USE OF LAYERED DOUBLE HYDROXIDES AS IONOPHORE FOR ANION SELECTIVE
ELECTRODE

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การใช้เลเยอร์ดับเบิลไฮดรอกไซด์เป็นไอโอโนฟอร์สำหรับขั้วไฟฟ้าเลือกจำเพาะต่อแอนไอออน

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เลเยอร์ดับเบิลไฮดรอกไซด์ (LDH) หรือ สารประกอบไฮโดรทาลไซต์ (hydrotalcites)
สารกลุ่มนี้มักถูกเรียกว่าเป็นแอนไอออนิกเคลย์ ที่คุณสมบัติในการดูดซับและแลกเปลี่ยนแอน
ไอออนที่จำเพาะได้ ซึ่งเป็นพฤติกรรมที่คล้ายคลึงกับการจำพวกสารกลุ่มไอโอโนฟอร์ และสารเติม
แต่งไอออนิก ที่ใช้ในขั้วไอออนเลือกจำเพาะ (ISE) จึงมีความเป็นไปได้ที่จะนำสารกลุ่มเลเยอร์
ดับเบิลไฮดรอกไซด์มาใช้เป็นไอโอโนฟอร์แบบตัดแต่งตามชนิดแอนไอออน และสารเติมแต่งไอ
ออนิกในการขึ้นรูปเมมเบรนสำหรับขั้วไอออนเลือกจำเพาะ ในงานวิจัยนี้เลเยอร์ดับเบิลไฮดรอกไซด์
ชนิดแมกนีเซียม-อะลูมิเนียมที่มีไนเตรตไอออนแทรกตัวอยู่ระหว่างเลเยอร์ (MgAl LDHs-NO_3^-) ได้
ถูกนำมาใช้ศึกษาขึ้นรูปร่วมกับพีวีซีเป็นไอออนซีเล็คทีฟเมมเบรน (ISM) พบว่าเมมเบรนที่เตรียมที่
โดยใช้ 30%(w/w) ของ MgAl LDHs-NO_3^- แสดงผลการตอบสนองทางศักย์ไฟฟ้าที่ดีที่สุด สำหรับ
การตรวจวัด NO_3^- โดยแสดงผลการวัดที่เป็นเส้นตรง ในช่วงความเข้มข้น 1.0×10^{-4} to
1.0×10^{-2} M และมีค่าความชันเนินส์เป็น -51.31 mV decade^{-1} จากการพยามศึกษา
ความจำเพาะเจาะจงด้วยเทคนิค SSM สำหรับการตรวจวัดแอนไอออนชนิดต่างๆ พบว่า SCN^- และ
NO_3^- มีความจำเพาะเจาะจงในการตรวจวัดที่ใกล้เคียงกัน โดยผลการศึกษาได้นำเสนอแนวคิด
สำหรับการนำสารกลุ่มเลเยอร์ดับเบิลไฮดรอกไซด์มาใช้ดัดแปลงเป็นไอโอโนฟอร์ เพื่อเป็นแนว
ทางการพัฒนาขั้วไอออนเลือกจำเพาะต่อแอนไอออนต่อไปในอนาคต

สาขาวิชา	เคมี	ลายมือชื่อนิสิต ....
ปีการศึกษา	2565	ลายมือชื่อ อ.ที่ปรึกษาหลัก ....

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Layered double hydroxides (LDHs) or hydrotalcite compounds are referred to anionic clays with specific anion adsorption and exchanging properties. These behaviors are similar to ionophores and ionic additives in ion selective electrodes (ISEs). Therefore, in this study LDHs was used to function as tailor-made ionophores for particular anions and ionic additives in ISEs. MgAl LDHs were prepared, and then modified the intercalated anions to be NO_3^-. The selective polymeric membrane was casted using PVC and MgAl LDHs-NO_3^-. The membrane containing 30%(w/w) MgAl LDHs-NO_3^- showed the best ISE characteristics toward NO_3^- with response slopes of -51.31 mV decade^{-1} in the concentration range 1.0×10^{-4} to 1.0×10^{-2} M. However, attempts of the selectivity studies using separate solution method (SSM) showed the selectivity coefficients of SCN^- and NO_3^- were not significantly different. The results present an idea for fabrication of tailor-made ionophores for anions which can lead to further development.

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CHAPTER I

INTRODUCTION

1.1.Background and Significance of Research

Nowadays, the development of sensors for anions has received considerable attention due to its essential roles in physiological and industrial processes. Many sensing techniques have been reported to detect anions using direct and indirect instrumental method including, high-performance liquid chromatography (HPLC), ion chromatography (IC) liquid chromatography-tandem mass spectrometry (LC-MS) and UV-Visible spectrophotometry. These methods require time consuming procedures [1]and use of sophisticated instruments, whereas electrochemical analysis is another approach which is simple, has low limit of detection and high sensitivity which breakdown the drawback of previously mentioned methods.

Ion selective electrode (ISE) is one of the electrochemical sensors that is widely used in environmental analysis, quality check and standardization because it is simple, durable, reusable and easy to prepare. The selectivity of ISEs is mainly due to ionophores (lipophilic complexing agents) which result from a stronger interaction between the ionophore and a target ion rather than a weaker interaction of the ionophore and interfering ions. A number of ISEs has been reported during the past 10 years especially cation selective electrodes. However, anion selective electrodes are less explored as compared to the cation one due to different shapes of anions. [1]

Layered double hydroxides (LDHs) or hydrotalcites-like compounds are referred to anionic clays which have anion adsorption capacity and anion exchange property. [2, 3] Therefore, LDHs was use as the green material for environmental applications such adsorbents, decontaminating and environmental catalysts. The LDHs prominent points, behavior of ion exchange and storage was like the function of organic synthetic ionophore which was probably used instead. LDHs is commercial inorganic compound,

cheap and easy to fabricate in laboratory. To the best of our knowledge, LDH based anion selective electrodes have been less reported. Thus, utilizing LDHs as ionophore in ISEs is interesting and challenging idea. [4, 5] Intercalated anions of LDHs can be modified to be specific anions by well-known techniques. Therefore, the modified LDHs can be use as ionophore tailor-made for a particular anion.

In this study, our goal is to use MgAl LDHs with NO_3^- as intercalated anion to be an ionophore, polyvinyl chloride (PVC) as polymer and *o*-nitrophenyl octyl ether (*o*-NPOE) as plasticizer to fabricate the polymeric membrane for NO_3^- ISEs.

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CHAPTER II

LITERATURE REVIEWS

2.1. Anion Pollution and Detection

According to its high solubility in water, anion is usually discovered in ground water, surface water and drinking water. Nowadays, apart from being found in water, anion also can be found and accumulated in foodstuffs such as vegetables, meats, fruits and edible crops due to increase of global population in recent years.[6, 7] Hence, as a water and food contaminant, anion has become severe environmental issue and affected to human health. Therefore, detection of anions is of importance to prevent environmental problems. There are many instrumental methods including ion chromatography (IC), liquid chromatography tandem mass spectrometry (LC-MS), Ultraviolet-Visible spectrophotometry (UV-Vis) for detection of anion. These methods have drawbacks such as time consuming, requiring skilled-labor and using sophisticated instrumentation. Some industries also use a classical technique such as titration to reduce the analytical cost. Electrochemical methods are less expensive and easy to develop efficient anion detectors and sensors, which break down limitations and drawbacks of previously mentioned methods. Ion selective electrode (ISE) is one of electrochemical techniques which uses basic principle of electrochemistry but has the high efficiency of ion detection.

2.2. Ion Selective Electrodes (ISEs)

Ion selective electrodes (ISEs) are the fundamental chemical sensors that have the longest history with the most frequent routine application. An example of ISEs is pH meter which has been widely used for more than 60 years.[1] The pH meter uses glass membrane ionophore which is specific for H^+. In general, ISEs are potentiometric sensors that are widely used to analyze both of cations and anions with rapid and accurate detection. For medical applications, the portable ISEs can be used for measuring ion concentration in biological fluids.[8] The potentiometric response is the

phase boundary potential (E_{PB}) that differs from other analytical techniques which ability to the real time detect an ion activity in aqueous phase (bulk solution) compare with organic phase (polymeric membrane), described by Nernst equation (equation 2.1)

$$E_{PB}=E^0+\frac{RT}{z_iF}\ln\frac{a_{i(aq)}}{a_{i(org)}}$$ (2.1)

Where E° incorporates all potential contributions of measuring cell that are constant for this measurement. The parameter R, T and F were referred to universal gas constant, temperature and Faraday constant in C/mol e^- unit, respectively while Z_i, $a_{i(aq)}$ and $a_{i(org)}$ are charge and activity of measured ion in aqueous phase and organic phase, respectively.[1, 9]
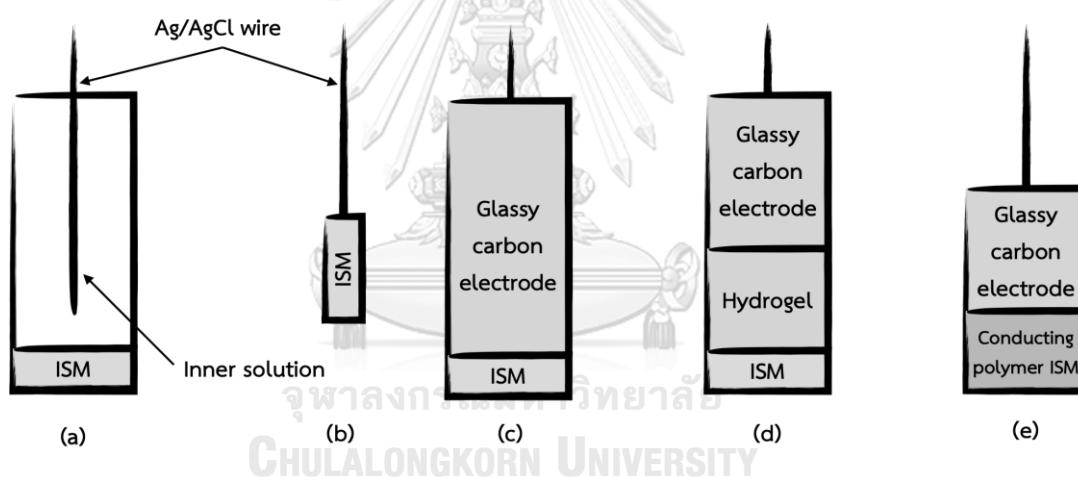
Figure 2.1 The ISE working electrode with several type (a) conventional electrode, (b) coated wire electrodes, (c) solid state, (d) hydrogel conventional electrode and (e) conducting polymer solid state.[9]

There are several types of ISEs an illustrated in Figure 2.1. A conventional ISE shown in Figure 2.1a composes of ion selective membrane (ISM) mount on the electrode body which has Ag/AgCl wire immersed in inner electrolyte solution (non-directly contract with ISM). Solid-state ISEs shown in Figure 2.1b and c compose of ion selective membrane (ISM) attached directly to Ag/AgCl wire or mount on glassy carbon

electrode. In Figure 2.1d, the inner electrolyte solution of conventional ISE was replaced with electrolyte hydrogel. In Figure 2.1e, the ISM of solid state ISEs was added the conducting polymer.[10]

2.3. Polymeric Membrane Based ISEs

Polymeric membrane based ISEs are the most versatile ISEs for selective ion detection. The membrane cloud be classified into three main components: plasticized polymeric phase, ionophore and ionic additive. Typically, polyvinyl chloride (PVC) was used as polymeric matrix, ionophores should be the lipophilic complexing agent with ion-exchange sites that specific for analytical ion and ionic additive was used as the ion balancing. Components were dissolved together in organic solvent to be a homogeneous mixture which called cocktail solution. The cocktail solution was casted and formed the ion selective membrane (ISM) via evaporation of solvent. The membrane was then put on an electrode body equipped with an Ag/AgCl wire and an inner filling solution of fabricate a working ISEs as shown in Figure 2.2.[1]
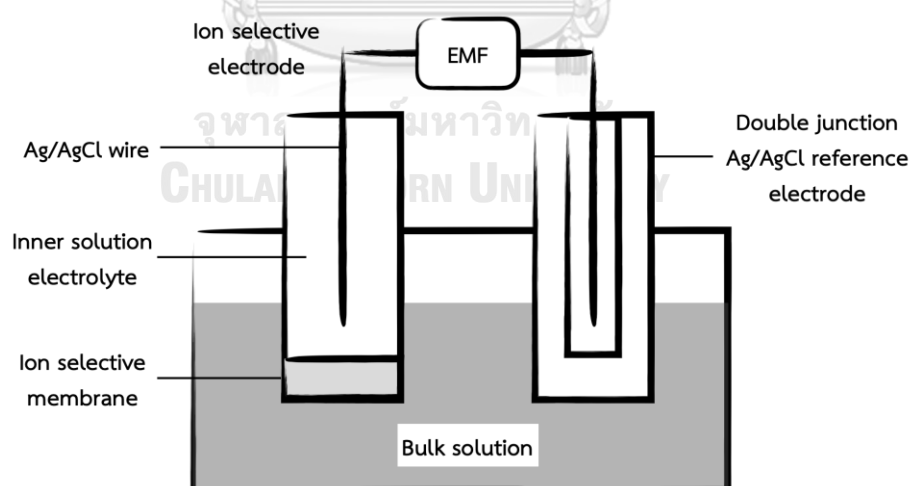
Figure 2.2 Schematic diagram of a membrane electrode measuring circuit and cell assembly.[1]

Selectivity of polymeric membrane based ISEs was expressed with the selectivity coefficients, $logK_{i,j}^{Pot}$ which can be measured from the separate solution method (SSM) as reported by Bakker et al.[1, 9] The SSM showed the potentiality of the primary ion or the analytical ion to replace the foreign ion. The $logK_{i,j}^{Pot}$ can be derived from Nernst's equation (equation 2.1) couple with two different measuring methods defined as Nicolskii- Eisenman Formalism (as shown in equation 2.2).

$$logK_{i,j}^{Pot} = \frac{nF(E_j - E_i)}{2.303RT} + log\left(\frac{a_i}{a_j^{n/m}}\right)$$

(2.2)

The subscript (i) and (i) refer to the parameter result from primary and interfering ions, respectively while E is potential response, a is ion activity, n and m are the charge of primary and interfering ions, respectively. The parameter R , T and F are referred to universal gas constant, temperature in °K and Faraday constant in C/mol e⁻ unit, respectively.

2.4. Ionophore

Ionophores are the group of compounds in polymeric membrane which can interact with analyte ion. The selectivity of polymeric ISEs stems from ionophores with ion specific ion binding. The commercial ionophores are organic molecules with ion binding and exchanging side that could be cyclic ether, supramolecular, porphyrin ring etc. (Figure 2.3) that can be synthesized in the laboratory and dissolved in PVC- based ISEs preparation.[1]
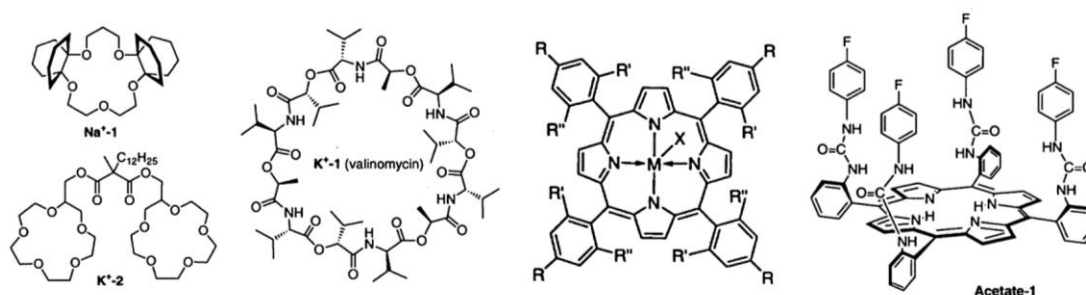
Figure 2.3 A selection of organic molecules using as ionophores in ISEs.[1]

The different shape anions are a challenge of anion ISEs. They require the specific binding ionophore for serve the anion detection while the most of cation has the only round shape. Organometallics are popular reported to use as anion ionophore which can be modified or synthesized as anion required. The example of thiocyanate ISEs, cyclopalladated amine, metal porphyrins, organotin complex and silver thiourea derivatives have been use as ionophore for polymeric ISEs.[11]

The synthesis of these organic molecules needs many steps in preparation which also need a lot of chemical and generate tremendous waste. Therefore, our group tries to use the inorganic compounds which has similar property to organic ionophores such as zeolite, layer double hydroxide (LDHs) and montmorillonite as ionophore in our fabricated ISEs.

2.5. Layered Double Hydroxides (LDHs)

The example of ion exchangeable inorganic compound as ionophore. Layered double hydroxides (LDHs) or hydrotalcite-like compounds are consisted of the positively charged of two-dimensional sheets (brucite-type structure) that have intercalated by the exchangeable charge-compensation molecules (water molecules or anions such as OH^-, CO_3^{2-}, NO_3^- etc.). LDHs are the family of anionic clay materials which have the formular structure $[M_{1-x}^{II}M_x^{III}(OH)_2][X_{x/q}^{q-}\cdot nH_2O]$, where M^{II} and M^{III} are divalent and trivalent metal cations, $[X_{x/q}^{q-}\cdot nH_2O]$ are the charge-compensation interlayer composition as shown in Figure 2.4. The interlayer molecules can be anions which have stored and exchanged with other ones.[2, 12, 13] The anion exchange behavior in LDHs depends mainly on electrostatic forces or coulombic forces between positively charged hydroxylated sheets and the intercalated anions as shown in equation 2.3. The ability of anion exchange depended on the charge and diameters of anions.[14]

$$|F|=K_e\frac{|q_1||q_2|}{r^2} \tag{2.3}$$

while F is coulomb force, K_e is Coulomb constant, q_1 and q_2 are the signed magnitudes of the charges which can refer to hydroxylated sheets and anion, r is the distance between the charges which can refer to anion's diameters.
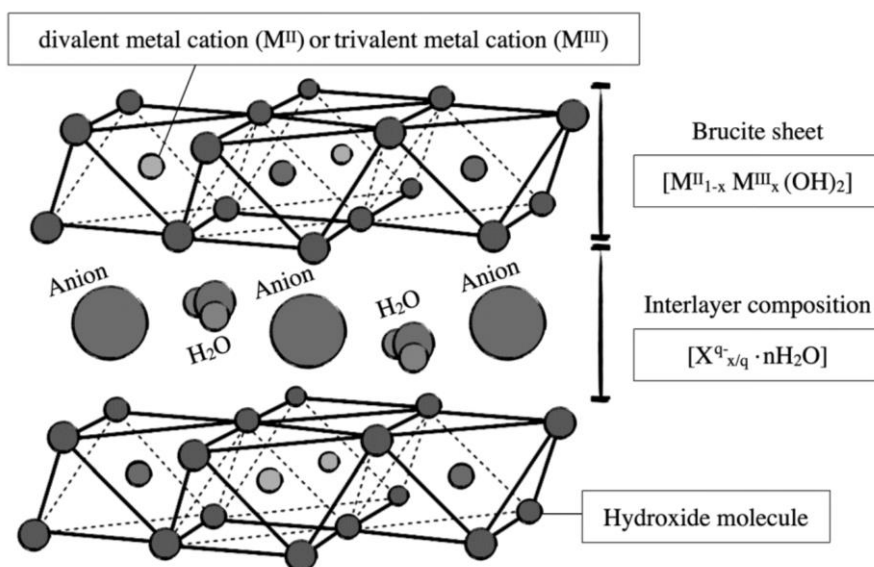
Figure 2.4 The structure of Layered double hydroxides.

LDHs are commercial and can be developed or designed to be the advanced materials with high potential applications such as adsorbent, catalysts, drug delivery etc. The synthesis of layered double hydroxides is simple and inexpensive on laboratory and industrial scales. There are many ways to prepare which achieve suitable physical and chemical properties LDHs for applications. The fundamental of LDHs preparation is co-precipitation of metal cation in basic condition which have substance flow rate, pH variation and nucleation. For the standard of coprecipitation, the urea method uses the hydrolysis rate of urea which can be controlled by temperature for continuous nucleation of mixed hydroxides simultaneous. The crystallinity and homogeneous of compounds were the result of controllable preparation which increase the LDHs ability and repeatable. For another technique, hydrothermal treatment is also used to improve the simultaneous growth of LDHs nucleation and increase the homogeneity in close systems under control pressure and temperature.[2, 15]

Anion-exchange, reconstruction and adsorption is the strength ability of LDHs which widely used for taking up a variety of contaminants and toxic substances directly

from the environment (Figure 2.5). For anions pollutant such as phosphate divertive, can be captured by the exchangeable anion forms of LDHs (such as NO_3^-, Cl^-) with anion exchange mechanism.[16] For hydrophobic environment pollutant such as surfactants or hydrophobic organic contaminants, can be eliminated by Organo-LDHs modified (such as dodecyl sulphate or organo-montmorillonite) with hydrophobic adsorbing mechanism.[17] For transition metal cations pollutant (such as Cu^{2+}, Ni^{2+}, Co^{2+}, and Zn^{2+}), can be harvested by adding Mg-based LDHs to aqueous pollutant solutions for increase pH which causes metal cations to co-precipitate to be the mix-metal hydroxide or LDHs with reconstruction mechanism.[18]
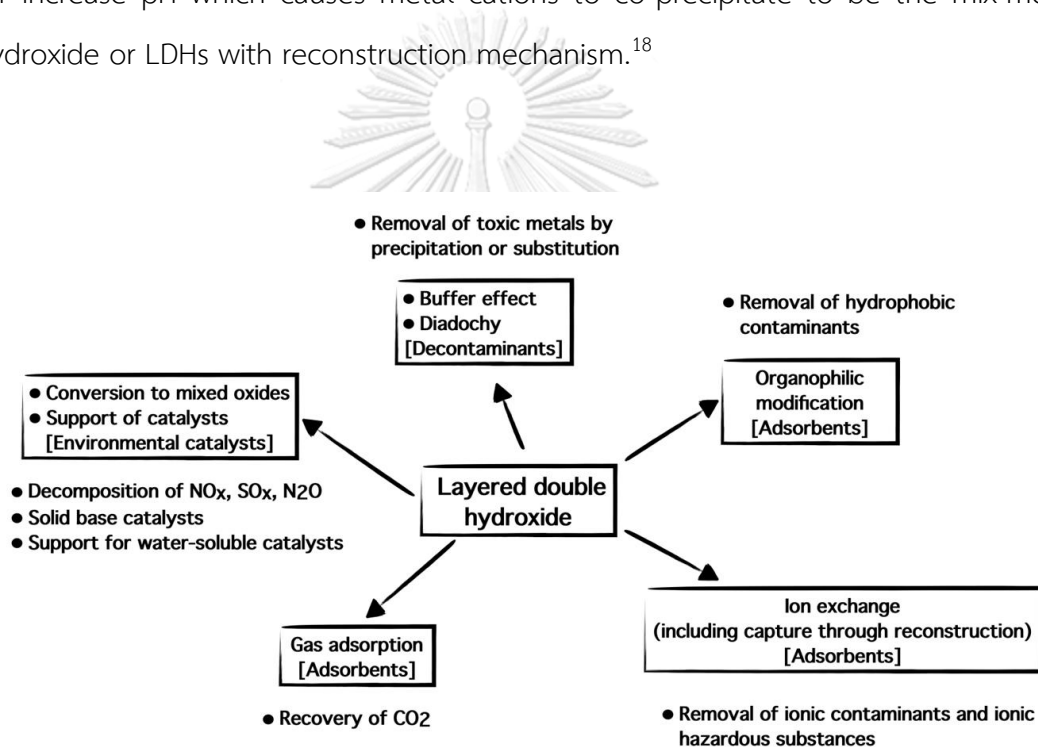
Figure 2.5 Environmental applications of LDHs.[17]

Regeneration is the unique property of LDHs, ascribable to a structural memory effect of LDHs which can be used in adsorbent reusing and LDHs decarbonating by hydration of the calcined LDHs (or layered double oxide, LDOs). In the first step, LDHs with a local anion containing was calcined into a mixture of oxides (LDOs). The second step, mix metal oxides were rehydrated in an aqueous solution containing the anion to be intercalated which can be repeat in cycle as showed in Figure 2.6.[2]
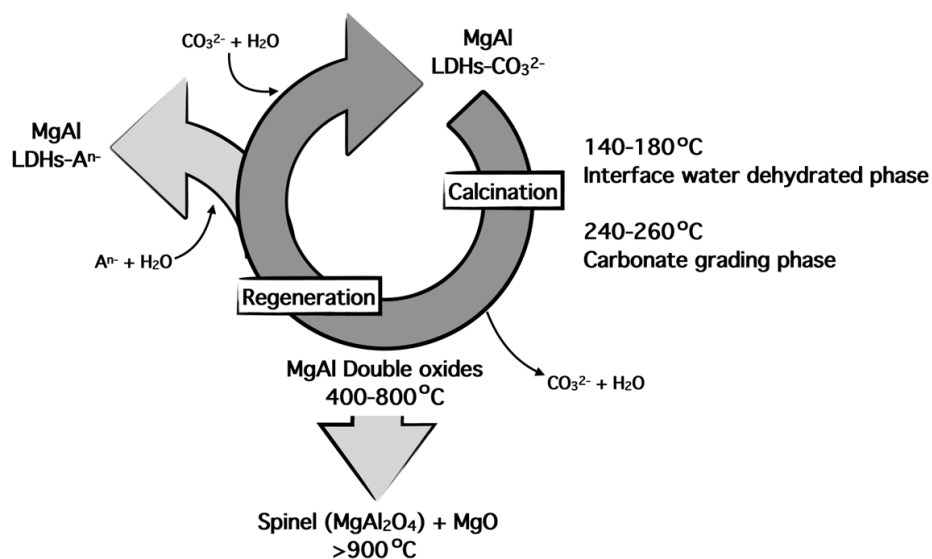
Figure 2.6 Decomposition of MgAl LDHs by calcinations and regeneration from calcined LDHs in aqueous solutions.[2]

2.6. Applied of Layered Double Hydroxides in Ion Selective Electrodes

Ballarin et al. demonstrated that synthetic MgAl LDHs can be used as ionophores for intercalated anion detection (MgAl LDHs-Cl$^-$ and MgAl LDHs- NO_3^- for chloride ion and nitrate ion detection, respectively). The membrane was composed of polyvinyl chloride (PVC) as polymer backbone and dibutyl phthalate (DBP) as plasticizer, tridodecylmethylammonium iodide (TDMAI) as cationic additive and co-precipitation MgAl LDHs amount 40-70 %(w/w) as ionophore. This case, the classical ISE was used as ISE working electrode then apply to solid contact ISE on glassy carbon electrode that displays the same sensitivity. The potentiometric response exhibited a linear concentration range from 5.0×10^{-5} to 2.0×10^{-1} M with average Nernstian slope -54.2 mV decade^{-1} for chloride ion, from 2.0×10^{-4} to 1.0 M with an average Nernstian slope -48.3 mV decade^{-1} for nitrate. The selectivity order was $CH_3COO^- < ClO_4^- < NO_3^- < I^- < SCN^- < IO_3^- <$ Phthalate $< Br^- < Cl^- < SO_4^{2-}$ which differ from the Hofmeister series but could be ascribed by an exchange mechanism of LDHs structural.[4]

Morigi et al. used MgAl LDHs intercalated with sulfate ion as ionophore for sulfate detection. The membrane was composed of polydimethylsiloxane (PDMS) as

lipophobic polymer with free plasticizer and ionic additive, co-precipitation MgAl LDHs-SO_4^{2-} amount of 29 %(w/w). The solid contact ISE was prepared in this case which showed the potentiometric response with a linear concentration range from 4.0×10^{-5} to 4.0×10^{-2} M with an average Nernstian slope -29.6 mV decade^{-1} for sulfate ion. The selective membrane exhibits the high selectivity for sulfate over all the univalent anions but also was interfere from the divalent and trivalent anions (phosphate, oxalate, sulfite, and thiosulfate) that was controlled by 2-[4-(2-hydroxyethyl)-1-piperarazinyl] ethanesulfonic acid (HEPES), the zwitterionic sulfonic acid buffer which presented into the solution.[5]

Tonelli et. al, synthesized MgAl LDHs with monohydrogen phosphate as exchangeable interlayer anion by the co-precipitation method. The plasticizer-free selective membranes without ionic additive were used in solid contact ISE on glassy carbon electrode (GCE) which composed of polyvinyl butyral (PVB) as polymer backbone and MgAl LDHs-HPO_4^{2-} as ionophore. The potentiometric response showed a linearity range from 5.0×10^{-5} to 2.0×10^{-2} M with Nernstian slope of -29.2 and -25.4 mV/decade when the solutions were buffered at pH 6.0 and 7.5, respectively. This case, the PVB/MgAl LDHs-HPO_4^{2-}/GCE do not display the superior selectivity from others work but they can discriminate the most lipophilic interfering anions (such as perchlorate and thiocyanate) of monohydrogen phosphate detection.[19]

CHAPTER III

EXPERIMENTAL SECTION

3.1. Material

The fresh Layered Double Hydroxides (LDHs) were prepared by urea method using hydrothermal process and modified by decarbonation via calcination and regeneration process.[13, 20] Magnesium nitrate hexahydrate, aluminum nitrate nonahydrate, urea powder and sodium nitrate were purchased from Sigma-Aldrich. High molecular weight polyvinyl chloride (PVC), o-nitrophenyl octyl ether (o-NPOE) and tetrahydrofuran (THF) were obtained in Selectophore® grade from Sigma-Aldrich. All chemicals and solvents were used as received without further treatment. Aqueous solutions for potentiometric experiments were prepared with ultrapure water from Milli-Q (Bedford, MA, USA) water purification system (Millipore).

3.2. Instrumentation

Preparation and modification process of LDHs were taken place in hot air oven (room 1539, MHMK) and calcination process was occurred in chambre furnace (Carbolite). A vortex meter (Scientific Industries Vortex-Genie 2) and a sonicator (Bendelin Sonorex Digitec) were used in casting of ISM. The crystalline and phase purity of LDHs were identified by powder X-ray diffraction analysis on an X-ray Diffractometer using Rigaku SmartLab X-Ray Diffractometer with Cu-Kα radiation (40 kV, 30 mA, λ =1544 Å). The Fourier Transform Infrared (FTIR) spectra were recorded with a Nicolet 6700 spectrophotometer via transmittance mode (KBr Disk) in the range of 550–4000 cm^{-1}. The surface morphology of samples was recorded by Scanning Electron Microscopy-Energy Dispersive Spectrometry (SEM-EDS) using JSM-IT100 InTouchScopeTM Scanning Electron Microscope. A Lawson Labs, Inc 16-channel potentiometer (Lawson Labs Inc., Malvern, PA 19355, USA) was used for measuring potentiometric response of ion selective electrode at room temperature (26 ± 1 °C). All potential measurement were

carried out with the following voltaic cell: Ag/AgCl reference electrode | sample solution | membrane | inner filling solution | Ag/AgCl wire.

3.3.   Preparation of Layered Double Hydroxides (LDHs)

The high crystalline magnesium-aluminum layered double hydroxides (MgAl LDHs) was prepared followed by Mohamed R. Berber protocol[13] with a slight modification.[1] The mixed metal salt ($Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ with total amount is 0.024 mol) and urea powder (urea: metal ratio is 3.5: 1) were dissolved in 50 mL of deionized water (the protocol was shown on Table 3.1). The reaction mixture solution was poured into a stainless-steel autoclave reactor and heated (at 120 and 140°C) for 12 hours. The high crystalline MgAl LDHs with CO_3^{2-} as intercalated ion (MgAl LDHs-CO_3^{2-}) precipitated in the reactor. It was then separated by vacuum filtration using double filter paper and dried at 60°C.

Table 3.1 Summary of all LDHs preparation protocol in reaction solution (50 mL).

Protocol	Metal salt ($M^{2+}: M^{3+}$)	Mg (m mol)	Al (m mol)	Urea (m mol)	Hydrothermal temperature (°C)
2:1-UH-120	2:1	16	8	84	120
2:1-UH-140	2:1	16	8	84	140
3:1-UH-120	3:1	18	6	84	120
3:1-UH-140	3:1	18	6	84	140

3.4.   Modification of Layered Double Hydroxides (LDHs)

The intercalated anion in high crystalline MgAl LDHs-CO_3^{2-} was changed to nitrate ion by 2 steps as shown in Figure 3.1. The first step was a calcination process using furnace (with heating rate 2 °C/ min and final temperature at 500°C for 3 h, the temperature profile were shown in Figure 3.2) to give the metal oxide form of LDHs which is called layered double oxide (LDOs). [20, 21] In the regeneration process of LDHs, a solution of $NaNO_3$ (0.20 M, 10 mL) was added to MgAl LDOs (0.200 g) and stirred for 24 hours at room temperature to obtain MgAl LDHs with NO_3^- as intercalated ion. MgAl LDHs-NO_3^- was then separated by vacuum filtration and dried at 60°C. [20, 21]
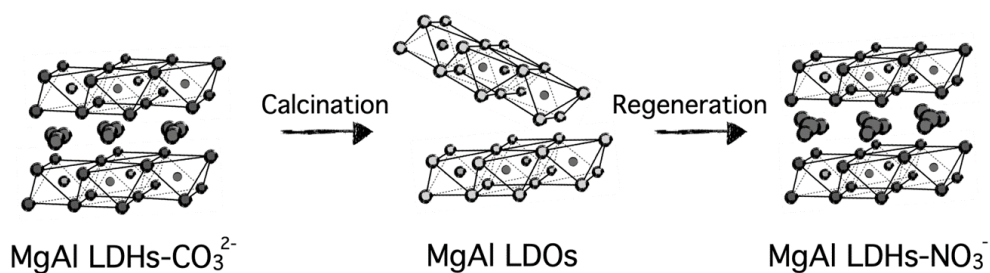
Figure 3.1 The 2 steps of LDHs modification pathways
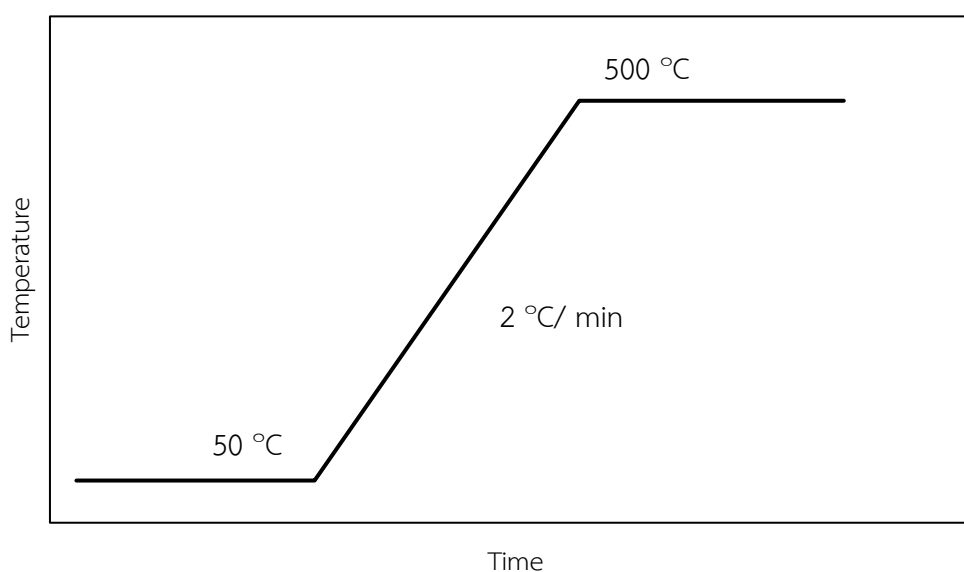
Figure 3.2 Temperature profile of calcination process.

3.5. Preparation of Ion Selective Membrane and Electrodes Assembly

Ion selective membranes were prepared by mixing MgAl LDHs-NO_3^-, PVC and *o*-NPOE (with specific ratio of polymer: plasticizer = 1:2, total weight 100.00 mg as listed in Table 3.2) in 2.000 mL of THF. The mixture was subjected to shake by vortex mixer and subsequence ultrasonicate to obtain a colloid. The colloid was transferred into a glass ring with 22 mm diameter affixed onto the clean glass plate. The solvent THF was allowed to evaporate overnight to obtain ion selective membranes.

Table 3.2 Membrane composition of the ISM with total weight 100.00 mg.

Membranes	Membrane components %(w/w)		
	MgAl LDHs-NO$_3^-$	PVC	NPOE
A	10.00	30.00	60.00
B	20.00	26.67	53.33
C	25.00	25.00	50.00
D	30.00	23.33	46.67
E	35.00	21.26	43.33
F	40.00	20.00	40.00

Note Membranes A-F referred to 10%(w/w) MgAl LDHs-NO$_3^-$, 20%(w/w) MgAl LDHs-NO$_3^-$, 25%(w/w) MgAl LDHs-NO$_3^-$, 30%(w/w) MgAl LDHs-NO$_3^-$, 35%(w/w) MgAl LDHs-NO$_3^-$, and 40%(w/w) MgAl LDHs-NO$_3^-$ respectively.

3.6.   The EMF Measurements

All EMF measurements were carried out with the following cell assembly: Ag/AgCl I 3 M KCl II 1 M LiOAc II bulk solution I ion selective membrane I inner solution I AgCl/ Ag. The membrane selective of the previously preparation was cut to be the small circle with 3 mm diameter. The cutting membrane was conditioned for analyte saturation by immersing in 1.0 x 10^{-2} M of the study ion for 12 hours then washed the excess ion by milli-Q water and assemble with classical ion selective electrode as shown the schematic illustration in Figure 3.3. The inner solution of ISE probe was 1.0 x 10^{-2} M of analyte coupled with 1.0 x 10^{-3} M of Cl$^-$. The reference electrode was double junction Ag/AgCl (type 6.0729.100, Metrohm AG, Ionenstrasse, 9100 Herisau, Switzerland) with 1 M LiOAc as salt bridge electrolyte.

For ISE characteristic study, 20.00 g of Milli-Q water in beakers (50 mL) was us as bulk solution, the standard ion solution at concentration 1.0 x 10^{-7} to 1.0 x 10^{-2} M was pipetted and measured the EMF with real time measurement by Lawson Labs, Inc 16-channel potentiometer. The potential analysis of any solution was recorded when the signal became stable after pipetting the standard concentration of each ion. Plots

between logarithmic function of anion activity and average potential were be used to calculate a Nernstian response slope.
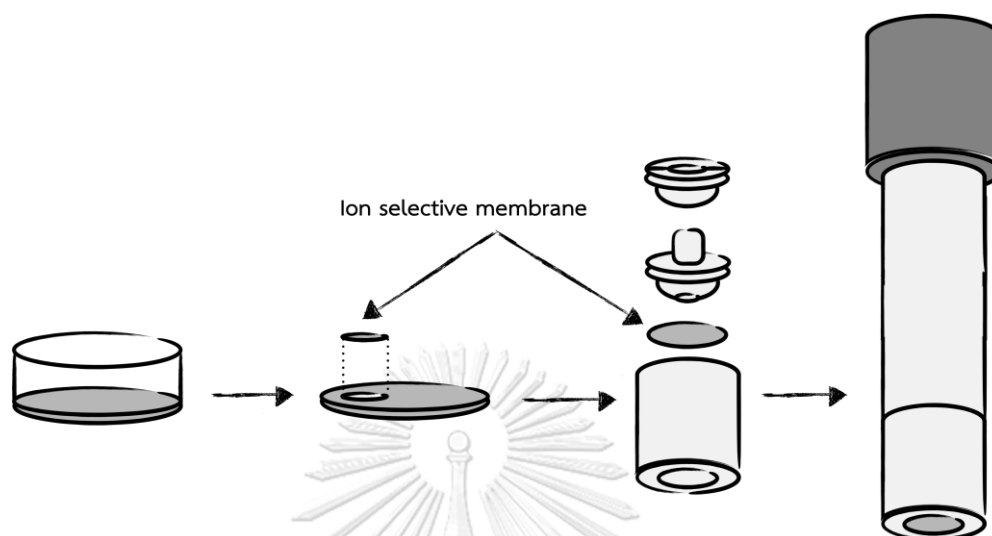
Figure 3.3 Schematic preview of the assembly of ion selective electrode.

3.7. Attempts to Study Selectivity of The Fabricated Membranes.

The selectivity was determined by the separate solution method (SSM). Four anions that gave the best Nernstian response slopes NO_3^-, SCN^-, ClO_4^- and SO_4^{2-} were used as primary anions, while interfering anions were NO_3^-, SCN^-, ClO_4^-, SO_4^{2-}, I^-, Cl^- and F^-. The membrane was conditioned with interfering ions. The interfering ions (j) solution was added to the bulk solution and EMF (E_j) was measured. The primary ion (i) solution was added and EMF (E_i) was then measured. The selectivity coefficients ($logK_{i,j}^{Pot}$) can be calculated using equation 2.2.[1, 8, 9]

CHAPTER IV

RESULT AND DISCUSSION

4.1 Preparation and Modification of Layered Double Hydroxides

All preparation processes shown in equations 4.1-4.4 occur in a hydrothermal autoclave reactor. The first reaction, urea was hydrolyzed to generate NH_3 which can control the amount of OH^- and pH of the solution (equation 4.1-4.2). Another product of urea hydrolysis, $CO_{2(g)}$, has occurred under high pressure. Then, $CO_{2(g)}$ would dissolve in aqueous solution as CO_3^{2-} (equation 4.3).

In equation 4.4, the co-precipitation of LDHs occurred by the formation of the mixed metal ion with OH^- to be mixed metal hydroxide which has crystal growth in a brucite sheet or layered structure. These composite metal hydroxide layers have a positive charge. Therefore, CO_3^{2-} and water molecule would stabilize the layered structure with coulombic forces.[2, 12] Each stabilized layer was stacked to be layered double hyd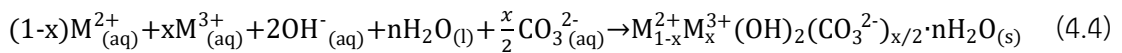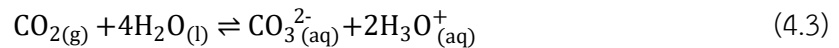roxides (LDHs) which contained CO_3^{2-} and water molecule between the layers. MgAl LDHs-CO_3^{2-} was obtained as white solid.

$$CO(NH_2)_{2(aq)} + 2H_2O_{(l)} \xrightarrow{\Delta} 2NH_{3(aq)} + CO_{2(g)} \tag{4.1}$$

$$NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons NH_{4\,(aq)}^+ + OH_{(aq)}^- \tag{4.2}$$

$$CO_{2(g)} + 4H_2O_{(l)} \rightleftharpoons CO_{3\,(aq)}^{2-} + 2H_3O_{(aq)}^+ \tag{4.3}$$

$$(1\text{-}x)M_{(aq)}^{2+} + xM_{(aq)}^{3+} + 2OH_{(aq)}^- + nH_2O_{(l)} + \frac{x}{2}CO_{3\,(aq)}^{2-} \rightarrow M_{1\text{-}x}^{2+}M_x^{3+}(OH)_2(CO_3^{2-})_{x/2} \cdot nH_2O_{(s)} \tag{4.4}$$
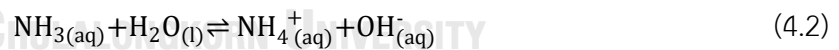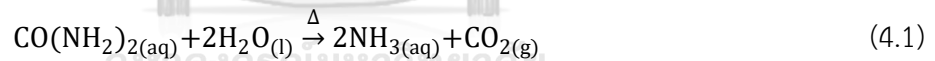
The structure of MgAl LDHs-CO_3^{2-} was similar to the natural LDHs which has high stability and low dispersiveness in polymer matrix due to the strengths of coulombic forces. Therefore, MgAl LDHs-CO_3^{2-} has poor anion exchange ability and cannot be immersible in PVC membranes while LDHs with other intercalated anions (such as NO_3^- and SO_4^{2-}) can be dispersive in the polymer matrix.[13, 20] In this work, the

intercalated anion of MgAl LDHs-CO_3^{2-} will be modified to NO_3^- in order to be used as a tailor made ionophore for NO_3^-.

The modification process composes of 2 steps, calcination and regeneration, as shown in equations 4.5 and 4.6. In the first step, MgAl LDHs-CO_3^{2-} was calcined to remove all organic compounds and water molecules resulting in the empty brucite sheet of mixed metal oxide layers called layered double oxides (LDOs) as shown in equation 4.5. Then, regeneration process of MgAl LDHs was carried out by addition of aqueous solution of NO_3^- to MgAl LDOs. NO_3^- stabilized the charge of regenerated metal hydroxide layers and acted as intercalated anions to form as MgAl LDHs-NO_3^- (equation 4.6).

$$MgAl\ LDHs\text{-}CO_{3(s)}^{2-} \rightarrow MgAl\ LDO_{(s)} + CO_{2(g)} + H_2O_{(g)} \qquad (4.5)$$

$$MgAl\ LDO_{(s)} + NO_{3\ (aq)}^- + H_2O_{(l)} \rightarrow MgAl\ LDHs\text{-}NO_{3\ (s)}^- \qquad (4.6)$$
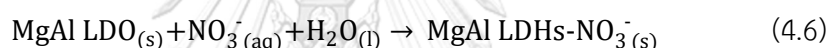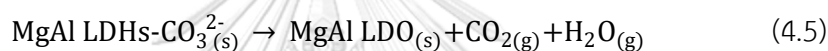
4.2.   Characterization Techniques of Layered Double Hydroxide

4.2.1. X-Ray Powder Diffractometry

The X-Ray Diffraction (XRD) patterns of all LDHs samples (described in Table 1) was shown in Figure 10 and the summary of the observe diffraction peaks was listed in Table 3.1. The protocol 2:1UH120 showed the diffraction peaks 2θ at $11.65°$, $23.55°$, $35.05°$, $39.65°$ and $47.20°$ which corresponded to the (003), (006), (012), (015) and (018) lattice planes of MgAl LDH ($Mg_6Al_3(OH)_{18}4.5H_2O$, JCPDS No. 00-035-0965) with high crystalline and high purity as shown in Figure 4.1. For 2:1UH140, an impure crystalline phase was found as the presence of an extra diffraction peak 2θ at $32.40°$. For the protocol 3:1UH120 and 3:1UH140, the impure crystalline phase (2θ at $9.5°$ and $31.5°$) were observed as extra diffraction peaks (as shown in appendix S1).

Therefore, 2:1UH120 was the best condition for LDHs preparation, which have the lattice planes close to the reference in both peak position and intensity ratio. This protocol was used to prepare MgAl LDHs-CO_3^{2-} for use in further experiments

Table 4.1 Summary of the observe diffraction peaks of all LDHs samples compare with LDHs reference.

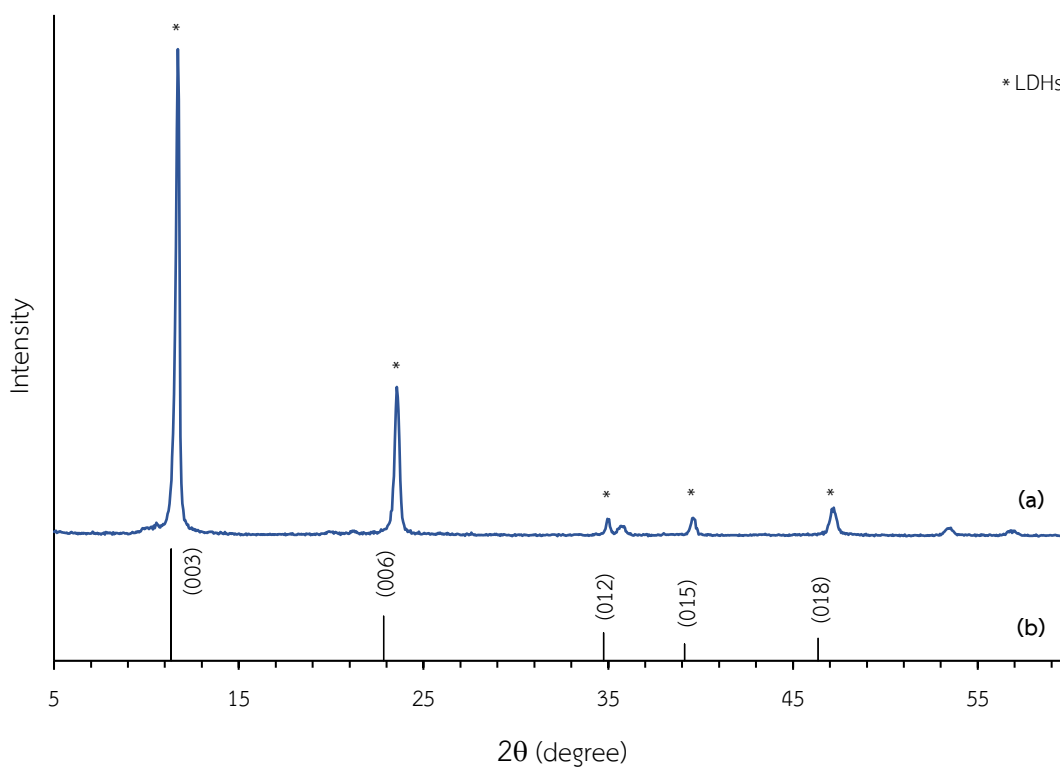| Protocol	Diffraction peaks at 2θ (°)								
2:1UH120		11.70	23.65		34.95	35.60	39.50		47.35
2:1UH140		11.70	23.50	32.40	35.50	35.95	39.70		47.00
3:1UH120	9.55	11.70	23.55	30.95	34.80	35.65	39.40	39.70	47.30
3:1UH140	9.65	11.70	23.45	30.55	35.05	35.80	39.00	39.70	46.95
Reference		11.34	22.84		34.74		39.13		46.36
$(Mg_6Al_3(OH)_{18}4.5H_2O$		(003)	(006)		(012)		(015)		(018)

Figure 4.1 XRD patterns of (a) synthesized MgAl LDHs-CO_3^{2-} using urea method (M2+/M3+ ration 2:1) and hydrothermal treatment at 120°C compare with (b) the pure phase LDHs reference (JCPDS no. 00-035-0965).

The XRD pattern of modified LDHs is shown in Figure 4.2. All diffraction peaks of LDHs lattice planes disappeared in the XRD pattern of MgAl LDOs because

the intercalated ions were removed and left only the calcined metal phases as mixed metal oxide. The diffraction peak 2θ at 43.70° could be ascribes to the mixed metal oxide phase, which implied the successful calcination (Figure 4.2a).[21]

The regenerated LDHs or MgAl LDHs-NO_3^- has the diffraction peaks 2θ at 11.55°, 23.50°, 34.95°, 39.50° and 47.30° which could correspond to the (003), (006), (012), (015) and (018) lattice planes similar the pre-modified LDHs with lower crystallinity. Other parameters of the diffraction peak, such as position and intensity ratio can signify the successful regeneration of MgAl LDHs-NO_3^- (Figure 4.2b).
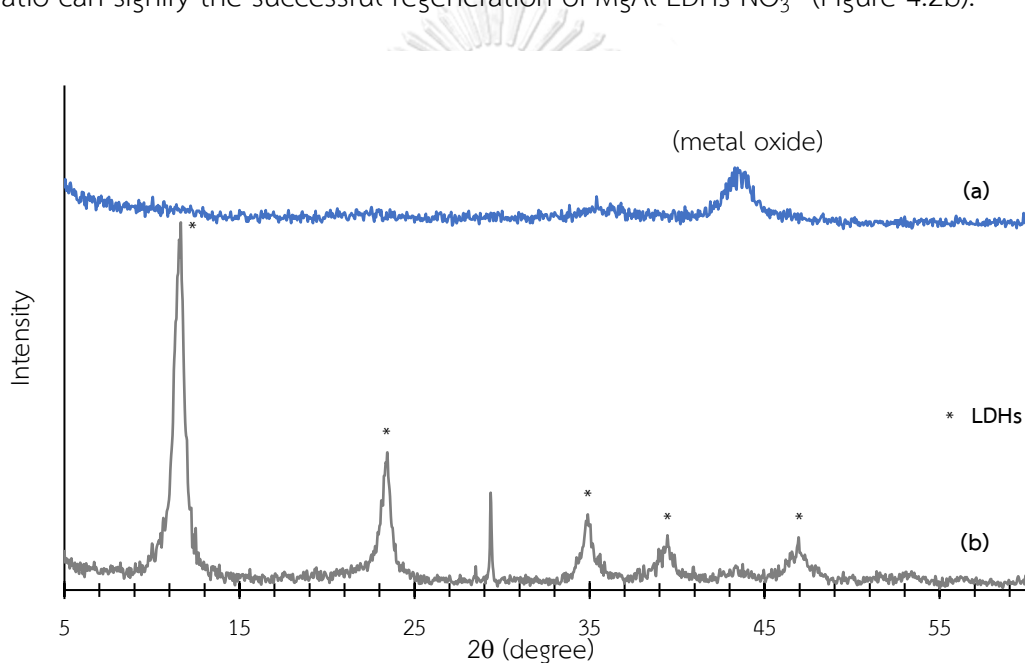
Figure 4.2 XRD patterns of (a) MgAl LDOs and (b) MgAl LDHs-NO_3^-.

4.2.2. Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared (FT-IR) spectra of samples were recorded with a Nicolet 6700 spectrophotometer via transmittance mode (KBr Disk). For the MgAl LDHs-CO_3^{2-}, the FT-IR spectra showed the absorption peaks at 1350 and 790 cm^{-1} belong to stretching and bending modes of CO_3^{2-} interlayer anion, respectively. The broad and strong band at 3450 cm^{-1} and the absorption peaks at 1650 cm^{-1} belong to the stretching and bending modes of interlayer water molecules. The absorption bands

below 800 cm^{-1} belong to the metal–oxygen (M–O) characteristic (Figure 4.3a). After calcine treatment to be MgAl LDOs, the FT-IR spectra show the increasing of absorption bands below 800 cm^{-1} which belong to the metal–oxygen (M–O).[22] The other characteristic peaks of LDHs were significantly decreased because of the carbonate removal. LDO was the desiccant and the good adsorbent which could adsorb the moisture and gas such as $CO_{2(g)}$ at room temperature.[2, 23] The broad peak at 3450 cm^{-1} and the absorption peaks at 1650 cm^{-1} probably represent the moisture in MgAl LDO. The absorption peaks at 1400 cm^{-1} probably be the $CO_{2(g)}$ that adsorbs on the surface of MgAl LDO (Figure 4.3b). For modified LDHs or MgAl LDHs-NO_3^-, the FT-IR spectra showed an obviously sharp peak at 1400 cm^{-1} belongs to the N–O stretching vibration mode of NO_3^- while the absorption peak at 1350 cm^{-1} representing CO_3^{2-} almost disappears, indicates that the large number of NO_3^- ions have been successfully introduced into the interlayer of LDHs (Figure 4.3c)
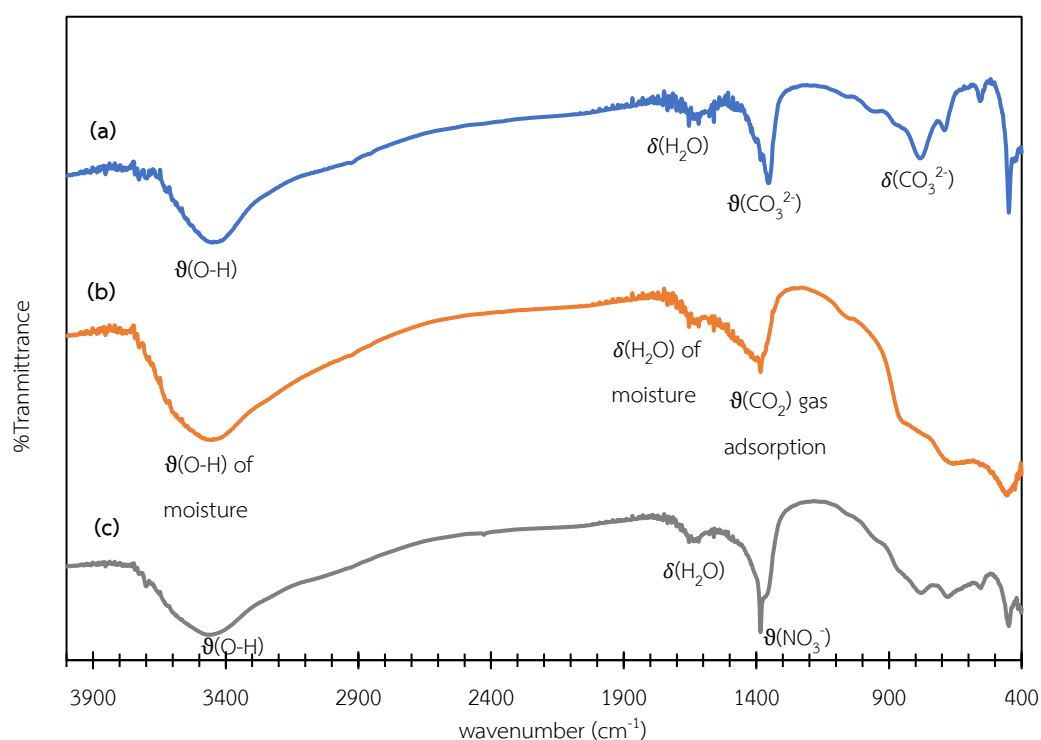

Figure 4.3 FT-IR spectra of (a) MgAl LDHs-CO_3^{2-}, (b) MgAl LDOs and (c) MgAl LDHs-NO_3^-

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4.3.   Potentiometric Studies

4.3.1. Preparation of Ion Selective Membranes

Membranes A-F were prepared using components shown in Table 3.2. Membrane A with 10%(w/w) loading was too low in percentage of LDHs causing a poor homogeneous membrane and could not be reproduced. Membrane F with 40%(w/w) was too high in percentage of LDHs causing the leak of inner solution through membrane. The characteristics of each membrane were investigated from the calibration curves by plotting between the potential responses for NO_3^- and its logarithm of concentration. As it was seen from the calibration curves (Figure 4.4) and summarized in Table 4.2, all membranes could respond to NO_3^- with slopes lower than the theoretical Nernstian slopes. Nernstian slopes increase upon increasing the percentage of LDHs loading. The 20%(w/w) and 25%(w/w) of MgAl LDHs-NO_3^- showed poor Nernstian slopes which cannot be approved. The 30%(w/w) and 35%(w/w) of MgAl LDHs-NO_3^- showed similar Nernstian slopes which are -51.31 and -51.45 (mV decade^{-1}), respectively in concentration range 10^{-4}–10^{-2} M. Therefore, 30%(w/w) LDHs loading was used for further studies.
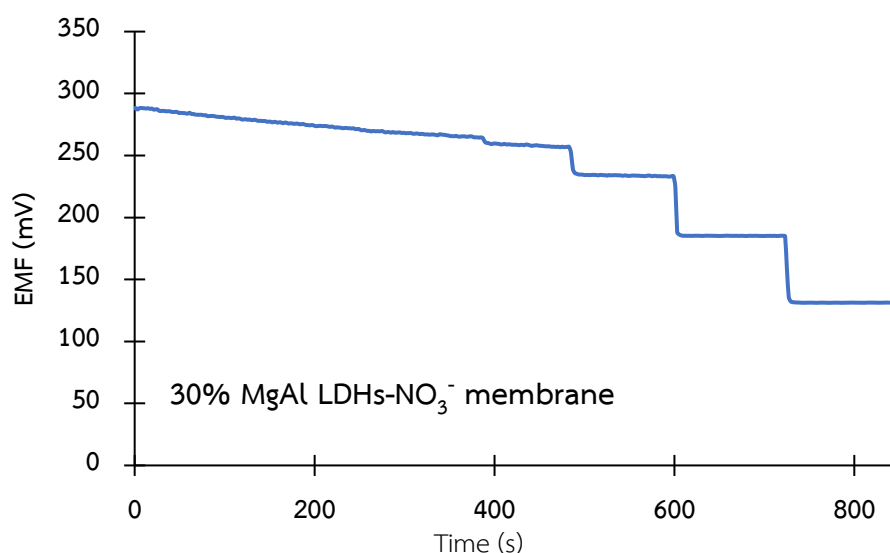

Figure 4.4 Time trace line of potentiometric response with NO_3^- of 30%(w/w) MgAl LDHs-NO_3^- membrane.

Table 4.2 Summary of potentiometric responses of different percentage LDHs membrane

Membrane	Percentage loading (w/w)	Nernstian slope (mV decade^{-1}) in linear range $1.0 \times 10^{-4} - 1.0 \times 10^{-2}$ M
A	10.00	(Poor homogeneous membrane)
B	20.00	-21.13
C	25.00	-35.16
D	30.00	-51.31
E	35.00	-51.45
F	40.00	(Inner solution was leaked through membrane)

4.3.2. EMF Responses of 30%(w/w) MgAl LDHs-NO$_3^-$ with Different Anions

The optimized LDHs membrane, 30%(w/w) MgAl LDHs-NO$_3^-$ was used for study EMF responses. Calibration curves (Figure 4.5) are summarized in Table 4.3. The NO$_3^-$ which is the intercalated anion of LDHs membrane gave the best ISE characteristics with Nernstian slope of -51.31 mV decade^{-1} in linear range of 10^{-4}–10^{-2} M. The Cl$^-$ may exchange in LDHs membrane due to the charge and size of Cl$^-$ was similar to NO$_3^-$. Therefore, Cl$^-$ shows a good Nernstian slope but not be the best. The SCN$^-$ and ClO$_4^-$ are high lipophilicity anions which easily pass through the polymer matrix (PVC-based membrane) coupled with anion exchange in the layered of LDHs membrane. Therefore, both anions show good Nernstian slope and become effective interfering anions. The molecular structure of ClO$_4^-$ was bigger than SCN$^-$ probably leading to the lower anion exchangeability. The SO$_4^{2-}$ has high charge and large molecular structure. Therefore, the exchangeability of SO$_4^{2-}$ in LDHs membrane was low implying by the poor Nernstian slope.

Table 4.3 Summary of potentiometric responses of 30%(w/w) MgAl LDHs-NO_3^-.

Anion	Nernstian slope (mV decade^{-1}) in linear range 1.0 x 10^{-4}– 1.0 x 10^{-2} M
NO_3^-	-51.31
SCN^-	-49.05
Cl^-	-47.16
ClO_4^-	-41.56
SO_4^{2-}	-13.32

4.3.3 Attempts in Selectivity Studies

We try to study the potentiometric selectivity of our fabricated ISE with 7 anions: NO_3^-, ClO_4^-, SCN^-, SO_4^{2-}, F^-, Cl^- and I^-. The logarithmic function of anion selectivity coefficients ($\log K_{i,j}^{pot}$) can be determined from equation 2.2. The example of calculation of selectivity coefficients is shown in Figure 4.6.

log conc. (mol/L)	Average EMF (mV)		$(E_j - E_i)$
	(i), NO_3^-	(j), ClO_4^-	
-7	168.00	165.09	-2.91
-6	162.17	160.27	-1.90
-5	156.23	155.10	-1.13
-4	142.73	144.49	1.76
-3	107.61	113.92	6.31
-2	59.18	67.22	8.04

$(E_j - E_i)$	$nF(E_j - E_i)$	$(2.30RT)$	$nF(E_j - E_i)/2.30RT$
8.04	-776000	5747	-0.135

$(log\ a_i)$	$(log\ a_j)$	(n/m)	$(log\ a_i) - (n/m)(log\ a_j)$
-2.015	-2.014	1.000	-1.392 x 10^{-3}

$log\ K_{i,j}^{POT}$
-0.136

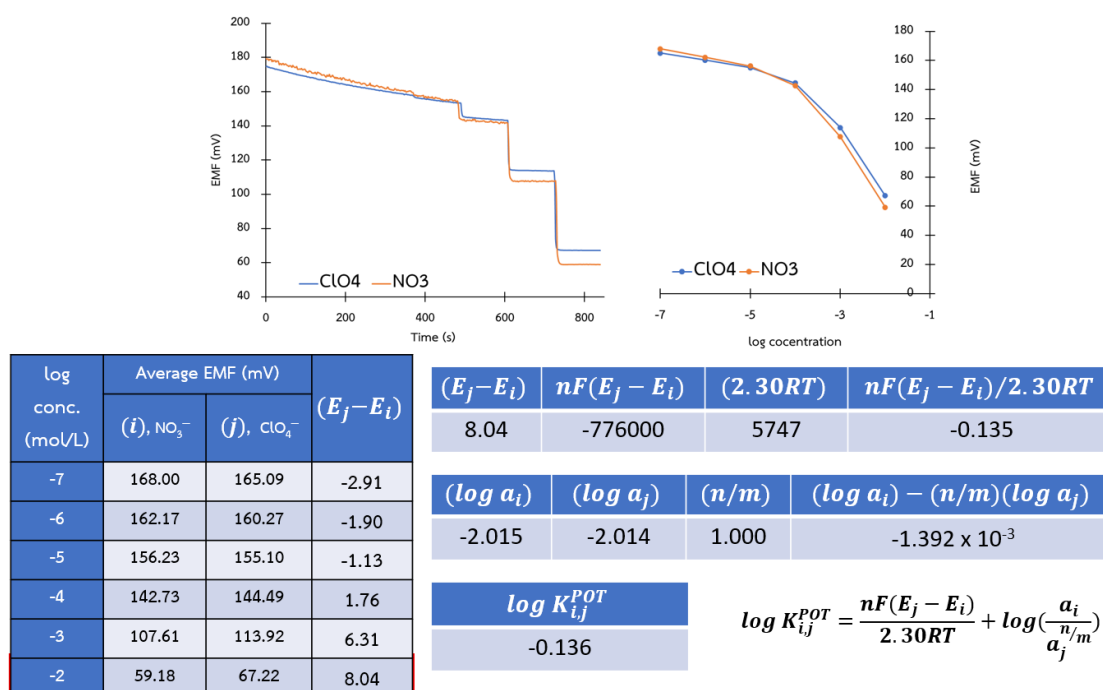$$log\ K_{i,j}^{POT} = \frac{nF(E_j - E_i)}{2.30RT} + log(\frac{a_i}{a_j^{n/m}})$$

Figure 4.5 An example of selectivity coefficient determination between NO_3^- (primary ion) substituted ClO_4^- (interfering ion).

Selectivity coefficients of 30%(w/w) MgAl LDHs-NO_3^- membranes are shown in Table 4.4. The selectivity coefficients ($\log K_{i,j}^{pot}$) of each anion shown in the Table are not significantly different. In the case of NO_3^- as primary ion, the selectivity coefficient of SCN^- as interfering ion was higher than that of NO_3^-. In the case of SCN^- as primary ion, the selectivity coefficients of all interfering ions were lower than SCN^-. These results suggested that for our fabricated ISEs were selective to SCN^- rather than NO_3^-. SCN^- is an anion with high lipophilicity and has a linear shape which probably more suitable to exchange NO_3^- in MgAl LDHs-NO_3^-. [11, 24]

Table 4.4 Selectivity coefficients of 30%(w/w) MgAl LDHs-NO_3^- membranes.

Interfering ion (j)	$\log K_{NO_3^-,j}^{pot}$	$\log K_{ClO_4^-,j}^{pot}$	$\log K_{SCN^-,j}^{pot}$	$\log K_{SO_4^{2-},j}^{pot}$
NO_3^-	0	0.059	-0.124	1.685
ClO_4^-	-0.136	0	-0.145	1.424
SCN^-	0.064	0.124	0	1.837
SO_4^{2-}	-0.505	-0.678	-0.599	0
F^-	-0.141	-0.201	-0.079	1.267
Cl^-	-0.015	0.039	-0.076	1.450
I^-	-0.057	0.015	-0.104	1.400

CHAPTER V

CONCLUSION

MgAl LDHs-CO_3^{2-} were prepared via urea method with hydrothermal treatment. The intercalated anion was then modified to be NO_3^- via calcination and regeneration process for use as tailor-made ionophore for NO_3^- anion. The XRD pattern and FT-IR spectra of all samples can confirm the success of preparation and modification of LDHs.

The potentiometric response of polymeric membrane electrodes prepared from with 30%(w/w) MgAl LDHs-NO_3^- showed the best ISE characters with response slopes of -51.31 mV decade^{-1} in the concentration range 1.0×10^{-4} to 1.0×10^{-2} M toward NO_3^-. For the attempt in the selectivity studies of our fabricated ISEs, the results showed that our fabricated ISEs were selective to SCN^- rather than NO_3^-. However, the selectivity coefficients of SCN^- and NO_3^- were not significantly different.

In this thesis, we have demonstrated to use modified MgAl LDHs-NO_3^- as a tailor-made ionophores for NO_3^- anion. However, the selectivity of fabricated ISE is not fulfilled yet. Therefore, the ISE characteristic may be improved in the future work by (i) changing the ISE platform from PVC membranes to other matrixes that allow better homogeneity of the material or using other type of ISEs such as solid contract ISEs and (ii) other components in the electrode such as ionic additive can also be added to improve the ISE characteristics.
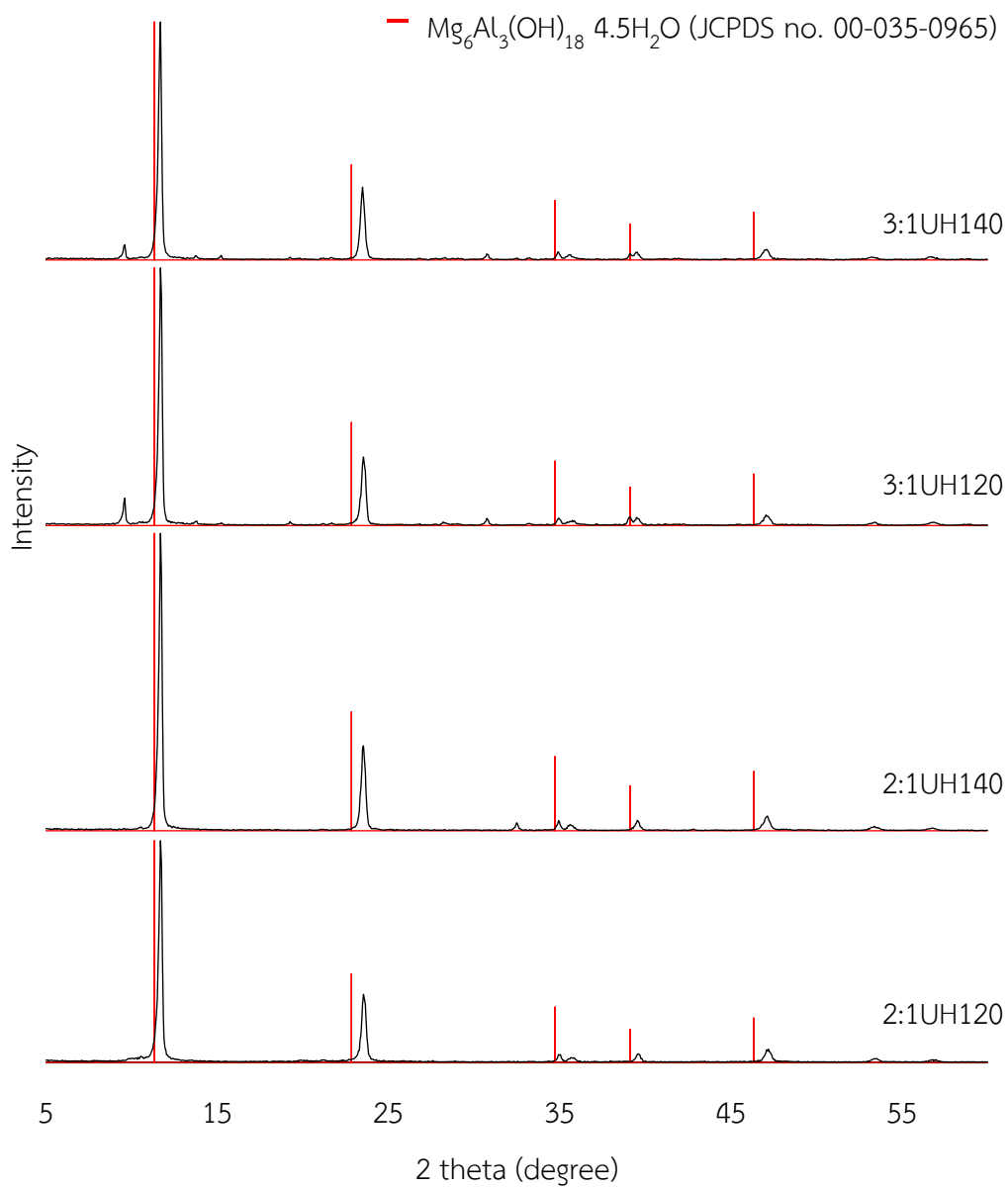
REFERENCES

Appendix

Figure S1 XRD patterns of all synthesized MgAl LDHs CO_3^{2-} using urea method (M^{2+}/M^{3+} ration 2:1 and 3:1) and hydrothermal treatment (120°C and 140°C) compare with the pure phase LDHs reference (JCPDS no. 00-035-0965)
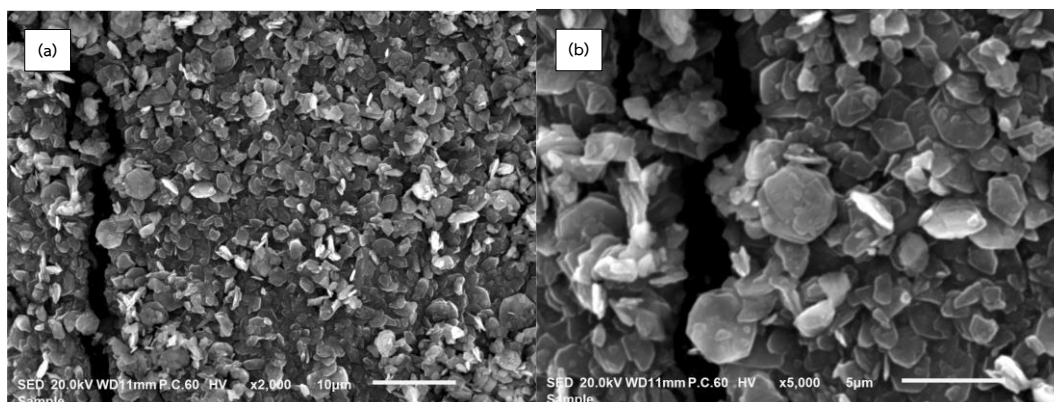
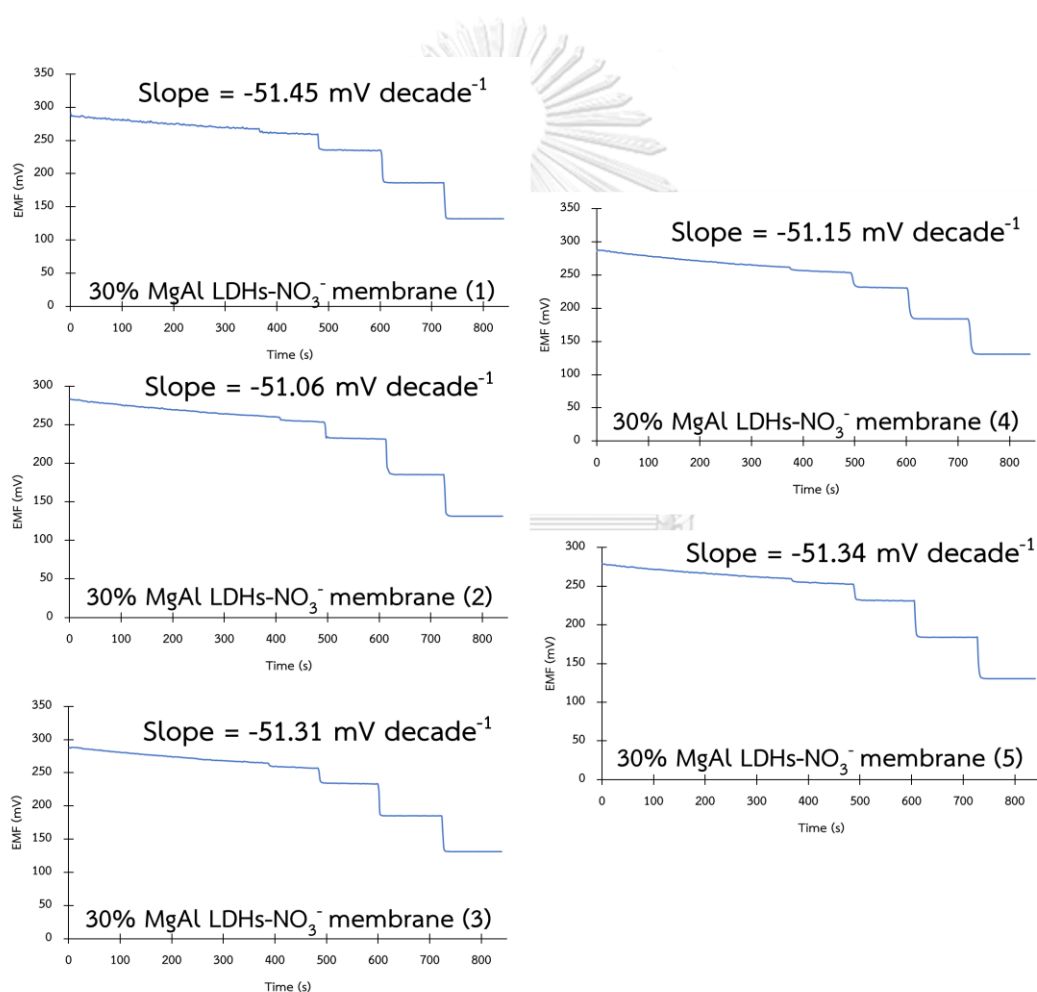**Figure S2** Morphology of MgAl LDHs-CO_3^{2-} with (a) 2k and (b) 5k magnification

Figure S3 Reproducibility of 30%(w/w) MgAl LDHs-NO_3^- membrane with linear

concentration range 1.0×10^{-4} to 1.0×10^{-2} M toward NO_3^-.
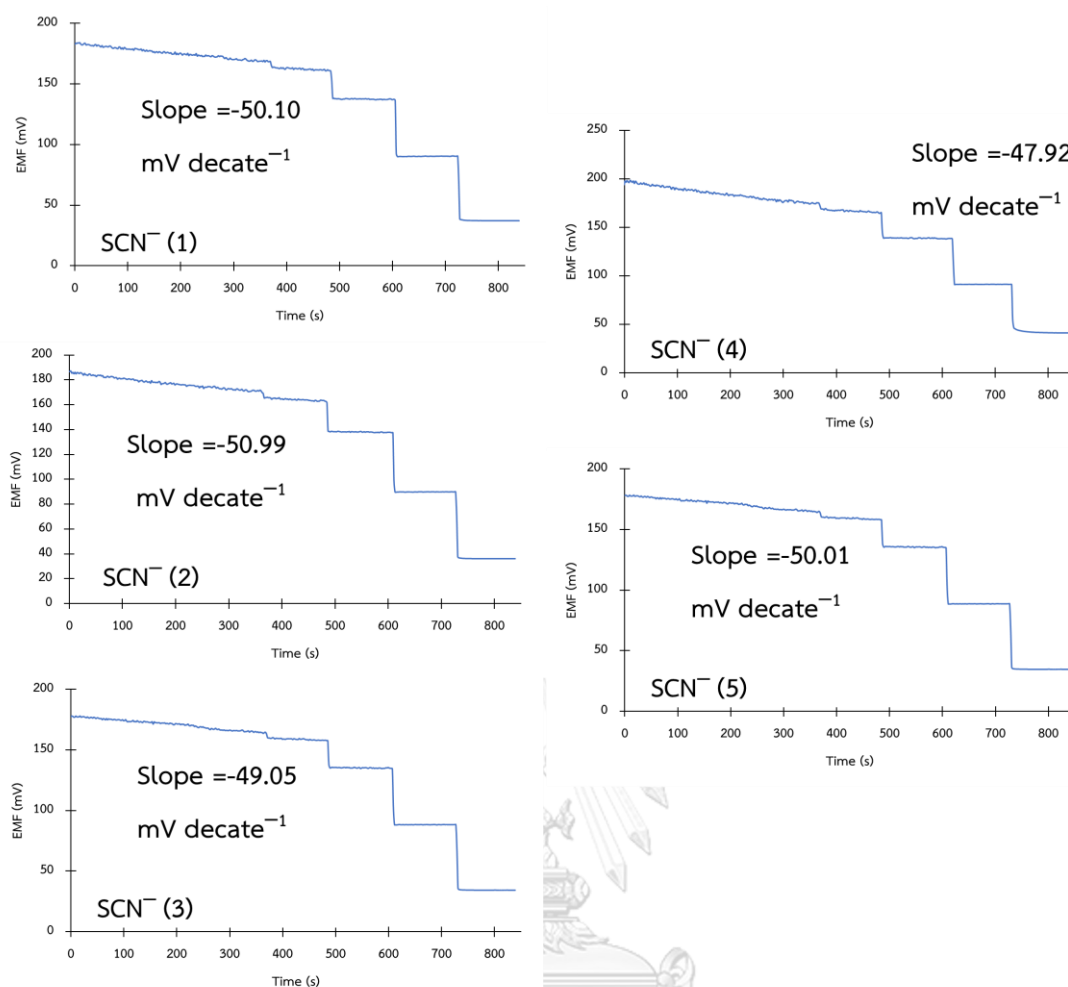
Figure S4 Reproducibility of 30%(w/w) MgAl LDHs-NO_3^- membrane with linear concentration range 1.0×10^{-4} to 1.0×10^{-2} M toward SCN^-.

Table S1 Summary of potentiometric responses of different percentage LDHs membrane

Membrane types	Percentage loading (w/w)	Nernstian slope (mV decade^{-1}) in linear range	
		1.0×10^{-4}–1.0×10^{-2} M	1.0×10^{-5}–1.0×10^{-2} M
B	20.00	-21.13	-15.68
C	25.00	-35.16	-26.18
D	30.00	-51.31	-43.26
E	35.00	-51.45	-43.33

Table S2 Summary of potentiometric responses of 30%(w/w) MgAl LDHs-NO_3^-.

Anion	Nernstian slope (mV decade^{-1}) in linear range	
	$1.0 \times 10^{-4} - 1.0 \times 10^{-2}$ M	$1.0 \times 10^{-5} - 1.0 \times 10^{-2}$ M
NO_3^-	-51.31	-43.26
SCN^-	-49.05	-39.58
Cl^-	-47.16	-37.76
ClO_4^-	-41.56	-32.22
SO_4^{2-}	-13.32	-11.98
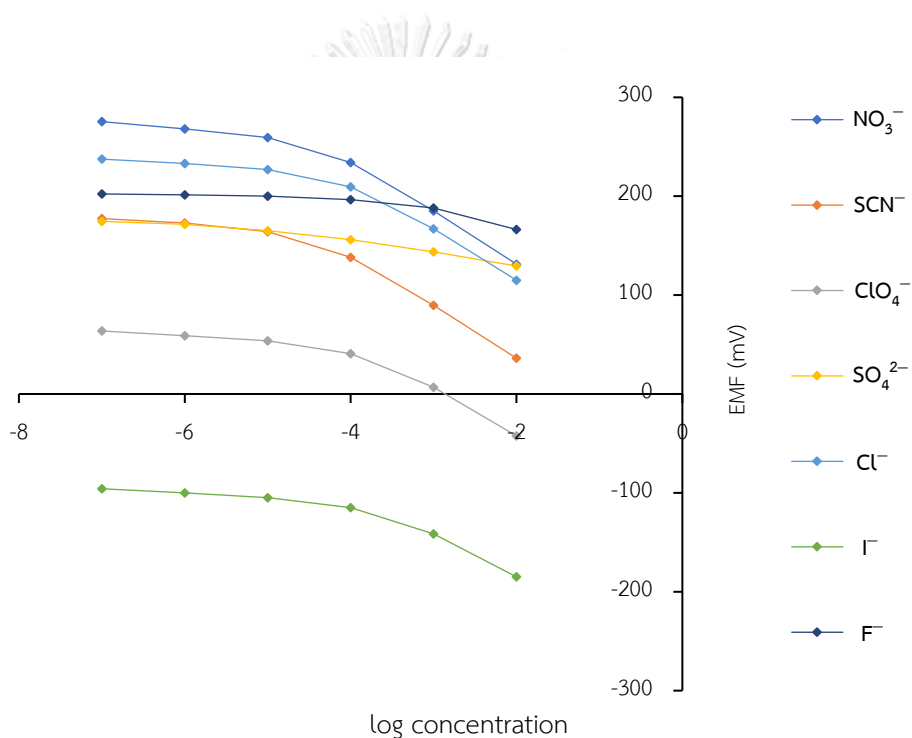
Figure S4 Calibration curves of anion responses for 30%(w/w) MgAl LDHs-NO_3^-.

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