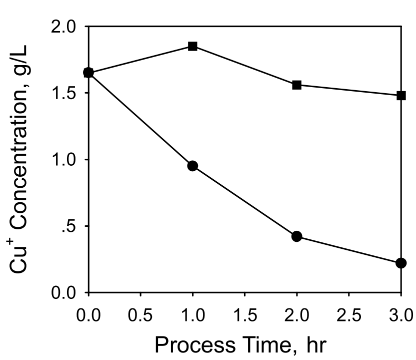

Fig. 4(a) The change of cuprous ion concentration in the anolyte (●) and catholyte (■) against process time
圖4(a). 陽極區與陰極區溶液一價銅濃度變化與時間關係

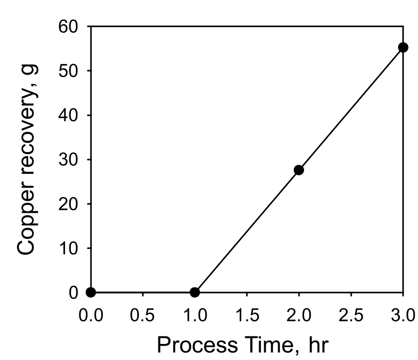

Fig. 4(b) The change of copper recovered in the cathode compartment against process time.
圖4(b). 陰極區回收銅變化與時間關係

It can be seen from Fig. 4 (a) that after regeneration, cuprous ion concentration was considerably reduced in the anode compartment. When the process time reached to 3 hr, nearly 90% of initial cuprous ion has been oxidized into cupric ion.

It was also observed that although there was negligible copper metal recovered when the process time was less than 1 hour, the copper recovered in the cathode compartment started to increase when the process time exceeded 1 hour.

3.3. Electricity utilization efficiency

It can be calculated from the process time between 2-3hr that the electricity utilization efficiency of anode and cathode compartments is about 100 %. Due to the co-existence of both Cu^{+} and Cu^{2+} in the solution which both contributed to the copper recovery, the current efficiency in the cathode cannot be measured directly. Despite this, the current efficiency in a typical cathode compartments can be generally considered 98 %. Under such circumstance, the electricity utilization is summarized in Table 1 (according to constant current of 20 A).

4. Conclusions

The continuous cupric regeneration system by means of BDD electrode proved to generate hydroxyl radicals which efficiently oxidized cuprous ions and regenerated copper etchant.

By balancing the ratio of Cu^{+} generated to Cu^{2+} consumed, it is possible to maintain the concentration ratio of Cu^{+} to Cu^{2+} in the solution by the above set up. An application example is shown in the Appendix.

5. Appendix: Application Example

Here is an example for the application of the above system. Supposing that a PCB factory uses $CuCl_2$ (initial Cu^{2+}=71g/L) as copper etchant. The copper coil with a thickness of 0.1mm is etched at 1 m^2/min (the copper forwarding speed is 2m/min and the width of the etching machine is 0.5m) and the etching tank has a volume of 1 m^3 (or 1000L). A regeneration

由圖4.(a)可見，再生後，陽極區一價銅濃度大幅減少，3小時後，幾近90%原有的一價銅氧化成二價銅。

圖4.(b)亦顯示出，雖則反應時間小於1小時只有很小量的回收銅，但當反應時間超越1小時後，陰極區的回收銅明顯地增加。

3.3. 電流使用效率

憑藉計算，處於反應時間2-3小時之間之電流使用效率達100%，由於溶液內Cu^{+} 及 Cu^{2+} 共存，二者均影響回收銅的數值，是故，陰極電流效率此時不能直接測定。儘管如是，標準陰極間隔區的電流效率一般可考慮為98%。在這種情況底下，於定電流20A，電流的使用效率可歸納如表1.所示：

	Change rate in the anode compartment after 20 Ahr of power input 20 Ahr 陽極區間變化率	Change rate in the cathode compartment after 20 Ahr of power input 20 Ahr 陰極區間變化率	Net change rate after 20 Ahr of power input 20Ahr 淨變化率
Cu^{2+}	+ 2.4 g/Ahr	- 0.5 g/Ahr	+ 1.9 g/Ahr
Cu^{+}	- 2.4 g/Ahr	- 1.4 g/Ahr	- 3.8 g/Ahr
Cu	0	+ 1.8 g/Ahr	+ 1.8 g/Ahr
Cu^{+}/Cu^{2+}	1.0	2.8	1.9 (theoretical value = 2) (理論值 = 2)

Table 1 Electricity Utilization of the Copper Etchant Regeneration System
表1. 蝕銅液再生系統電流使用效率

4. 結論

採用BDD電極產生氫氧自由基的連續式二價銅再生系統，可高效地氧化一價銅離子，從而再生蝕銅液。

由以上裝置，對比所生成的Cu^{+}+ 以及所消耗的Cu^{2+}的比率，可維持溶液中Cu^{+} 以及Cu^{2+} 的濃度，應用實例見以下附錄：

5. 附錄：應用實例

假定某線路板工廠蝕槽寬0.5m、容積 1m^3 (1000L)，採用初始濃度 Cu^{2+}=71g/L的$CuCl_2$ 作為蝕銅劑，厚度0.1mm的銅板被蝕液按1m^2/min的條件蝕刻(蝕銅速度

system can be designed as below to stabilize the etching rate.

Fig. 5 shows the schematic setup of the regeneration system.

The calculation of operating parameters is as follows:

a) Copper etching rate: Given the area of copper coil to be etched is 1m^2 /min, the total copper to be etched is 53.5kg/hr [= 8.92 x 10^{6}g/m^3 (copper density) x 1 m^2 / min (copper area) x 0.1 x 10^{-3}m (copper thickness) x 60 min]. This copper etching rate corresponds to the reduction of cupric ion at 53.5kg/hr and accumulation of cuprous ion at 107.0kg/hr.

b) Regeneration current: The regeneration tank aims to regenerate cupric ion and recover copper both at 53.5kg/hr in order to make balance. Table 1 shows that 1Ahr of power input can resume 1.9g of cupric ion and recover 1.8g of copper metal. Therefore, it requires 28.2kA [= 53.5 x 10^3(g/hr) / 1.9(g/Ahr)] and 29.7kA [=53.5 x 10^3(g/hr) / 1.8(g/Ahr)] of power input rate to resume cupric ion and recover copper metal at the expected rate. If the regeneration tank operates at constant current of 29kA, the cupric ion can be regenerated at 55.1kg/hr [= 29kA x 1.9(g/Ahr)] and copper recovery rate at 52.2kg/hr [= 29A x 1.8(g/Ahr)], respectively.

c) Flow rate of etchant circulation: It has been estimated from literature (Processing and Economic Aspects of Etchant Regeneration, R. E. Markle, 1983, Plating and Surface Finishing, 59-62) that the specific gravity of the copper etchant has to be controlled between 1.280 and 1.295g/mL so that the copper etching rate is maintained at 25 μm/min. The increase in specific gravity is due to the increase of total copper ions in the solution (cupric ion + cuprous ion). Therefore, when the total copper ion has been increased by 15kg [= (1.295 - 1.280g/mL) x 1000L], the etchant has to be disposed and regenerated. As the net change of total copper ion is 53.5kg/hr (=increase of cuprous ion at 107.0kg/hr decrease of cupric ion at 53.5kg/hr), as calculated in step (a), the maximum turnover time of the etchant is 0.28hr [= 15kg / 53.5(kg/hr)]. As the total volume of the etching

2 m/min)，為穩定蝕銅率，再生系統裝置可設計如圖5.所示：

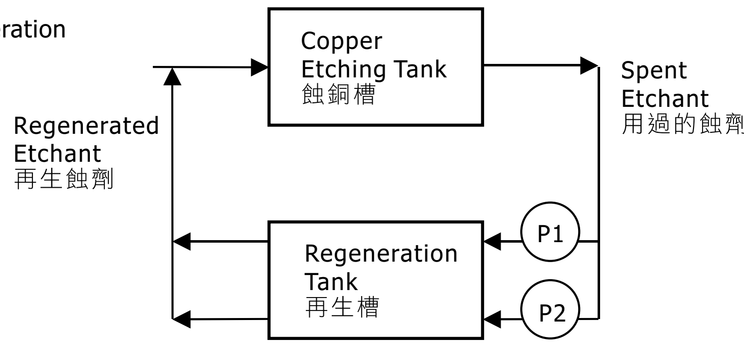

Fig. 5 Schematic Diagram of the Regeneration Setup
圖5. 再生裝置示意圖

操作參數計算如下：

a) 蝕銅速率：

己知單位時間銅板被蝕面積1m^2 /min，總蝕銅量53.5kg/hr， [= 8.92 x 10^{6}g/m^3 (銅密度) x 1m^2 / min (已知條件) x 0.1 x 10^{-3}m (銅厚度) x 60 min]，此蝕銅速率相當於二價銅離子以53.5kg/hr還原以及一價銅離子以107.0kg/hr積聚。

b) 再生電流：

再生槽目標在於以53.5kg/hr的蝕銅量同時再生二價銅離子以及回收銅，並使達於平衡。表1.顯示輸入1Ahr 的電量可恢復1.9g 二價銅離子及回收1.8g 金屬銅，所以，需要28.2kA的功率輸入[=53.5 x 10^3(g/hr) / 1.9(g/Ahr)]以及29.7kA的功率輸入[=53.5 x 10^3(g/hr) / 1.8(g/Ahr)]，方可使二價銅離子以及金屬回收銅達到預期的指標。如再生槽於29kA定電流的條件下操作，二價銅可再生55.1kg/hr [= 29kA x 1.9(g/Ahr)]，金屬銅可回收52.2kg/hr [= 29A x 1.8(g/Ahr)]。

c) 蝕劑循環流量：

參考有關文獻 (Processing and Economic Aspects of Etchant Regeneration, R. E. Markle, 1983, Plating and Surface Finishing, 59-62)，為維持25 μm/min 的蝕銅率，蝕劑比重應控制於1.280 及1.295g/mL 之間。比重增加意味著溶液內總銅離子(二價離子與一價離子之和)增加。所以，當銅離子增至15kg [= (1.295 - 1.280g/mL) x 1000L]時，蝕劑應該處理及再生。由於總銅離子的淨變化是

tank is 1000L, the flow rate is 3571L/hr (= 1000L / 0.28hr).

Table 2 shows the summary of the above system.

Change 變化	Cu^{+}	Cu^{2+}	Cu
Etching Tank 蝕槽	+ 107.0kg/hr	- 53.5kg/hr	- 53.5kg/hr
Regeneration Tank 再生槽	- 110.2kg/hr	+ 55.1kg/hr	+ 52.2kg/hr

Table 2 Summary of the regeneration system
表2. 再生系統銅離子變化

53.5kg/hr (一價銅離子以 107.0kg/hr的增量與二價銅離子以 53.5kg/hr的減量之差)、已於步驟(a) 計算出，蝕劑的最大周轉率是 0.28hr [= 15 kg / 53.5(kg/hr)]。蝕槽總容積是1000L，流量是3571L/hr (= 1000L / 0.28hr)。系統銅離子變化如表2.。

It can be seen from the above table that after 1 hour of running, 97% of etched copper can be recovered and 100% of the Cu^{2+} can be refreshed.

After regeneration, the system runs as below figure.

由表2.可見，再生系統經1小時的運作，蝕劑內可回收97% 的金屬銅以及可更新100% 的Cu^{2+} 。

再生後，系統操作如圖6.：

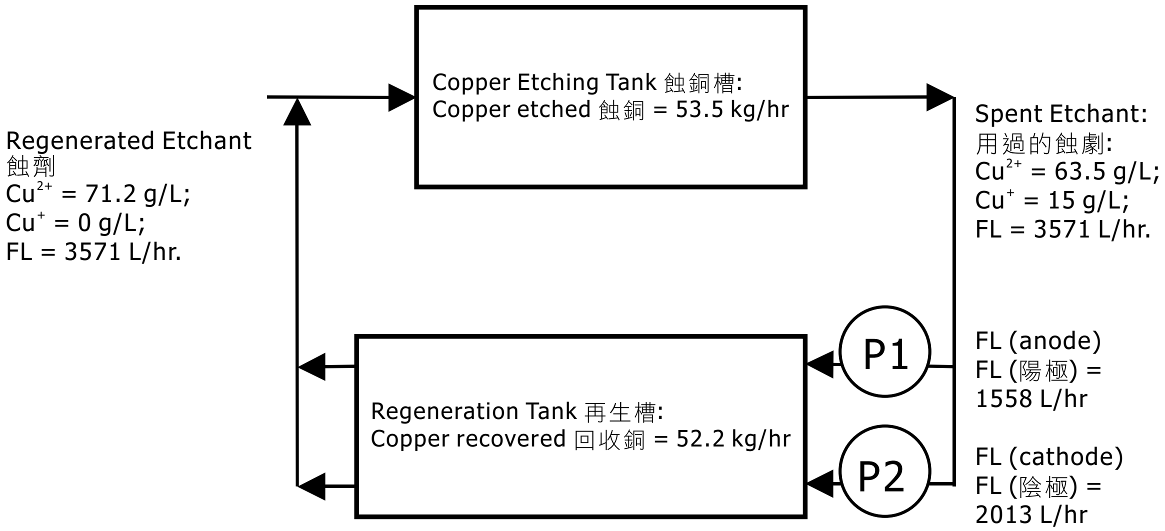

Fig. 6 Summary of the Operation of the Regeneration System
圖6. 再生系統操作總結

6. 鳴謝

《發展一個再循環蝕銅系統來增強HDI線路板生產過程的精密度》獲香港特區政府創新科技基金撥款資助，特此鳴謝。