In-line System to Produce High-Purity Acid Solutions

Hiroto MASUNAGA,*† Yuji HIGO,* Mizuo ISHII,* Noboru MARUYAMA,* and Shigeo YAMAZAKI**

*Nichiri Mfg. Co., Ltd., 324-5 Takatsu, Yachiyo, Chiba 276-0036, Japan
**Department of Applied Science, Okayama University of Science, 1-1 Ridaicho, Okayama 700-0005, Japan

Herein, we report a new device that generates a high-purity acid solution. It comprises three compartments divided by anion-exchange membranes and filled with ion-exchange resins. Fluorochemical cation-exchange membranes, which tolerate electrochemical wear and permit bulk flow, are inserted between each electrode and the anion-exchange resin. A bipolar boundary is a composite boundary comprising anion and cation exchangers. This device has four bipolar boundaries to separate the location of acid generation from the location where water is electrolyzed. It can tolerate high pressures, resist degradation due to electrolysis at the electrodes, and produce high-purity acid solutions that are free from gases and cationic impurities. The acid solution is generated on the basis of an electrokinetic phenomenon at the surfaces of ion-exchange resins and membranes in an electric field; its concentration can be controlled at rates from 0.01 to 100 μmol/min by adjusting the electrical current applied to the device.

Keywords Ion chromatography, cation analysis, acid solution generation, electrokinetic phenomenon, separation of acid solution generation place from water electrolysis place, fluorochemical cation exchanger

(Received December 2, 2015; Accepted February 24, 2016; Published June 10, 2016)

Introduction

Acid solutions have been widely used in analytical techniques employed by scientists and engineers. They have been used as carriers, eluents, and diluents for techniques, such as HPLC, LC. In all applications, the acid solutions have been prepared and replenished by the user. This paper specifically addresses the production of methanesulfonic acid (MSA) and HCl solutions. Conventional acid solution preparation methods involve dilution of concentrated acid; the resulting solutions contain varying amounts of dissolved cations, such as Na+, NH4+, and K+. Acid purification involves removing these cations, which is extremely difficult, time consuming, and often tedious. Therefore, automated methods for acid preparation are desirable. Dasgupta et al.1,2,3 pioneered the application of electrolytic methods to the generation of eluents for ion chromatography (IC) and demonstrated electrical control of concentration. Small et al.4,5 introduced a new method called ion reflux, wherein eluent generation and suppression were integrated into an automated form of IC that has the potential to continuously operate. Dionex introduced the EG40 eluent generator,6,7 which uses one of two cartridges to produce either a KOH solution (for anion analysis) with a cation exchanger or MSA (for cation analysis) with an anion exchanger. The eluent’s concentration is controlled by the amount of current applied to the ion exchange unit. The device cartridges have a dead volume of less than 300 μL. Since this device generates MSA solutions by the reaction of methanesulfonate ions (MS–, arriving at the anode) with H+ (generated by electrolysis of water on the anode), the generated MSA solution is pumped into the degas module inlet to remove the byproduct of electrolysis—O2 gas—at the anode. Therefore, the dead volume between the device and the separation column is increased.8,9 The strong anion exchanger is known to undergo Hofmann elimination by attack of the hydroxyl group on the quaternary amine, and to be electrolyzed by oxidation and reduction at the electrodes.10

This study aims to develop a new device that can tolerate high pressures, resist degradation due to electrolysis at the electrodes, and produce a continuous stream of high-purity acid solution in line, which does not contain gases (H2 or O2), produced by electrolysis of water at the electrodes and impurity cations. The device is schematically displayed in Fig. 1. It comprises three compartments that are isolated from each other by two anion-exchange (AE) membranes, and electrodes are placed at the far ends of the outside compartments. The three compartments are filled with ion-exchange resins, and the fluorochemical cation exchange membrane (FCEM), which permits bulk flow, is installed between each electrode and its adjacent AE resin. A center compartment contains both AE and cation exchange (CE) layers packed with AE and CE resins, respectively. A bipolar boundary is a composite boundary comprising an AE resin and a CE membrane, an AE resin and a CE resin, or an AE membrane and a CE resin. We anticipate that the bipolar boundary will show properties that are analogous to a bipolar membrane. The current-voltage (I-V) properties of the bipolar boundary show the following rectification properties: A) a rapid increase of the electric current with the applied voltage under forward bias (V > 0 in Fig. 2, where V is the applied voltage) results in ions (anions and cations) becoming concentrated at the bipolar boundary (hereinafter referred to as the ion concentration junction, ICJ) and B) a region of high...
resistance when the membrane is reverse biased \((V < 0, \text{low reverse-bias voltages})\) can be seen in Fig. 2. Under high reverse bias voltages, however, C) a rapid increase in current with the applied voltage \((V < 0\) in Fig. 2, high reverse bias voltages) due to an anomalously high water dissociation rate is observed (hereinafter referred to as the water-dissociation junction, WDJ). It is widely accepted that the large electric field occurring at the WDJ under reverse bias enhances the water dissociation rate via protonation-deprotonation reactions involving the ion-exchanger and the water molecules in the WDJ,12–18. This device has four bipolar boundaries (ICJs 1 and 2 and WDJs 1 and 2). Consequently, the MSA (or HCl) solution is generated at a separate position from where the water is electrolyzed. These specifications enable the four-bipolar-boundary device to tolerate high pressures, resist degradation from electrolysis on the electrodes, and produce a high-purity MSA (or HCl) solution that is free from gases and cationic impurities. This paper introduces the four-bipolar-boundary device developed for in-line MSA (HCl) generation and examines the mechanism of its operation. An MSA (or HCl) solution is generated by an applied current \((0 \sim 200 \text{ mA})\) and the resulting concentration varies at rates from 0.01 to 100 μmol/min.

**Experimental**

**Architecture of the four-bipolar-boundary device and comparison device**

The four-bipolar-boundary device architecture is schematically displayed in Fig. 1. The device comprises three compartments isolated from each other by two AE membranes \((φ12 \text{ mm, AHA, Astom, Tokyo})\). An electrode is placed at the far ends of the two outside compartments. The cathode compartment (CC, 15 mm in length) is packed with AE resin (Amberlite IRA-402BL, 0.6 – 0.8 mm, ≥ 1.25 meq/mL, Organo, Tokyo, Japan) and FCEM 1 (CMF, physically modified to increase water permeability, φ12 mm, Asahi Glass, Tokyo) is inserted between the cathode and the AE resin. WDJ 2 consists of FCEM 1 and AE resin. The preparation compartment (PC, 15 mm in length) consists of both CE (Dowex 5WX8, 200 – 400 mesh, 1.7 meq/mL) and AE resins (Dowex 1X8, 200 – 400 mesh, 1.2 meq/mL). ICJ 1 consists of both AE and CE resins. The anode compartment (AC, 15 mm in length) is filled with AE resin (Amberlite IRA-402BLB) and FCEM 2 (CMF) is installed between the cathode and AE resin. WDJ 1 consists of CE resin and an AE membrane. ICJ 2 consists of AE resin and FCEM 2. There is bulk flow through FCEMs 1 and 2. Inlets 1, 2 and 3 are connected to Pump 1 (peristaltic pump, with a 1 mL/min flow rate, controlled by a home-made flow control driver), Pump 2 (1.3 mL/min, DP-8020, Tosoh, Tokyo, Japan) and Pump 3 (peristaltic pump, with a 1 mL/min flow rate, controlled by a home-made flow control driver), respectively. A 100-mM MSA or a 200-mM NaCl solution is pumped into Inlet 1, pure water is pumped into Inlets 2 and 3,
and the purified MSA (or HCl) solution is eluted from Outlet 2 of the PC.

A comparison device without a bipolar boundary, the CDboundary0,6–8 was built to test the proposed mechanisms of the four-bipolar-boundary device; this is schematically displayed in Fig. 3. CDboundary0 is packed with only AE resin between the electrodes, so there is no bipolar-boundary between the electrodes. A 100-mM MSA or a 200-mM NaCl solution is pumped into Inlet 1, pure water is pumped into Inlets 2 and 3, and the purified MSA (or HCl) solution is eluted from Outlet 2 of the AC.

Electrical conductivity measurement of the MSA solution produced by the four-bipolar-boundary device and CDboundary0

The system used herein is schematically displayed in Fig. 4. Outlet 2 of the four-bipolar-boundary device and CDboundary0 was connected to an electrical conductivity detector (ECD, iCM8401, Nichiri, Japan) to measure the electrical conductivity of the effluent streams.

Ion chromatograph equipped with the four-bipolar-boundary device

An ion chromatograph (ICA-2000) was equipped with a pump (1 mL/min, ICA-2000), a four-bipolar-boundary device, an injector (20 μL, ICA-2000), a separation column for cation analysis (IonPac CS14, 40°C, Dionex, USA), a suppressor (iSC8010,18 Nichiri), and an electrochemical detector (ECD, ICA-2000). The four-bipolar-boundary device was connected between the pump and the injector. Effluent (~10 mM MSA solution, 3861 μS/cm, pH 2.04) from Outlet 2 of the four-bipolar-boundary device was used as an eluent for IC. The injected sample was separated using the column, MS– was removed from the eluent using the suppressor, and the suppressor effluent was characterized using the ECD.

Results and Discussion

Reaction mechanisms

Ion-exchange resins and membranes have mobile counter ions and are good electronic conductors.19 We consider CDboundary0, which retains only an anion exchanger between two metal electrodes in a chamber. When a DC potential is applied across the electrodes, the electrical field drives the negative counter ions toward the anode.4,5

In the case of our proposed four-bipolar-boundary device, when a DC potential is applied across the electrodes, we anticipate that the following reactions occur at the four bipolar boundaries in addition to the oxidation-reduction reaction at the electrodes. The cathodic reduction of water produces OH− and H2 gas:

\[
2H_2O + 2e^- \rightarrow 2OH^- + H_2 (g)
\]  \hspace{1cm} (1)

The anodic oxidation of water produces O2 gas and H+:

\[
2H_2O \rightarrow 4H^+ + O_2 (g) + 4e^- \hspace{1cm} (2)
\]

Water dissociation produces OH− and H+ at WDJ 1 and 2 (OH− and H+ produced by water dissociation are hereinafter referred to as DOH and DH, respectively):

\[
H_2O \rightarrow DH + DOH \hspace{1cm} (3)
\]

Water dissociation produces OH− and H+ at WDJ 1 and 2 (OH− and H+ produced by water dissociation are hereinafter referred to as DOH and DH, respectively):

\[
2H_2O \rightarrow 4H^+ + O_2 (g) + 4e^- \hspace{1cm} (2)
\]

Water dissociation produces OH− and H+ at WDJ 1 and 2 (OH− and H+ produced by water dissociation are hereinafter referred to as DOH and DH, respectively):

\[
H_2O \rightarrow DH + DOH \hspace{1cm} (3)
\]

Ion concentration produces MSA solution at ICJ 1:

\[
MS^- + H^+ \rightarrow MSA \text{ solution} \hspace{1cm} (4)
\]

Ion concentration also produces H2O at ICJ 2:

\[
H^+ + DOH \rightarrow H_2O \hspace{1cm} (5)
\]

DH and DOH are produced by water dissociation at WDJ 2. DH migrates through FCEM 1 to the cathode and reacts with the OH− generated by electrolysis of water at the cathode. The byproduct of electrolysis at the cathode—H2 gas—is eluted out with the MSA solution stream passing from Inlet 1 to Outlet 1, because the CC is separated from the PC by the AE membrane. Trace amounts of NH4+ in the MSA solution are also eluted out with the stream. DOH sequentially migrates into the AE resin in the PC, displacing other anions (OH− and MS−). Therefore, OH− and the MS− propagate a net motion toward the anode. The PC has two bipolar boundaries (ICJ 1 and WDJ 1); ICJ 1 comprises the CE and AE resins, and WDJ 1 consists of an AE membrane and CE resin. DH and DOH are also generated by water
Location of water dissociation at WDJs 1 and 2 and ion concentration at ICJs 1 and 2

Spatially separating the generation of the acid solution from gas evolution

Electrochemical durability of the four-bipolar-boundary device resulting from FCEMs 1 and 2

Effect of FCEMs 1 and 2 on the potential across the electrodes as a function of time: (○) both membranes are present and (△) both membranes are absent.
evident in the effluent for the four-bipolar-boundary device but is evident for that of \( \text{CD}_{\text{boundary}0} \). This proves that the MSA solution produced by the four-bipolar-boundary device is free from gas. We conclude that the four-bipolar-boundary device separates the location where MSA solution is generated from the location where water is electrolyzed.

**Performance of the four-bipolar-boundary device: purity of the generated MSA solution**

The pressure resistance of the four-bipolar-boundary device was determined. The measurement was performed using an ICA-2000, installing the four-bipolar-boundary device between a pump and an injector. A separation column for cation analysis (CS14) generated a pressure of approximately 9 MPa, causing less than 1% of the water pumped from Inlet 2 to Outlet 2 to leak into the CC and the AC. Moreover, the membranes in the system did not break during the pressure test. A chromatogram of the standard cations measured by the ICA-2000 is shown in Fig. 8(a). The result illustrates that the four-bipolar-device can be used at a pressure of 9 MPa. Furthermore, the concentration of cationic impurities was determined in a sample of the generated MSA solution. Ultra-pure water (without ions) was pumped into the PC of the four-bipolar-boundary device. A chromatogram of the MSA solution (~10 mM, 3861 \( \mu \text{S/cm}, \text{pH 2.04} \)) generated by the four-bipolar-boundary device is shown in Fig. 8(c). For comparison, an MSA solution was prepared by the conventional method (10 mM MSA prepared from a 1 M MSA stock solution) to examine the relationship between the applied electrical current and the generated acid solution concentration. The resulting concentration of HCl was determined. The concentration of the HCl solution can be estimated from the electrical conductivity measured by the ECD. The relationship between the HCl concentration and the applied current was linear (\( r = 0.999 \)), passing through the origin with a slope of 0.566 mM/mA. In a separate experiment, the electrical current applied was fixed at 5 mA, and the electrical conductivity of the purified HCl solution was measured to be 1186 \( \mu \text{S/cm} \), corresponding to an HCl concentration of 2.84 mM per 1 mL/min. The electrical current was increased to 10 mA, and the concentration increased to 5.81 mM per 1 mL/min. This result confirms the linear dependence of the concentration of the HCl solution on the applied electrical current. We have demonstrated the ability to control the concentration of the HCl solution using the applied electrical current. The rate of generation of HCl was 100 mM HCl per 1 mL/min when the maximum applied electrical current (200 mA) was applied to the four-bipolar-boundary device. This result illustrates that acid solution is generated at a rate of 0.01 – 100 mM per 1 mL/min by an applied electrical current (0 – 200 mA).

**Conclusions**

All the experimental results presented in this paper were consistent with the mechanisms described herein. The four-bipolar-boundary device comprised three compartments...
(AC, PC and CC) separated by two AE membranes; the PC was equipped with two bipolar boundaries that spatially separated the generation of acid solution from the electrolysis of water. Moreover, the AC and the CC were equipped with FCEMs 1 and 2 to prevent electrolysis of the AE resin on the electrodes. The four-bipolar-boundary device tolerated high pressures, resisted degradation due to electrolysis at the electrodes, and produced a high-purity acid solution that was free from gases and cationic impurities. The acid solution’s concentration was precisely controlled by varying the current applied to the electrodes.

References

1. SeQuant, “A Practical Guide to Ion Chromatography”, 2007. SeQuant AB, Sweden, ISBN 978-91-631-8056-9.
2. D. L. Strong and P. K. Dasgupta, Anal. Chem., 1991, 63, 480.
3. D. L. Strong, C. U. Joung, and P. K. Dasgupta, J. Chromatogr., 1991, 546, 159.
4. H. Small and J. Riviello, Anal. Chem., 1998, 70, 2205.
5. H. Small, Y. Liu, and N. Avdalovic, Anal. Chem., 1998, 70, 3629.
6. B. E. Erickson, Anal. Chem., 1999, 71, 465A.
7. J. S. Fritz and D. T. Gjerde, “Ion Chromatography”, 1999, Wiley-VCH, Weinheim.
8. Y. Liu, K. Srinivasan, C. Pohl, and N. Avdalovic, J. Biochem. Biophys. Methods, 2004, 60, 205.
9. Y. Liu, P. Alto, C. A. Pohl, M. J. Mcadams, L. Gatos, H. Small, Z. Lu, M. Liu, and K. Moshfeh, “High Pressure Degas Assembly for Chromatography System and Method”, US patent, 2013, 0213225 A1.
10. M. A. Hickner, A. M. Herring, and E. B. Coughlin, J. Polym. Sci. B. Polym. Chem., 2013, 51, 1727.
11. A. Tanioka and K. Shimizu, Bull. Soc. Sea Water Sci. Jpn., 1993, 47, 230.
12. P. Ramirez, H. J. Rapp, S. Mafe, and B. Bauer, J. Electroanal. Chem., 1994, 375, 101.
13. I. C. Bussignana and H. Reiss, J. Membr. Sci., 1983, 15, 27.
14. S. Mafe, J. A. Manzanares, and P. Ramirez, Phys. Rev., 1990, 42, 6245.
15. P. Ramirez, H. J. Rapp, S. Reichle, H. Strathmann, and S. Mafe, J. Appl. Phys., 1992, 72, 259.
16. R. Simons, Electrochim. Acta, 1984, 29, 151.
17. R. Simons, Nature, 1979, 280, 824.
18. H. Masunaga, Y. Higo, M. Ishii, N. Maruyama, and S. Yamazaki, Anal. Sci., 2014, 30, 477.
19. M. C. Sauer, P. F. Southwick, K. S. Spiegler, and M. R. J. Wyllie, Ind. Eng. Chem., 1955, 47, 2187.
20. The Chemical Society of Japan, “The Chemical Handbook Basic Edition”, 1993, II-446.