# การพัฒนาชุดการทดลองเซลล์กัลวานิกแบบย่อส่วนและต้นทุนต่ำ เพื่อใช้เป็นอุปกรณ์ในการสอนเคมีไฟฟ้า

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### บทคัดย่อ

้งานวิจัยนี้ได้พัฒนาเซลล์กัลวานิกแบบย่อส่วนและต้นทุนต่ำ มีวิธีการสร้างที่ง่าย เพื่อใช้เป็นอุปกรณ์สำหรับการสอนเคมี ้ไฟฟ้าในระดับมัธยมศึกษาตอนปลาย การออกแบบครั้งนี้ใช้แนวคิดเคมีรักษ์สิ่งแวดล้อมคือ ลดปริมาณการใช้สารเคมี ทำให้ของเสีย ้จากสารเคมีมีปริมาณน้อยลง และใช้เวลาในการทดลองน้อยลง แต่ยังคงรักษาภาวะที่สมบรูณ์ของการทดลองไว้ได้อย่างต้นแบบ ในงานวิจัยนี้พัฒนาเซลล์กัลวานิกที่ประกอบด้วยขั้วไฟฟ้า Cu Zn Al Mg และ Fe สะพานเกลือทำมาจากเส้นด้ายชนิดฝ้ายราคา ถูก (ยาว 18 เซนติเมตร) ชุบด้วยสารละลายอิเล็กโทรไลต์ อุปกรณ์ที่พัฒนาขึ้น มีความสอดคล้องกับการทดลองแบบเดิม แต่ใช้ ้ปริมาตรสารละลายอิเล็กโทรไลต์น้อยลง (2.00 มิลลิลิตร) จากการศึกษาพบภาวะที่เหมาะสมดังต่อไปนี้ ความเข้มข้นของสาร ้ละลายอิเล็กโทรไลต์ที่เหมาะสมของแต่ละเซลล์ (0.01 โมลต่อลิตร) สารละลายที่ใช้ชุบสะพานเกลือ (โพแทสเซียมไนเทรต ความ เข้มข้น 0.01 โมลต่อลิตร) และศึกษาอายุการใช้งานของสารละลายอิเล็กโทรไลต์ในภาวะที่เหมาะสม (720 ชั่วโมง) ผลการทดลอง ้ที่ได้จากการสร้างเซลล์กัลวานิกเปรียบเทียบกับวิธีแบบเก่า เมื่อใช้ *t*-test ทดสอบศักย์ไฟฟ้าของวิธีทั้งสองไม่มีความแตกต่างกัน ้อย่างมีนัยสำคัญ (t<sub>stat</sub> = 2.414, t<sub>critical</sub> = 2.447) ที่ระดับความเชื่อมั่นร้อยละ 95 การวิเคราะห์คะแนนก่อนเรียนและหลังเรียนของ ้นักเรียน (ก่อนและหลังการใช้เซลล์ที่พัฒนาขึ้น ตามลำดับ) พบว่า มีผลสัมฤทธิ์ทางการเรียนเฉลี่ยก่อนเรียนและหลังเรียนมีค่าเท่ากับ 4.69 และ 8.15 ตามลำดับ โดยมีร้อยละความแตกต่างสำหรับคะแนนก่อนเรียนและหลังเรียนเท่ากับร้อยละ 34.89 ค่าสัมประสิทธิ์ การกระจายตัวมีค่าเท่ากับร้อยละ 24.09 และ 15.82 สำหรับคะแนนก่อนเรียนและหลังเรียนตามลำดับ เมื่อใช้ *t*-test แบบกลุ่ม ้ ตัวอย่างไม่อิสระต่อกันทดสอบคะแนนของการสอบทั้งสองครั้ง พบว่า มีความแตกต่างกันอย่างมีนัยสำคัญ (t<sub>observed</sub> = 9.55, t<sub>critical</sub> = 2.07) ที่ระดับความเชื่อมั่นร้อยละ 95 นอกจากนี้นักเรียนยังมีความเข้าใจที่เพิ่มมากขึ้นต่อการทดลองเซลล์กัลวานิกแบบย่อส่วน ้และต้นทุนต่ำ วิธีการนำเสนอนี้คาดว่าจะเป็นเครื่องมือในการสอนที่มีประสิทธิภาพและมีประโยชน์ในการศึกษาระดับมัธยมศึกษา ตอนปลาย

**คำสำคัญ:** การทดลองแบบย่อส่วน เซลล์กัลวานิก สะพานเกลือ โรงเรียนมัธยมศึกษาตอนปลาย

## The Development of Small Scale and Low-Cost Galvanic Cells as a Teaching Tool for Electrochemistry

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#### Abstract

A simple method for construction of small-scale and low-cost galvanic cells was developed as a teaching tool for electrochemistry of high school students. The method was designed based on the concept of "Green chemistry" reducing use of chemicals, less waste generation, and time consumption while retaining the experimental concepts. The galvanic cells contain various electrodes, including Cu, Zn, Al, Mg and Fe, and a low cost salt bridge which was made from a cotton thread (with the length of 18 cm) soaked with electrolyte solutions. Our experimental setup corresponded to the conventional platform; but with lesser use of electrolyte solution (2.00 mL). The cells were studied for the optimum conditions including concentration of electrolyte of each cell (0.01 M), the solutions employed as salt bridge (0.01M KNO<sub>3</sub>) as well as the study of reagent lifetime of electrolyte (720 h). The results obtained from the constructed galvanic cells were compared to those from the galvanic cells developed through conventional method. According to the t-test, the cell potential values obtained from both methods were comparable ( $t_{stat}$  = 2.414, t<sub>crictical</sub> = 2.447) at p= 0.05. The analysis of pre-test and post-test scores of the students (before and after using the developed cells, respectively) was also performed revealing the mean values of 4.69 and 8.15, respectively, with the difference of mean percentage for the pre-test and post-test scores being 34.89%. CV (coefficient variation) was 24.09% and 15.82% for the pre-test and post-test, respectively. According to the paired-samples t-test analysis, the scores of the two examinations were significantly different ( $t_{observed}$  = 9.55,  $t_{critical}$  = 2.07) at p=0.05. The improved posttest scores obtained from the students indicate their increased understanding towards the small scale and low cost galvanic cells. The approaches presented herein are expected to be cost-effective and useful teaching tool incorporated into high school education.

Keywords: Small scale, Galvanic cell, Salt bridge, High school

#### Introduction

In several parts of the world, higher education institutions are still depending on use of macro scale experiments (traditional approach) for an educational illustration in chemistry. Thus, lack of instrumentations, apparatuses, chemicals or laboratories in many schools suppresses learning process to students. There are two important aspects in "Green Chemistry" (modern approach) which can be applied for the improvement of the learning process. One is based on the idea of miniaturization in way that experiments in chemistry (oxidation and reduction, electrochemistry, galvanic cell, electron transfer, acid and base etc.) can be

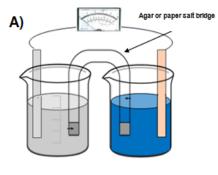
scaled down which are carried out in simpler and smaller platforms (*e.g.* using injection bottles, dropper bottles, syringes, well plates, plastic pipettes) as well as being more economic than the traditional macro scale approach (*e.g.* employing glassware in the laboratory). The other aspect is to perform effective chemical experiments which consume less chemical and reduces generation of waste with high product yields. Thus, the small-scale and effective experiments have a potential to enable teaching materials for students in huge classes, as well as for many institutions in developing countries lacking technical services (*i.e.* electricity, running water) and standardtype equipments.

Electrochemistry has been regarded as one of the most difficult topics by both students and teachers (Finley et al., 1982). High school students find it difficult to understanding the fundamental concepts of electrochemical cells and electrolytes which involve the processes of oxidation-reduction, electron transfer and ion conduction (Ebenezer, 2001; Lin et al., 2002; Ringnes, 1995). A key challenge is to provide better insight into the flow directions of ions in electrolyte and electrons in electrodes (Sanger and Greenbowe, 1997). Chemists normally apply particle models to provide an explanation for such problems. However, the chemist's conceptual models have been found to be complex for many students (Ahtee et al., 2002; Garnett et al., 1990; Garnett and Treagust, 1992; Özkaya, 2002). As a result, the students are not enthusiastic in learning electrochemical phenomena. This also results in difficulty for many teachers teaching electrochemistry.

Electrochemical processes involve oxidationreduction (redox) reactions transferring electrons from one species to the others. Galvanic cells (traditionally presented in the form called Daniell cells) are widely used for illustration of the electrochemical processes applied in either qualitative or quantitative analysis. In most applications, a galvanic cell contains two electrodes partly immersed into two separated electrolyte solutions. The two electrode ends, which are not in contacted with the electrolytes, are connected via conductive wires. Providing that there is potential difference between the two electrodes, redox reactions occur at the electrode/electrolyte interfaces facilitating flows of electrons (or electric current in the wires) and ions (in electrolytes) (Varkey et al., 2014). The two separated half-cells (each of which contains the electrode and electrolyte) are connected via a salt bridge resulting in a closed electrical circuit within the cell. The salt bridge functions as an electrical contact between the two electrolyte solutions maintaining the ion flow as well as preventing a mixing of the solutions (Umland and Bellama, 1999; Whitney, 1903). Conventionally, a galvanic cell is constructed by using considerably large volume of electrolyte with the use of either agar or paper as a supporting material in the salt bridge (Figure 1A).

The concepts of microscale chemistry and "Green Chemistry" have been further described in many articles (Anderson, 1996; Bradley 2002; Craig et al., 1989; Epp 1995; Grønneberg et al., 2007; Grønneberg et al., 2006; Kamata and Yajima 2013; Kelkar and Dhavale 2000; Kvittingen and Verley 2004; Liberko 2007; Singh et al., 1999; Waterman and Thompson, 1995). Mini galvanic cells were developed as a teaching platform illustrating semi quantitative analysis in electrochemistry (Craig et al., 1989). The cell consists of two droppers clogged by cotton plugs which were dipped into a 2dram vial (17 mm  $\times$  60 mm) containing ammonium nitrate (functioning as a salt bridge in aqueous state). Each dropper contains electrolyte solution and a small metal electrode. Although the cell performance was good, such a platform is slightly different from the conventional platform employing a solid supporter as a salt bridge (e.g. as illustrated in Figure 1A) which is usually shown in many text books. The unsteady voltage of the previously reported cell caused by inconsistency in

cotton plug packing was also noted (Craig et al., 1989) as well as short cell lifetime which may be another disadvantage. This study aimed to develop small-scale and low-cost galvanic cells as teaching materials in electrochemistry for high school students. To the best of our knowledge, a small platform of galvanic cells with approximately 10-fold reduction of electrolyte volume using cotton thread as a material in the salt bridge has not been previously reported. The aim of this work is to develop such a platform (Figure 1B) aimed to be used in high school laboratories.



20.00 mL, 1 M MgSO4

20.00 mL. 1 M CuSO

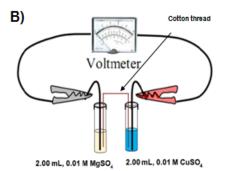


Figure 1 Comparison between (A) conventional and (B) developed platforms of galvanic cells.

#### Experimental

Preparation of electrolytes and electrodes

All electrolytes were prepared with laboratory grade reagents and distilled water. A 0.01 M solution of each electrolyte was separately prepared by dissolving 0.2496 g of  $CuSO_4$ ·5H<sub>2</sub>O (CARLO ERBA), 0.2874 g of  $ZnSO_4$ ·7H<sub>2</sub>O (CARLO ERBA), 0.24647 g of

MgSO<sub>4</sub>·7H<sub>2</sub>O (Ajax Finechem), 0.27801 g of FeSO<sub>4</sub>·7H<sub>2</sub>O (CARLO ERBA), 0.6659 g of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·18H<sub>2</sub>O (Ajax Finechem), 0.1019 g of KNO<sub>3</sub> (Ajax Finechem), 0.0846 g of NaNO<sub>3</sub> (Ajax Finechem) or 0.0584 g of NaCl in 100 mL of deionized water. All 0.01 M electrolyte solutions (2.00 mL) were transferred into separated vials. Electrodes (strips of different metals) were cleaned by sanding and/or dipping in 3 M HCl and cut into the dimension of 0.54 mm  $\times$  9 cm.

#### Preparation of galvanic cells

A small-scale galvanic cell was made from two vials (7 cm height). A cotton thread (with the length of 18 cm) pretreated in 2.00 mL of 0.01 M of saturated potassium nitrate solution (Ajax Finechem, AR.) was used as a salt bridge. The pretreated thread was dipped into vials, left for hardening (about 5 minutes) and then carefully adjusted into an appropriate position as shown in Figure 1B. Each vial was then filled with electrolyte and a metal electrode the length of which was slightly longer than the depth of the vial. The used equipments are shown in Figure 2.

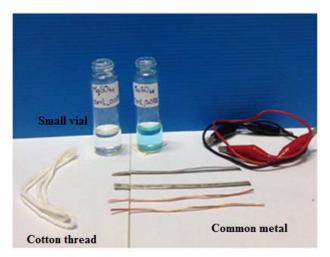


Figure 2 Apparatus used for small-scale galvanic cells

#### Measurement and optimization of galvanic cell potential

Measurement of potential of the studied galvanic cells was performed as followed. The black wire was connected to the electrode with smaller reduction potential (anode), and the red wire was connected to the other electrode with higher reduction potential (cathode). After connecting each wire to a digital multimeter (model AT9205B, ATTEN® INSTRUMENT), the cell potential ( $E_{cell}$ ) produced by each pair of the half-cells was measured as shown in Figure 1B. Optimization of cell potential was performed involving types, concentrations and volumes of electrolytes as well as reagent life time and stability of the cells.

#### Application of the developed method

The developed galvanic cells were applied as teaching materials in electrochemistry. A total number of 31 students (11 male, 35.48% and 20 female, 64.52 %) within the age range of 14-16 years participated in the study conducted in July, 2014. They are from Satree-siriket School, Amphoe Sisaket, Sisaket province, Thailand. Performance of the galvanic cells was evaluated which is based on how well the students' knowledge can be improved. This was performed by the comparison of pre-test and post-test scores in electrochemistry of the students before and after using the galvanic cells.

#### Analysis of data for developed method

The mean scores for each test were analyzed by using software statistics, involving sample mean, standard deviation, coefficient of variation (CV), relative standard deviation, percentage of score, and *t*-test.

#### **Results and discussion**

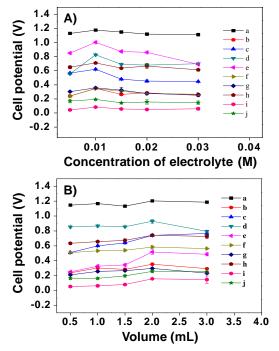
#### Optimization of the cell potential

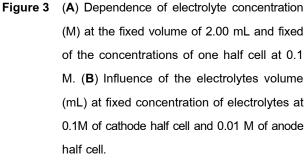
Parameters affecting cell potential were examined using the separated cells. Figure 3A shows that the cell potential increased with the increasing electrolyte concentration. The experiment was performed by fixing concentration of one half-cell (0.1M) and increasing the concentration of the other half-cell up to 0.01 M; whilst, further increase in the concentration from 0.005 M to 0.03 M resulted in the potential decrease. Therefore, 0.01 M was chosen for further experiments. The potential values of the galvanic cells with different pairs of electrodes and electrolytes using cotton thread as salt bridges were compared to the theoretical values which were calculated by using Nernst's equation as followed.

$$\mathsf{E}_{\text{cell}} = \mathsf{E}_{\text{cell}}^{0} - \frac{0.591}{n} \log \mathsf{Q} \tag{1}$$

where  $E_{cell}^{0}$  is the standard reduction potential the cell which can be calculated from the standard reduction potential of each half cell. Q is the reaction quotient depending on activity ratio of ions in electrolytes employed in the two half-cells. The activity ratio can be approximated to be the ratio of ion concentrations. According to the Equation 1, values of  $E_{cell}$  relative to that of  $E_{cell}^{0}$  depend on Q. A Q value being more than, less than, or equal to 1 corresponds to  $E_{cell}^{0}$  being less than, more than, or equal to 1, respectively.

Any increase in Q of the cell results in reduction of E<sub>cell</sub>, while decrease in Q increases E<sub>cell</sub>. Thus, E<sub>cell</sub> can be tuned by changing Q value which can be simply performed by varying concentration ratio of two electrolytes used in the cell (Oldfield, 1988) For a galvanic cell prepared using  $[Zn^{2+}] = [Cu^{2+}] = 1.0$  M, the Q value is 1 ( $\log_{10}$ Q 1 = 0). The potential of this cell ( $\mathsf{E}_{Zn\,|Zn^{2+}||Cu^{2+}|Cu}$  ) is the same as the cell potential at the standard state ( $E^0_{Zn |Zn^{2+}||Cu^{2+}|Cu}$ ) which is calculated to be 1.10 V, for instance. When the concentration of  $Zn^{2+}$  (aq) is increased to be 10 times of  $[Cu^{2+}]$  (with  $[Zn^{2+}] = 1.0$  M and  $[Cu^{2+}] = 0.1$ M), the corresponding Q value is 10 ( $\log_{10}$ Q = 1). The calculated  $E_{Zn |Zn^{2+}||Cu^{2+}|Cu}$  is decreased to be 1.07 V. If  $[Zn^{2+}] = 0.01M$  and  $[Cu^{2+}] = 0.1M$ , the resulting Q is 0.1(log<sub>10</sub>Q = -1). The calculated  $E_{Zn |Zn^{2+}||Cu^{2+}|Cu}$ is increased to be 1.13 V which corresponded to our experiment shown in Figure 3A.

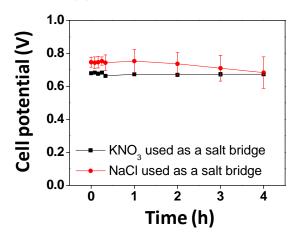


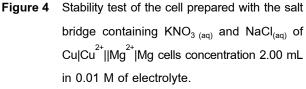


(a) Cu Cu <sup>2+</sup>   Mg <sup>2+</sup>  Mg,	(b) Cu Cu <sup>2+</sup>   Zn <sup>2+</sup>  Zn,
(c) Cu Cu <sup>2+</sup>   Fe <sup>2+</sup>  Fe,	(d) Cu Cu <sup>2+</sup>   Al <sup>3+</sup>  Al,
(e) Zn Zn <sup>2+</sup>   Fe <sup>2+</sup>  Fe,	(f) Zn Zn <sup>2+</sup>   Al <sup>3+</sup>  Al,
(g) Zn Zn <sup>2+</sup>    Mg <sup>2+</sup>  Mg,	(h) Al Al <sup>3+</sup>   Fe <sup>2+</sup>  Fe,
(i) Fe Fe <sup>2+</sup>   Mg <sup>2+</sup>  Mg, and	t (j) Al Al <sup>3+</sup>   Mg <sup>2+</sup>  Mg.

The effect of electrolyte volume on the cell potential is shown in Figure 3B. The cell potential increased with increasing volume of electrolyte until 2 mL since the contact surface areas between electrodes and electrolytes increased which enhanced  $E_{cell}$ , *e.g.* due to reduction of resistance within the electrode/ electrolyte junction (Allen, 1995). The increasing  $E_{cell}$  values reached the saturated values at 2–3 mL. Thus, this condition was selected minimizing amount of used solution.

The effect of salt types used as salt bridges on the cell potential was also studied. Although high E<sub>cell</sub> was obtained with the use of 0.01 M NaCl<sub>(aq)</sub>, the cell lifetime is relatively short (about 0.33 h). 0.01 M KNO3(aq) was observed to be better salt resulting in very stable cells as well as providing high cell potential, as illustrated in Figure 4. Potassium ion is remarkably nonreactive, and most potassium salts are soluble in water (Whitney, 1903). Also noted that NaCl<sub>(aq)</sub> might not be a good choice when zinc, silver or lead electrodes were applied due to the precipitation of many common anions, e.g. ZnCl<sub>2</sub>, AgCl, PbCl<sub>2</sub>, which is caused by the presence of NaCl<sub>(aq)</sub> (Iverson and Duke, 1957; Ohno 2011). The long term use of this salt solution also causes imbalance of ions in the electrochemical cell. The results of other studied cells were also in good agreement with Figure 4. Therefore, 0.01M KNO<sub>3 (aq)</sub> was selected for further study.





The lifetime of the developed small-scale cells is investigated as shown in Table 1 for the lifetime of the Cu(s)|Cu<sup>2+</sup>(aq)||Mg<sup>2+</sup>(aq)|Mg(s) cell and the other cells studied also corresponded to Table 1. The cell potential values measured in different sets of the experiments were not significantly different within %RSD < 2, suggesting that the precision of the developed small-scale cells

Table 1 Mean ( $\overline{X}$ ), standard deviation (SD) and relative standard deviation (%RSD) values of E<br/>Cu |Cu<sup>2+</sup>||Mg<sup>2+</sup>|Mg<br/>using 2.00 mL and 0.01 M of electrolytes in both half-cells at different application time.

			(	Cell voltage (V	/)			
Cell of Cu Cu <sup>2+</sup>   Mg <sup>2+</sup>  Mg	Time (h)							
-	0	1	2	3	4	24	720	
Set 1	1.38	1.40	1.39	1.40	1.42	1.41	1.43	
Set 2	1.38	1.41	1.39	1.37	1.42	1.38	1.40	
Set 3	1.40	1.43	1.42	1.39	1.44	1.40	1.39	
М	1.39	1.41	1.40	1.39	1.43	1.40	1.41	
SD	0.01	0.01	0.01	0.01	0.01	0.01	0.02	
%RSD	0.83	1.08	1.23	1.10	0.80	1.09	1.47	

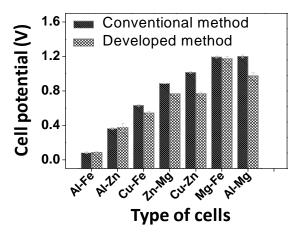
is high and workable. It could also be concluded that the reagent can be effectively used up to one month.

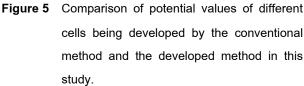
# Comparison of small scale method and conventional method

The comparison between conventional and developed cells was illustrated in Figure 5 for different half-cell couples. Both methods were observed to be comparable. According to the *t*-test, the cell potential of each 7 cell was not significantly different ( $t_{stat} = 2.414$ ,  $t_{critical} = 2.447$ ) at p = 0.05. The Cu-Fe, Zn-Mg, Cu-Zn and Al-Mg cells developed in this study reveals significantly lower  $E_{cell}$  compared to the conventional cells. However, qualitative analysis of different cells is considered to be the same using either conventional or herein approaches. With the benefits of low cost and small scale, it is worthwhile applying the developed cells in this study as teaching materials in the future.

#### The students learning outcome

The learning potential of the developed method were determined using pre-test and post-test scores of the students before and after experiencing the developed cells. The data imply that the application of the smallscale and low-cost galvanic cells was able to meet the desirable goal with higher post-test scores of the students as shown in Table 2. This table reveals student's posttest scores were significantly higher (with  $\overline{X}$  = 8.15 and SD = 1.29) than their pre-test scores (with  $\overline{X}$  = 4.69 and SD = 1.13).





This outcome indicates an applicable teaching innovation to improve students' knowledge in electrochemistry. According to the result of CV showed that the post-test scores (CV = 15.82) is improved when compared with the pre-test (CV = 24.09), suggesting that the improvement of students' s understanding (the criteria of consideration of CV value in education study were divided into 3 parts 0-15 was an excellent method, 15.1-20 was a good method and > 20 was a poor method). According to the *t*-test, the *t* values of two examinations were  $t_{\text{observed}} = 9.55$  and  $t_{\text{critical}} = 2.07$  with p = 0.05. This observation indicates significant degree of difference between the two data. The students learning experience with the small-scale experiments is very satisfactory.

**Table 2** Descriptive statistics, being number of students (N), mean value of scores ( $\overline{X}$ ), standard deviation (SD),coefficient of variation (CV), of pre-test and post-test of scores for small scale and low cost of galvanic cellwith p = 0.05 and Total mean = 10.

Variable	Ν	М	SD	Percentage	CV (%)	<i>t</i> -test
Pre-test	31	4.69	1.13	46.90%	24.09	9.55
Post-test	31	8.15	1.29	81.50%	15.82	2.07

#### Conclusions

The small-scale and low-cost galvanic cells have been developed and successfully applied as the teaching materials in electrochemistry which was confirmed by the improved post-test scores of the high school students after using the cells. It was found that the developed cells have a potential to reduce the solution consumption, at least by 15 mL per experiment as well as producing less amount of waste in the laboratory. The application of this approach is thus environmentally friendly and worthwhile. Besides the 'Green' chemistry aspect, the developed cell efficiency is comparable to the results obtained from the conventional macro-scale cells. The presented concept is expected to be a model example of small-scale experiments for sustainable future.

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