Electrochemical analysis study of rare earth element: Lanthanum under the effect of magnetic field and its application as an additive for chrome magneto electrodeposition

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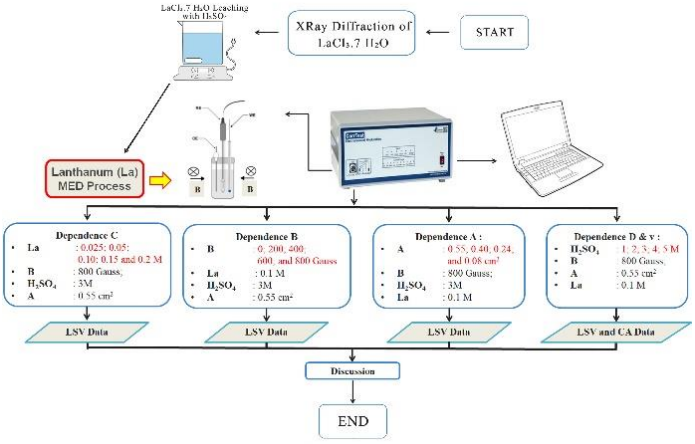
Abstract

Lanthanum is a rare earth group that is increasingly needed for a variety of applications. In this study, we analyze the effect of magnetic fields on lanthanum electrodeposition. Electrochemical analysis techniques used are linear sweep voltammetry (LSV) and Chronoamperometry (CA). LSV is used to measure the maximum current (limiting current). To determine the maximum current, the result of the LSV must be plotted in a Tafel plot. Tafel generated from LSV is the electrode potential (mV) with the logarithm of the current density (Log i_L ($A \cdot cm^{-2}$)). The diffusion coefficient of the electroactive species was determined using chronoamperometry (CA). The results showed that the effect of increasing the working electrode area (*A*), magnetic field strength (*B*), and electroactive concentration (*C*) gave a certain increase in limiting current. Meanwhile, the addition of solution viscosity (*v*) and diffusion coefficient (*D*) will reduce the limiting current value for lanthanum electrodeposition. This study also carried out a chrome-plating process with the addition of lanthanum which was studied previously, it was found that the plating process using magnetic field produced a more uniform; thicker; more compact, and more mass deposit.



Keywords: Lanthanum; Magneto electrodeposition; Linear sweep voltammetry; Chronoamperometry

Introduction

The need for Rare Earth Element (REE) minerals in the world have recently increased enormously. This is because REE is a very strategic commodity for future technological advances. Significantly, the presence of REE commodities is able to contribute to the improvement of modern technology that is around us, such as cellular phones, computers, rechargeable batteries, magnets, fluorescent lamps and other electronic equipment for civil and military purposes [1]. Lanthanum is a rare earth group that is a soft bluish-white metal. This metal was discovered in 1893 and is one of the group III B transition metal elements in the lanthanide series of elements. Lanthanum reserves are more abundant than gold or platinum and are always found among the fission products of uranium, thorium and plutonium. Lanthanum metal is widely used as a material for x-ray screens, glass lenses, optical fiber, capacitor batteries, and ceramics [2]. If lanthanum processing can be carried out optimally, Indonesia in the future has the potential to become a producer of lanthanum metal based on rare earth minerals in the world. Because since 2014, with the issuance

of the Minister of Energy and Mineral Resources No. 1 (updated with the Minister of Energy and Mineral Resources Regulation No. 25 of 2018) the minimum requirement for REE that must be purified is to reach a purity value of more than 98%, making research for lanthanum metal processing increasingly important to do [3].

Lanthanum can be obtained by electrodeposition process. Electrodeposition is a metal deposition process using a DC current by electrolysis. Electrodeposition has a major problem, namely the roughness of the resulting layer (non-uniform crystal growth) [4]. As for magneto electrodeposition (MED), the coating process is carried out under the influence of a magnetic field. The presence of a magnetic field has an influence on the fractal growth or morphology of the resulting deposit. The presence of a magnetic field results in an increase in the limiting current and a uniform growth and a more uniform metal deposition surface [5 – 7].

Limiting current is the maximum current that can be obtained by the reaction of the electrode in the reactant concentration in the presence of a large supporting electrolyte [8]. The presence of a uniform magnetic field direction can produce a good limiting current value. In addition to the influence of the magnetic field, the influence of the electrode area, the concentration of electroactive species, the kinematic viscosity of the electrolyte, the diffusion coefficient of the electroactive species, and the number of electrons involved in the redox process also affect the electrodeposition results. When compared to the conventional electrodeposition process, MED technology is easier because it can be carried out at room temperature [9].

Materials and Methods

The material used in this research were Lanthanum (III) chloride heptahydrate 98% ($LaCl_3 \cdot 7H_2O$) and sulfuric acid (H_2SO_4) from Merck Ltd., Potentiostat-Galvanostat Instrument (Wuhan CorrTest Electrochemical Workstation) for MED process to get limiting current value, X-ray Diffraction (XRD Pan Analytical X'pert PRO MRD 1 from Netherland) and X-Ray Fluorescence (XRF, Panalytical Epsilon 3 XLE from Netherland) were used to analyze raw-material, and Scanning Electron Microscope (SEM) for analysis of chrome plating added with $LaCl_3 \cdot 7H_2O$ additives using a magnetic field and without using a magnetic field. The electrolyte solution ($LaCl_3 \cdot 7H_2O$ which has been dissolved in sulfuric acid at a certain concentration) was carried out by the MED process with several parameters. A total of 19 runs were obtained according to Table 1 until Table 4. Fig. 1 is a schematic of the Lanthanum MED research tool circuit.

Electrochemical analysis techniques used are linear sweep voltammetry (LSV) and Chronoamperometry (CA). In this study LSV is used to measure the maximum current (limiting current). To determine the maximum current, the result of the LSV must be plotted in a Tafel plot. Tafel generated from LSV is the electrode potential (mV) with the logarithm of the current density (Log i_L ($A \cdot cm^{-2}$)). The diffusion coefficient of the electroactive species was determined using chronoamperometry (CA). Under static conditions, the reaction rate and current response measurements can be determined from the diffusion rate. For the reduction reaction at electrodeposition, the current is described by the Cotrell equation. By using the Cotrell equation, the value of the diffusion coefficient (D) can be calculated. The maximum current (limiting current) is the highest current on the cathodic curve, which is an increase in electrode potential that does not give an increase in current density. The limiting current (i_B) was calculated using the following equation (1) [10].

$$i_B = 10^{iL} \times A \quad (1)$$

Where i_B is the limiting current value, i_L is the current density logarithmic, and A is electrode area (cm^2).

Table 1 Experimental design dependence on $LaCl_3 \cdot 7H_2O$.

Run	$LaCl_3 \cdot 7H_2O$ (M)	Magnetic field strength (Gauss)	Working Electrode Area (cm^2)	H_2SO_4 (M)
1	0.025	800	0.55	3
2	0.05	800	0.55	3
3	0.10	800	0.55	3
4	0.15	800	0.55	3
5	0.20	800	0.55	3

Table 2 Experimental design dependence on magnetic field strength.

Run	$LaCl_3 \cdot 7H_2O$ (M)	Magnetic field strength (Gauss)	Working Electrode Area (cm^2)	H_2SO_4 (M)
1	0.10	0	0.55	3
2	0.10	200	0.55	3
3	0.10	400	0.55	3
4	0.10	600	0.55	3
5	0.10	800	0.55	3

Table 3 Experimental design dependence on working electrode area.

Run	$LaCl_3 \cdot 7H_2O$ (M)	Magnetic field strength (Gauss)	Working Electrode Area (cm^2)	H_2SO_4 (M)
1	0.10	800	0.08	3
2	0.10	800	0.24	3
3	0.10	800	0.40	3
4	0.10	800	0.55	3

Table 4 Experimental design dependence on H_2SO_4 concentration.

Run	$LaCl_3 \cdot 7H_2O$ (M)	Magnetic field strength (Gauss)	Working Electrode Area (cm^2)	H_2SO_4 (M)
1	0.10	800	0.55	1
2	0.10	800	0.55	2
3	0.10	800	0.55	3
4	0.10	800	0.55	4
5	0.10	800	0.55	3

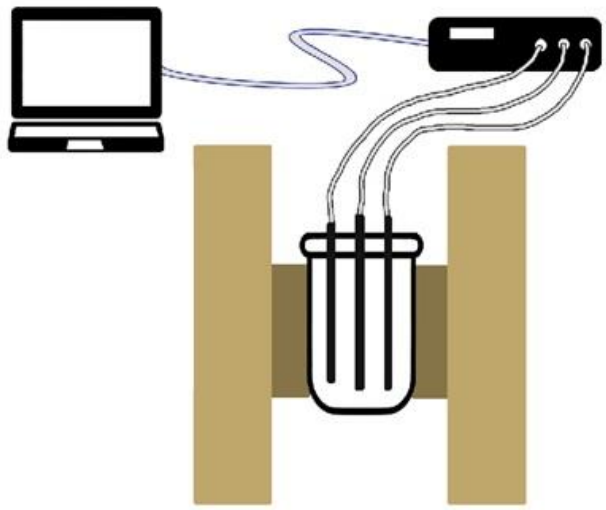


Fig. 1 Schematic of the magnetic electrodeposition of lanthanum research tool circuit.

Table 5 XRF result of Lanthanum (III) chloride heptahydrate.

Element	Wt (%)
Al	0.16
Ca	0.22
P	0.25
Cl	38.39
Sn	0.30
Te	0.11
La	60.29
Si	456.80 ppm

Results and Discussion

See Fig. 2 for XRD result of raw-material used, and we can see in Table 5 that Lanthanum content in Lanthanum (III) chloride heptahydrate (raw-material) is about 60%. The effect of magnetic field strength (B) on the limiting current value with the MED method on lanthanum has increased the limiting current value, As can be seen in Fig. 3. The increase in limiting current occurs due to the increase in mass transfer in the MED process. The increase in limiting current occurs due to the effect of Magneto Hydro Dynamic (MHD). The MHD effect is present, due to the presence of a magnetic field that affects the current thereby changing the convection flow of the electrolyte [10]. The MHD effect can increase the transfer of electroactive species from or to the electrode, due to the presence of a strong magnetic field, the force acting is known as the Lorentz force [11]. The Lorentz force acts when the magnetic field and the electrode cell are mounted horizontally, so that the greater the magnetic field strength, the greater the working current [12].

Lanthanum (III) Chloride Heptahydrate ($LaCl_3 \cdot 7H_2O$) in the MED experiment was the electroactive species (C) which was then mixed with H_2SO_4 solution (supporting electrolyte). The concentration of $LaCl_3 \cdot 7H_2O$ used was 0.025, 0.05, 0.10, 0.15 and 0.20 M diluted with 3 M H_2SO_4. The effect of the concentration of $LaCl_3 \cdot 7H_2O$ on the limiting current value in lanthanum MED can be seen in Fig. 4. Based on Fig. 4, the experimental results show that the limiting current value increases with increasing lanthanum concentration. As the electroactive concentration increases, the free cations in the electrolyte will increase as well, this can cause stirring at the working electrode to be more efficient [13].

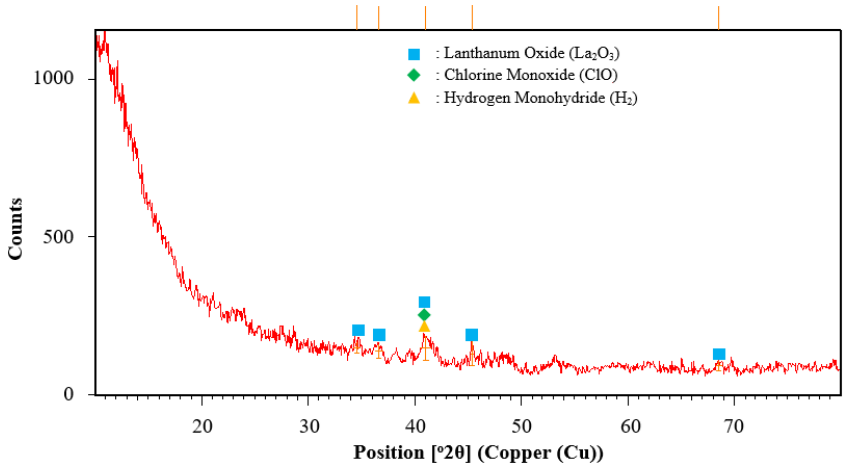


Fig. 2 XRD Result of Lanthanum (III) Chloride Heptahydrate.

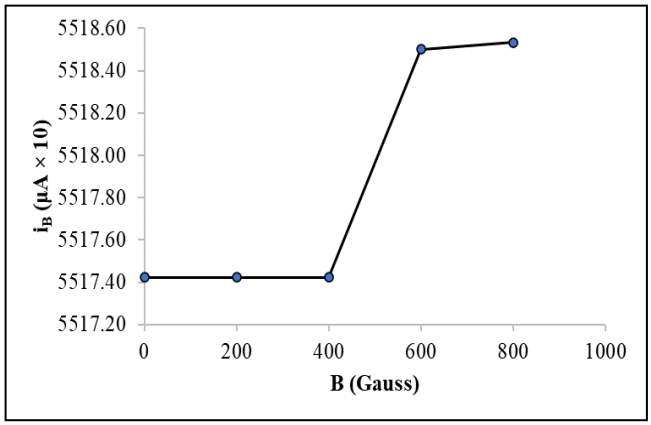


Fig. 3 Effect of Magnetic Field Strength on Limiting Current, Using 3M H_2SO_4; 0.10 M Lanthanum (III) Chloride Heptahydrate; A= 0.55 cm^2; Platinum Electrode.

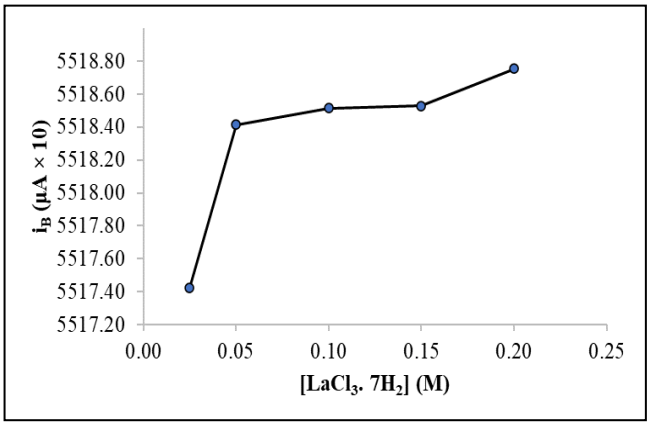


Fig. 4 Effect of Lanthanum (III) chloride heptahydrate concentration on limiting current, using 3M H_2SO_4; A = 0.55 cm^2; B = 800 Gauss; Platinum electrode.

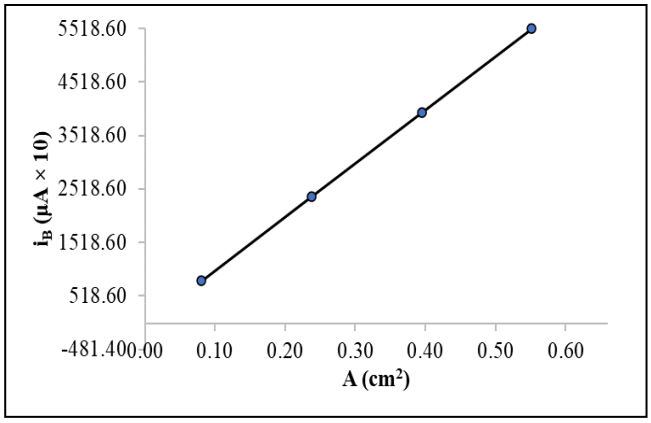


Fig. 5 Effect of working electrode area on limiting current, using 3M H_2SO_4; 0.10M Lanthanum (III) chloride heptahydrate; B = 800 Gauss; Platinum electrode.

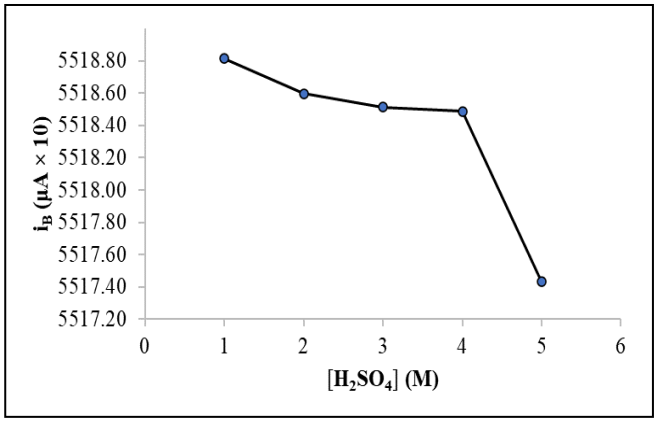


Fig. 6 Effect of H_2SO_4 concentration on limiting current, using 0.10 M Lanthanum (III) chloride heptahydrate; B = 800 Gauss; A= 0.55 cm^2; Platinum electrode.

Increasing concentrations of electroactive can also induce turbulent flow in the electrolyte. The induced turbulent flow facilitates mass transfer, so that the greater the electroactive concentration, the limiting current value also increases [14].

The effect of the working electrode area on the limiting current value in lanthanum MED can be seen in Fig. 5. Based on Fig. 5, it is found that the increasing limiting current occurs because the electrode area is increasing. The larger the working electrode area, the greater the efficiency of magnetic stirring in the diffusion area [13]. This causes the mass transfer at the electrode to increase so that the limiting current also increases.

The supporting electrolyte used in lanthanum MED is H_2SO_4, the concentration of the H_2SO_4 solution is 1, 2, 3, 4 and 5 M. The supporting electrolyte can affect the diffusion coefficient (D) and viscosity (v). The greater the concentration of H_2SO_4 solution, the limiting current value will decrease, this can be seen in Fig. 6 and Table 6. The value of the diffusion coefficient (D) is influenced by the electrons involved (n) in the lanthanum MED, the electrons involved are 2, which is obtained from equation (2) for the H_2SO_4 reaction as follows;

$$H_2SO_4 \rightarrow 2H^+ + SO_4^{2-} \quad (2)$$

The two electrons involved in lanthanum MED are used to calculate the value of diffusion coefficient, using equation (3).

$$D^A = \frac{X}{n \times A} \quad (3)$$

Where, n = number of electrons, A = surface area of the working electrode (cm^2), X = coefficient value of the line equation for 2 variable and D = diffusion coefficient ($cm^2 \cdot s^{-1}$).

Table 6 Effects of supporting electrolytes on D, v, and i_B.

$LaCl_3 \cdot 7\ H_2O$ (M)	H_2SO_4 (M)	Viscosity (Poise)	D ($cm^2 \cdot s^{-1}$)	i_B (μA)
0.10	1	1.10	4.42×10^{-12}	551.881×10^{-2}
0.10	2	1.25	3.34×10^{-12}	551.860×10^{-2}
0.10	3	1.48	1.37×10^{-12}	551.851×10^{-2}
0.10	4	1.66	1.65×10^{-13}	551.849×10^{-2}
0.10	5	2.02	7.22×10^{-14}	551.743×10^{-2}

Based on Table 6, it is found that the viscosity value of the electrolyte solution is increasing because the concentration of the supporting electrolyte is also increasing. This happens because, viscosity is a measure of the viscosity of a solution, the greater the concentration of the solution, the higher the viscosity value. Viscosity determines the ease with which a molecule can move due to friction between layers of material [15]. Based on Table 6 the value of the diffusion coefficient (D) and the limiting current obtained is decreasing. The decreasing limiting current is caused by increased friction in the electrolyte solution, this reduces the

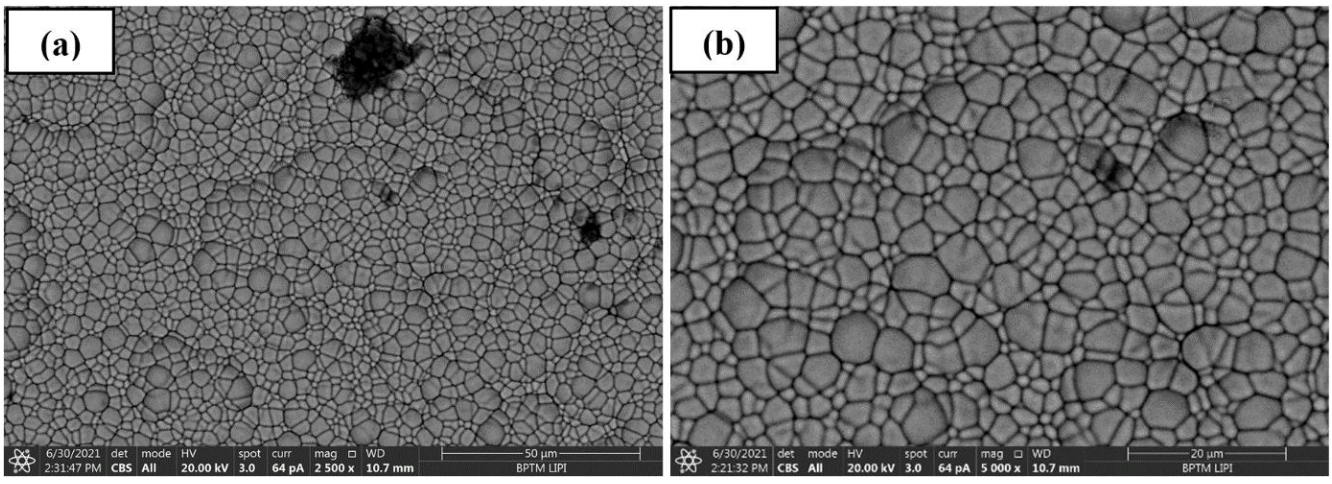


Fig. 7 (a) SEM 2500x magnification result of plating process without magnetic field and (b) SEM 5000x magnification result of plating process without magnetic field.

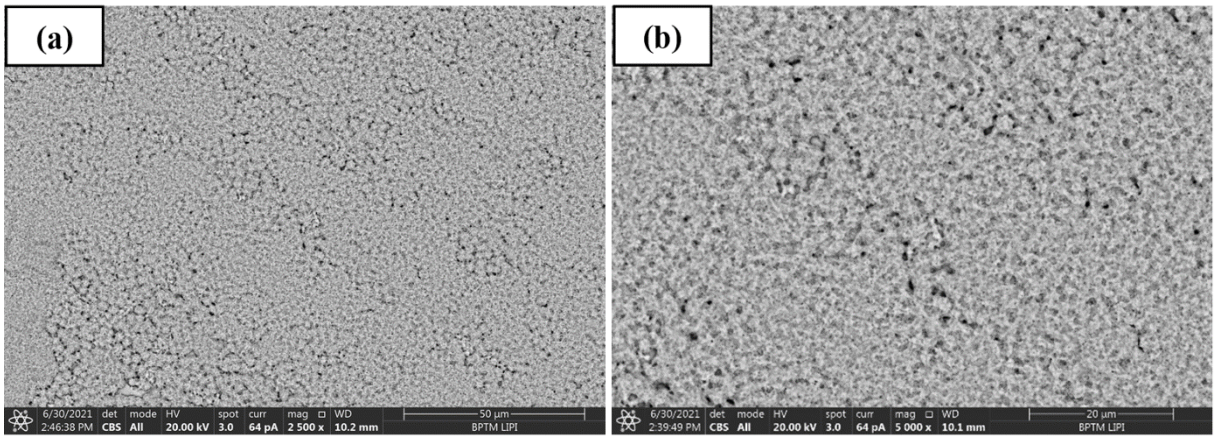


Fig. 8 (a) SEM 2500x magnification result of plating process using magnetic field and (b) SEM 5000x magnification result of plating process using magnetic field.

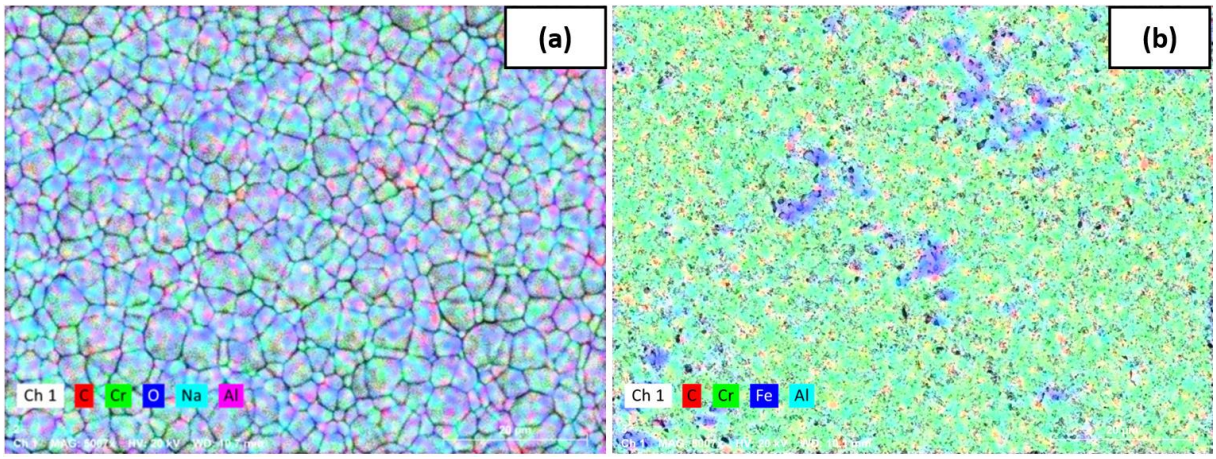


Fig. 9 Energy distribution (keV) visualizes variation of chemical elements in deposited area (a) Deposition without magnetic field and (b) Deposition using magnetic field.

effect of MHD on the electrolyte solution [13]. The decreasing MHD effect causes the mass transfer at the electrode to decrease, so that the value of the diffusion coefficient (D) and limiting current also decreases.

Wang Dan et al. in their study has shown that Nickel plating prepared by adding $LaCl_3 \cdot 7H_2O$ in the electrolyte turned out to be better surface quality, with more compact, less micropores. Because the special out-layer electronic structure of element La raised the polarization of Ni cathode deposition, accelerated the nucleation of Ni and reduced hydrogen evolution from cathode surface [16]. So, in this study, we want to see how the effect when the plating of the metal that is one periodic with nickel, namely chromium (Cr), with the addition of $LaCl_3 \cdot 7H_2O$ additive when using the influence of a magnetic field and without magnetic field. The result of SEM images, Fig. 7 is a sample without a magnetic field in the plating process. It was found that the surface was not uniform (relatively different in size) and not compact.

In contrast to the results of sample which uses the influence of a magnetic field (800 Gauss) during the plating process, a uniform surface was found (see Fig. 8) the results of the plating process with the influence of a magnetic field, obtained a more uniform surface, thicker and more compact**.**

Fig. 9(a) shows a photo of the energy distribution (keV) which visualizes the variation of chemical elements scattered in the deposited area, without the influence of a magnetic field. In Table 7, the chemical composition of the results of energy dispersive X-ray spectroscopy (EDX) shows that the percentage of chromium metal deposited is quite good (91%), but it can be seen in the Fig. that the oxide element dominates (blue color). This can indicate that

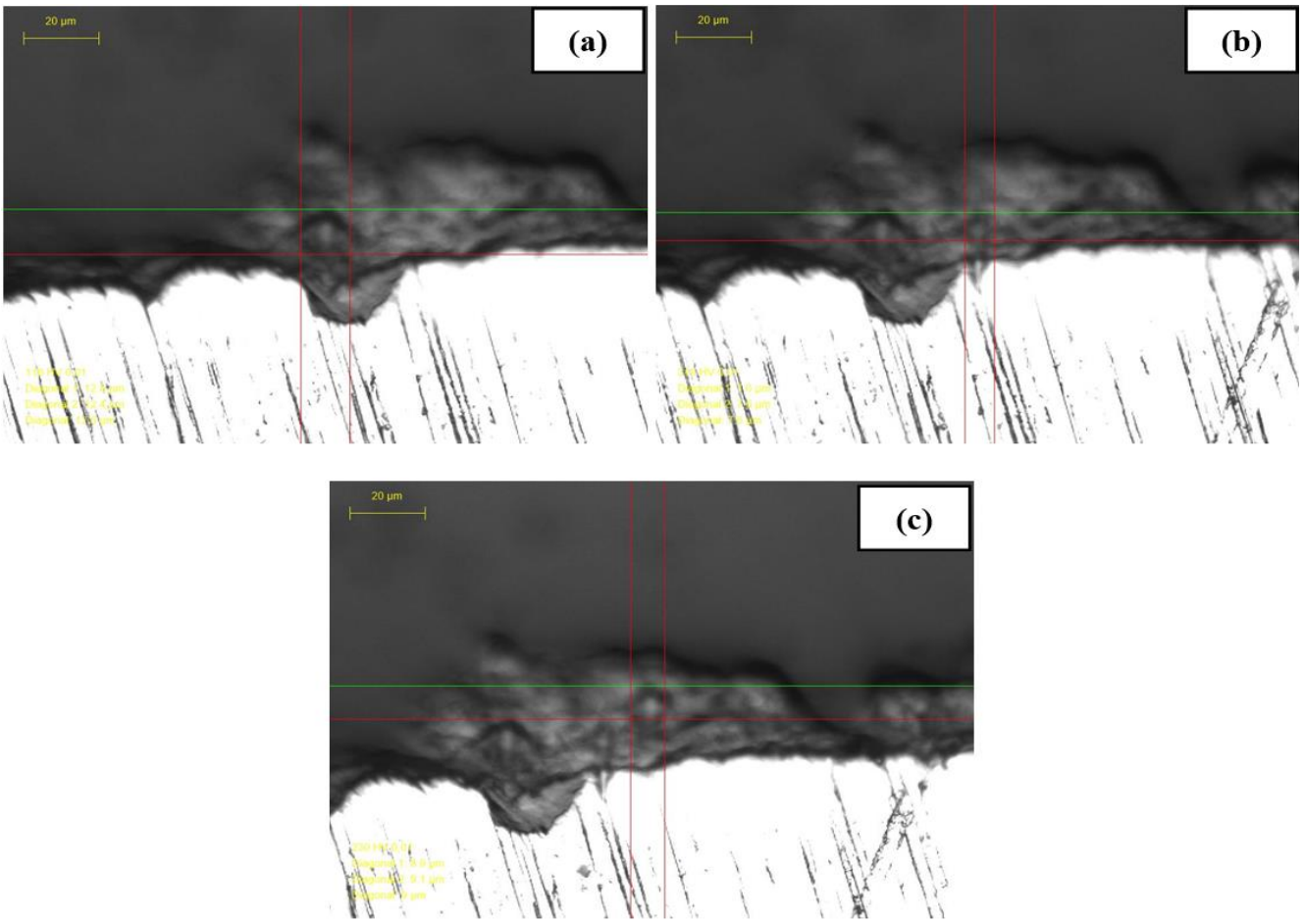


Fig. 10 Deposited microvickers result when without magnetic field.

visually, the coating process without the influence of a magnetic field is not very effective to get the optimum metal deposit.

This is different from the observations of EDX results of the deposition process involving the influence of a magnetic field (MED). Fig. 9(b) shows a photo of the energy distribution (keV) which visualizes chemical elements scattered in the coating area under the influence of a magnetic field. It can be seen clearly that chrome metal (green color) predominates, which is the desired result. Light-elements such as oxides and carbon were not found to be significant. This indicates that the deposition process using a magnetic field is more effective and produce less hydrogen evolution than without the influence of a magnetic field.

Table 7 Composition of EDX deposited results and deposited mass.

Description	Using Magnetic Field	Without Magnetic Field
Chrome (Cr)	86%	91%
Carbon (C)	2%	4%
Oxygen (O)	Not-found	2%
Deposited Mass	2.42 g	0.96 g

In Table 7 and Fig. 9, it can be seen that there is no lanthanum (La) element from the EDX results. This is because the $LaCl_3.7H_2O$ used in this plating only functions as an additive to the chromium sulfate solution. Based on Wang's research, it was found that the hardness of nickel

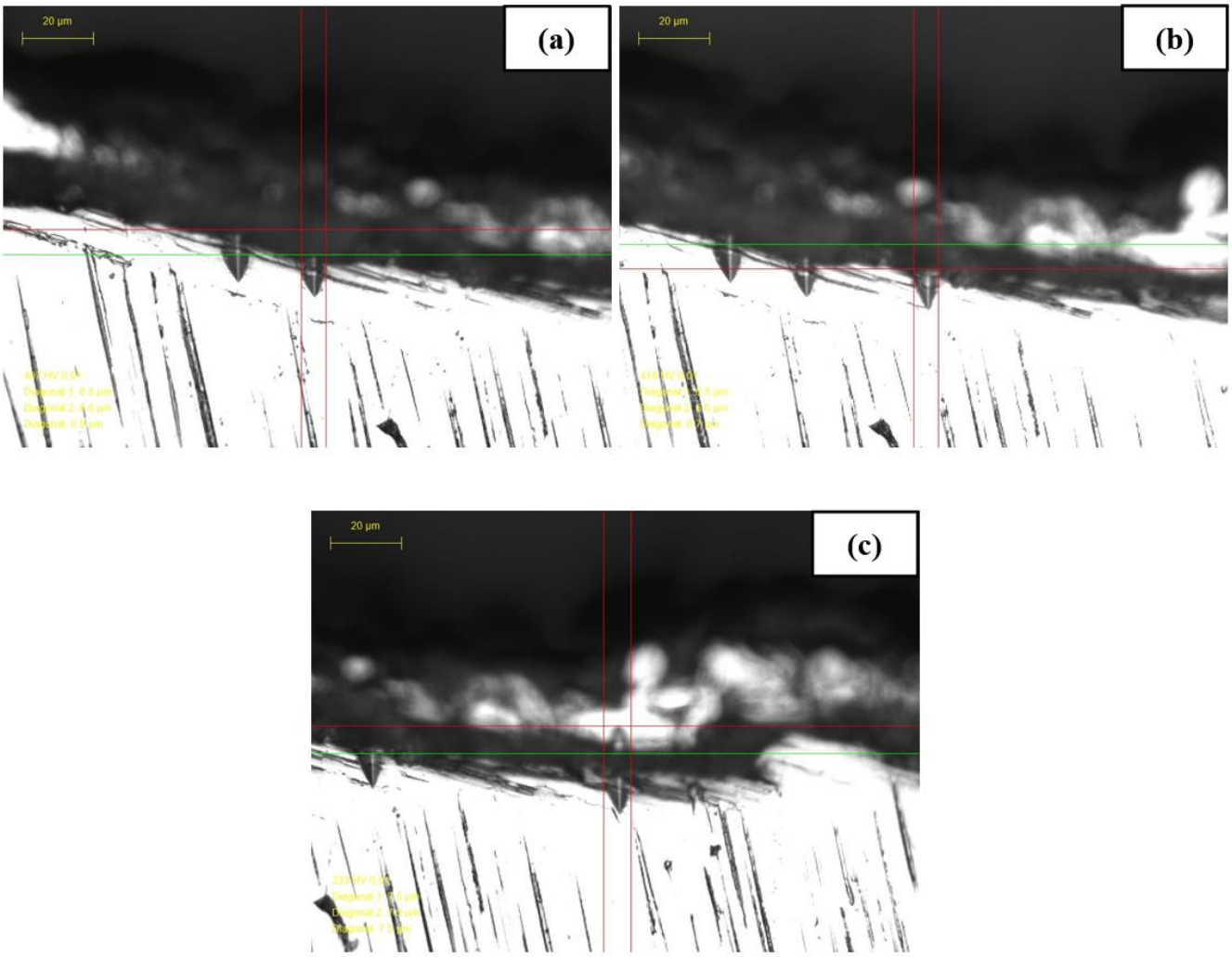


Fig. 11 Deposited microvickers result when using magnetic field.

deposits was highest when 1 g L^{-1} $LaCl_3.7H_2O$ was added to the nickel solution (Fig. 11). The value of 1 g L^{-1} is also used in this study of chromium plating. The deposited results of the pores are smaller and denser. This is because the special out-layer structure of Lanthanum increases the polarization of Nickel cathode deposition, supports Nickel nucleation and reduces hydrogen evolution from the cathode surface [16].

In the Volta-Order, lanthanum metal has a more negative electrode potential than chrome, so chrome is a stronger oxidizing agent (easier to reduce). So chrome metal will be much more easily reduced (deposited) compared to lanthanum. In addition, the concentration of chromium sulfate is dominant in the electrolyte solution, while the concentration of lanthanum is small because it acts as a catalyst only [16]. The following is an example of a volta-order:

Li, K, Ba, Ca, Na, La, Mg, Al, Mn, Zn, Cr, Fe, Cd, Co, Ni, Sn, Pb, H, Cu, Hg, Ag, Pt, Au

Testing the hardness value of the plating process without a magnetic field at 3-points was also carried out, the results were 116 HV (Fig. 10(a)); 318 HV (Fig. 10(b)); and 230 HV (Fig. 10(c)) with a mean value of 221 HV. While the plating process with a magnetic field at 3-point obtained a hardness value of 407 HV (Fig. 11(a)); 418 HV (Fig. 11(b)); and 333 HV (Fig. 11(c)) with a mean value of 386 HV.

Based on this analysis, it can be seen that the hardness of the deposit resulting from the plating process with the influence of a magnetic field has a better mechanical value,

in this case the hardness value. The better hardness value in the MED process is largely influenced by the less light-elements deposited. A good electrodeposition process is a process that produces a suitable/desired metal deposit, with the least amount of impurities. In order to visually and the application to be better.

Besides the effect of impurities, differences in hardness values can also be studied from different grain sizes as shown in Fig. 7 and Fig. 8. According to the Hall-Petch Law (HPL), the microhardness of the coating will increase with grain size refinement. The relationship between yield stress (or microhardness) and grain size, based on the dislocation theory of materials, can be expressed as shown in equation (4):

$$\sigma = \sigma_0 + K_H \cdot d^{-1/2} \quad (4)$$

Where σ_0 = Lattice friction to be overcome when removing a single dislocation, K_H = Constant and d = Average grain diameter

Based on equation (4), we can see that the relationship between (sigma) and d (grain diameter) is inversely proportional. Then the finer the grains produced in the deposition process, the higher the hardness value. Vice versa. Therefore, the electrodeposition process with the influence of a magnetic field (MED) is better than that without a magnetic field, because it produces good grain uniformity; small deposit of light-element impurities due to reduced hydrogen evolution; as well as higher deposit hardness values.

Conclusion

The results showed that the effect of increasing the working electrode area (*A*) gave a linear increase in limiting current value (i_B) for lanthanum electrodeposition. Magnetic field strength (*B*) with 600 Gauss or more also can increase the limiting current value, due to the paramagnetic properties that lanthanum have. Lanthanum (III) Chloride Heptahydrate concentration (*C*) gave a certain increase in limiting current for lanthanum electrodeposition as well. Meanwhile, the effect of the solution viscosity (*v*) and diffusion coefficient (*D*) which is influenced by the number of electrons involved in lanthanum (*n*) on the limiting current, namely the greater v and D, the limiting current value will decrease. This study also carried out chrome-plating process with the addition of Lanthanum which was studied previously, using magnetic field and without using magnetic field. It was observed that the morphological results of SEM images observations on the electroplating process of Chromium Sulfate with $LaCl_3 \cdot 7H_2O$ additive which was influenced by a magnetic field of 800 Gauss, resulted in a more uniform deposit; thicker; and more compact than without the influence of a magnetic field. The average hardness value of Chrome Sulfate coating with $LaCl_3 \cdot 7H_2O$ additive without a magnetic field is 221 HV, and with a magnetic field of 386 HV. The plating process with the addition of the influence of a magnetic field (MED) produces a harder layer deposit.

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References

[1] J. Ignasius, Potential of Rare Earth Metals in Indonesia. Indonesian Ministry of Energy and Mineral Resources, Jakarta, 2019.

[2] R. Herlani, Muljono, S. Widiyati, Mujari, Study the Effect of the Rare Earth Metals Cerium (Ce) and Lanthanum (La) on Thorium Analysis Using the X-Ray Fluorescent Method, Mujari Pusat Teknologi Akselerator dan Proses Bahan, BATAN. (2011) 237 – 248.

[3] Peraturan Menteri Energi dan Sumber Daya Mineral ini mulai berlaku pada tanggal, BN 2018/ NO 595. Indonesia, 2018.

[4] M.H. Uzir, Sudibyo, N. Aziz, Magneto-electro deposition of Tin Dendrites, Surf. Coat. Technol. 264 (2015) 66 – 71

[5] A. Levesque, S. Chouchane, J. Douglade, R. Rehamnia, Chopart, Effect of Natural and Magnetic Convections on the Structure of Electrodeposited Zinc–Nickel Alloy, Appl. Surf. Sci. 255(18) (2009) 8048 – 8053.

[6] K. Tschulik, J.A. Koza, M. Uhlemann, A. Gebert, L. Schultz, Effects of Well-defined Magnetic Field Gradients on the Electrodeposition of Copper and Bismuth, Electrochem. Commun. 11(11) (2009) 2241 – 2244.

[7] J.A. Koza, F. Karnbach, M. Uhlemann, J. McCord, C. Mickel, A. Gebert, S. Baunack, Schultz, Electrocrystallisation of CoFe Alloys Under the Influence of External Homogeneous Magnetic Fields–Properties of Deposited Thin Films, Electrochim. Acta. 55(3) (2010) 819 – 831.

[8] V.G. Levich, Physicochemical Hydrodynamics. Englewood Cliffs, N.J., Prentice-Hall, New Jersey, 1962.

[9] M.T. Fernanda, T.A. Paulo, Electrodeposition of Magnetic CoPd Thin Films Influence of Plating Condition, 28th ECS Meeting, Los Angeles USA. 16 October 2005, 89 – 101.

[10] Sudibyo, A.S. Handoko, U. Herlina, N. Aziz, Y.A. Sukma, Application of artificial neural network model to predict limiting current for cobalt magneto-electrodeposition, AIP Conf. Proc. 2232(1) (2020) 020009.

[11] S. Sandhaya, R.R. Vaishaka, A.C. Hedge, Magnetoelectrodeposition of Sn-Ni alloy coating for better corrosion protection, IJCEP. 2(1) (2016) 29 – 42.

[12] T.R.N. Mhíocháin, G. Hinds, A. Martin, E. Chang, A. Lai, L. Costiner, J.M. Coey, Influence of the magnetic field and gravity on the morphology of zinc fractal electrodeposit, Electrochim. Acta. 49(27) (2004) 4813 – 4829.

[13] Sudibyo, Modeling of Limiting Current ang Growth Fractal for Electrodepotition Under Magnetic Field Influence, M.Sc. Universiti Sains Malaysia, Penang, 2010.

[14] S. Taruli, Development of Limiting Current Semi-Empiric Equation for Vanadium Under the Effect of a Magnetic Field Thesis, Sultan Ageng Tirtayasa University, Banten, 2020.

[15] N.A. Lubis, The influence of liquid viscosity on falling time by falling ball method, Fisitek. 2(2) (2018) 26 – 32.

[16] D.Wang, Y. Cheng, H. Jin, J. Zhang, J. Gao, Influence of $LaCl_3$ addition on microstructure and properties of nickel-electroplating coating, J. Rare Earths. 31(2) (2012) 209 – 214.