recommended that the method should be used in combination with the relevant assignments and evaluations of the traditional performance assessment.

## CONCLUSIONS

The main purpose of the study was to describe the application of the free word association method in the analysis of learners' knowledge structure. The topic we chose for our analysis was 4th and 7th graders' conceptual systems related to the concept of renewable energy, which we evaluated from the aspect of the role of age as well as of gender and size of settlement. The word association test has helped in demonstrating that, as learners age, their knowledge turns into a more and more complex structure comprising of more and more concepts and connections in the given topic. In terms of settlement size, the knowledge of city children proved to be more complex, which can presumably be attributed to the difference in the learners' cultural and social background as well as the more favourable infrastrucure and teaching methodology applied in city schools. In our analysis we first constructed the network of connections among the stimulus words followed by the descripiton of the relationship between the stimulus words and the associations attached to them as well as the quantitative and qualitative characteristics of the associations. We concluded here, too. that the word association method is descriptive, simultaneously giving a good overview of students' knowledge structure, and its quantitative and qualitative aspects. However, it is time-intensive and hence should be applied on small sample sizes. Yet, due to its informative character, it can be recommended as a method of evaluation to teachers, too, who can use it at school to assess students' current knowledge or the changes in that knowledge. To teachers we recommend a simplified, less time-intensive version of the free word association test, which considers only the analysis of the associations and the connection between the stimulus words and the associations. In this case the maps containing the associations simultaneously make clear the strength and nature of the connections between the stimulus words, too. Thus the word association test can complement the traditional, descriptive statistical analysis of school evaluation.

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# Misconceptions sequencing the chemical processes in Daniell and electrolysis cells amongst first-year science and mathematics education university students Conceptos alternativos de los estudiantes sobre los procesos químicos en las células de Daniell y de electrólisis

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## Abstract

This study aims to analyse a number of misconceptions amongst first-year students from the Department of Mathematics and Science Education, Academic Year 2013/2014, at the University of Tadulako, Indonesia. The purpose is to explore the students' understanding of the concepts and the processes involved in electrolysis cells. In addition, the use and purpose of a salt bridge in these cells are also considered. A two-part test instrument was used to obtain the data. The test instrument involved a paper for the students to answer. The paper encompassed a series of stages for the mechanisms and processes that take place in (i) the Daniell cell (Zn-Cu) and (ii) the electrolysis cell for molten NaCl. Both processes were summarised into seven stages. Each stage consisted of three scientific illustrations for the students to choose from, with only one considered to be chemically correct. In addition, the students were asked to give a brief description of the mechanism they thought occurred at each stage and why. The results demonstrated that there was a higher level of misconception within the students' understanding of the electrolysis cell of molten NaCl (44%) when compared to their understanding of the Daniell cell (31%). For the Daniell cell, the half-reduction reaction (51%) was the most common misconception amongst the students, whilst for the molten NaCl cell ion migration (65%) appeared to be so.

Key words: misconceptions, chemistry learning, Daniell cell, electrochemistry, electrolysis cell, molten NaCl, salt bridge.

#### Resumen

Este estudio tiene como objetivo analizar una serie de conceptos erróneos entre los estudiantes de primer año del Departamento de Matemáticas y Educación Científica, (2013/2014), en la Universidad de Tadulako, Indonesia. El propósito es explorar la comprensión en los estudiantes de los conceptos y los procesos involucrados en las células de electrólisis y además, el uso y propósito de un puente de sal en estas células, también. Se utilizó un instrumento de prueba de dos partes para obtener los datos. Se hicieron una serie de pasos para determinar los procesos en la célula de Daniell (Zn-Cu) y la célula de electrólisis con el NaCl, fundido. Ambos procesos se resumieron en siete etapas, cada una consistió en tres ilustraciones científicas para los estudiantes, a elegir. Además, se pidió a los estudiantes que proporcionaran una breve descripción del mecanismo que pensaban que había ocurrido en cada etapa y por qué. Los resultados demostraron que había un mayor nivel de concepción errónea dentro de la comprensión de los estudiantes de la célula de electrólisis de NaCl, fundido (44%) en comparación con su comprensión de la célula de Daniell (31%). Para la célula de Daniell, la semireacción de la reducción era el error más común entre los estudiantes.

**Palabras clave:** conceptos alternativos, aprendizaje de la química, célula de Daniell, célula de electrólisis, NaCl fundido, puente salino.

## **INTRODUCTION**

Studies on misconceptions of electrochemical cells have attracted the interest of a number of researchers and educators over the years (Barral, Fernández, and Otero, 1992; Ceyhun andKaragölge, 2005; De Jong, Acampo, and Verdonk, 1995; Garnett, Garnett, and Treagust, 1990; Nakhleh, 1992; Ogude and Bradley, 1994; Sanger and Greenbowe, 1997b; Schmidt, Marohn, and Harrison, 2007). The subject of electrochemistry has long been regarded as something that is difficult to understand either by high school students and/or teachers (Davies, 1991; De Jong and Treagust, 2002; Griffiths, 1994; Johnstone, 1983). In particular, high school students reinforce that the conceptual understanding within the Daniell cell (Figure 1) and the electrolytic cell of molten NaCl (Figure 2) are of particular concern (Okpala andOnocha, 1988). It was proposed by Butts and Smith (1987) and supported by Garnett and Treagust (1992) that this may be due to the abstract concepts of electrolysis in general. Hence, the overall understanding of the processes involved in the cell is preventing the students writing the oxidation-reduction reactions correctly. This opinion was supported by a study in high schools in Nigeria which reported that more than 50% of grade XII students (age range from 16 to 20) considered that the concept of electrolysis was one of the most difficult concepts in science (Okpala andOnocha, 1988). This is plausible due to the abstract nature of the chemical concepts associated with electrochemical cells according to Huddle, White, and Rogers (2000).



Figure 1. Illustration for the Daniell Cell (Spencer et al., 2010).



Figure 2. Illustration for the molten NaCl cell (Reger et al., 2009). Figures 1 (Spencer, Bodner, and Rickard, 2010) Figure 2 (Reger, Goode, and Ball, 2009)

It is apparent that the electrochemical misconceptions that first-year mathematics and science students possess can hinder the assimilation of new conceptual understanding as they progress through their studies (Sanger andGreenbowe, 1997a). A number of authors have tried to address these misconceptions by focusing on the barriers to learning by using computer animations (Andersson, 1986; Greenbowe, 1994; Niaz, 2002; Sanger andGreenbowe, 2000) and modelling (Huddle et al., 2000) to support conceptual understanding. Some authors have introduced various methods of measuring the misconceptions held by their students. For example, Hasan, Bagayoko, and Kelley (1999) applied a CRI (certainty, response, index) method; Treagust (1988) and Loh, Subramaniam, and Tan (2014) proposed a diagnostic test; and finally Brandt et al. (2001) and Kose (2008) utilized concept mapping and drawings to ascertain their students' understanding.

There are many different known electrochemical cells discussed in the literature for example; the Clark cell (Zn-Hg system); the De La Rue cell (Zn-Ag system); the Helmholtz cell (Zn-Hg system); the Guoy cell (Zn-Hg system); the Weston cell (Cd-Hg system) and finally the Daniell cell (Zn-Cu system) (Hamer, 1965). The electrolysis of molten or fused sodium chloride was first introduced in a Downs cell early in the last century (Downs, 1924). Subsequently, together with the Daniell cell (Boulabiar, Bouraoui, Chastrette, and Abderrabba, 2004), they both became an important feature in key physics and chemistry texts of the time.

Most teachers and educators often deliver both of these topics in the context of the electrochemical series, using very similar diagrams to Figures 1 and 2. They often treat the chemical theory as a whole process and they do not discuss each chemical transition as a separate stage. This often leaves the students' self-constructing the concepts and compounding their already developed misconceptions (Walanda andNapitupulu, 2013).

This paper aims to investigate the misconceptions that first-year undergraduate students from the Department of Mathematics and Science at the University of Tadulako, have on their conceptual understanding of the processes within an electrochemical cell.

## METHODOLOGY

The study was introduced to a group of the first year Mathematics and Science Education Department students (n=184) at the University of Tadulako, Indonesia in the academic year 2013/2014 (see Table 1).

			Table	1					
Summary	table	of the	cohort	of	students	in	this	study	7.

Program Study	Male	Female	Total
Mathematics Education	11	32	43
Chemistry Education	9	41	50
Biology Education	8	36	44
Physics Education	17	30	47
			184

All the students were registered on a course in basic chemistry subject knowledge and they all had previously been taught the theory within electrochemical cells in their last year of high school, including both the Daniell and the molten NaCl electrolysis cells.

The diagnostic test instrument utilized had previously been trialled with high school students (Walanda and Napitupulu, 2013), the results of which informed the final version of the test instrument that was used here. The first section of the test instrument was devoted to the Daniell cell and focussed on examining the sequence of mechanisms involved within the cell; whilst the second section reinforced the same but in the context of an electrolysis cell (molten NaCl). The tests were designed to explore the students' thorough understanding of the chemical concepts within each cell. This was done by summarizing the electrochemical concepts independently for both cells into seven stages. For each stage of the chemical process, the students could choose one of the three illustrations that had been suggested; only one of these was correct for each stage. Once the students had made their choice for each stage of the process they were then asked to articulate a brief description quantifying their choice, based on their chemical knowledge and understanding. In addition, they were also asked to articulate at what stage a salt bridge should be introduced in the Daniell cell to ensure the process was sustainable. The data collected from this study was then analysed using a data processing program (MS Excel).

## **RESULTS AND DISCUSSION**

Figure 3 illustrates the percentage of student response for each stage of the Daniell cell, whilst Figure 4 demonstrates the percentage of student response for the electrolysis of molten NaCl (for both of these the dark grey bar indicates the correct choice). For the Daniell cell (Figure 3 and Table 2) it is evident that a vast majority of students understand two of the stages really well, matching the electrodes and electrolyte (94%) and the ion majority contained in each cell (97%). However, there were still challenges in the students' conceptual understanding of oxidation (49%) and the cell (57%). It appears that the students' understanding of the electrolysis of molten NaCl (Figure 4 and Table 3), held more misconceptions than

the Daniell cell. The students had good knowledge and understanding of the movement of the ions (73%) and the charge at the electrode (68%), although they had difficulty with the phase of the electrolyte (65%) and ion migration (53%).



Figure 3. Graph summarising the percentage of student choices on the mechanism for each stage in the Daniell cell ( choice I, choice II and choice III; dark grey bar indicates the correct response for the stage).



Figure 4. Graph summarising the percentage of student choices on the mechanism for each stage in the molten NaCl electrolysis cell.

Based on the data presented in Tables 2 and 3, it is evident that students have clear misconceptions in sequencing the mechanistic stages for both of the electrochemical cells studied, but especially the molten NaCl cell. This demonstrates that the chemical concepts that are used in the electrolysis cell are still poorly understood by the majority of the students. The concept of the ions migrating in the molten NaCl cell was perceived as a misconception by 53% of students. This reinforces that students still do not have a fully developed conceptual understanding regarding the movement and consequently the migration of the ions once the electrodes have been 'dipped' into the molten NaCl.

Table 2. Summary of misconceptions held by the students when questioned about their understanding of the chemical stages in the Daniell cell.

Stage	Concepts	Percentage with Misconceptions
1	Matching Electrode and electrolyte	6
2	Oxidation half-reaction	49
3	Reduction half-reaction	51
4	Metallic Conduction	18
5	Cations or Anions Dominance	3
6	The role of Salt Bridge	57
7	The net cell reaction	35
Averag	e	31

Table 3. Summary of misconceptions held by the students when questioned about their understanding of the chemical stages in the electrolysis of molten NaCl.

Stage	Concepts	Percentage with a Misconception
1	Phase of Electrolyte	65
2	Ion Movement	27
3	Electricity/ion Source	43
4	Ion Migration	53
5	Electrolyte conduction	37
6	Electrode Charge	32
7	The net cell reaction	52
Averag	e	44

In the Daniell cell, it is obvious that a large percentage of students had misconceptions regarding the concept of the reduction half-reaction (51%) and the use of a salt bridge (57%). The individual half-reactions in the Daniell cell are as follows:

Cathode: 
$$\operatorname{Cu}_{(aq)}^{+} + 2e \rightarrow \operatorname{Cu}_{(s)}$$
 (1)  
Anode:  $\operatorname{Zn}_{(s)} \rightarrow \operatorname{Zn}_{(aq)}^{+} + 2e$  (2)







Figure 6. An illustration of the proposal for the reasoning behind the reaction stopping prior to a salt bridge being included.

Figure 5 illustrates part of the diagnostic test that was used to elicit students' understanding of the third stage in the seven mechanistic stages of the above reactions. Two of the options here show the movement of ions towards the solution thus distracting the students from the true conceptual understanding. The equation for the reduction half-reaction above demonstrates that there is a change in the phase of the Cu ions from dissolved in a solution into a solid, by consuming twice their number of electrons. Review of the diagnostic test given to students reinforced that generally they could write the above reduction reaction correctly. Thus, it is evident that the students have a good understanding about writing the redox equations for these types of reactions, but their understanding falters when abstract/diagrammatic representation is used to portray the concept. Hence, they all could not interpret the stages successfully when the abstract images/diagrams were used, and must, therefore, have gaps in their knowledge and understanding when challenged with the separate stages in these systems.

The function of the salt bridge in the Daniell cell is to support the process within the cell, to ensure the reaction is maintained over time. In the case of this cell, the oxidation half-reaction is the first chemical stage of the processes involved in the redox reactions that subsequently take place. Figure 6 illustrates a proposal for how the saturation of positive charge from the Zn<sup>2+</sup> ions acts as a barrier for the continuation of the reaction if current cannot flow through the cell (The Zn reaches an equilibrium with the solution). If this proposal is true, it offers an explanation for the prevention of the further oxidation of the Zn metal. If this does happen the electrons that are sourcing the reduction reaction are now not available and overall this results in no electrons flowing from the zinc electrode to the copper electrode, which in turn results in no electricity flowing between these cells. This problem is overcome by placing a salt bridge that connects the two individual half-cells. The salt bridge's main function is to maintain the balance of electrical charge across the two half-cells. It often contains an inert concentrated salt (such as KCl or KNO<sub>3</sub>) mixed with a gel.

The findings from the diagnostic tests indicate that there are misconceptions from the students in determining what stage the salt bridge is introduced to the system. There was great disparity between the students' responses here. A third (34%) indicated that the salt bridge was introduced in the early stages. An explanation for this could be due to them being provided with diagrams of this nature in high school, prior to undertaking a practical activity based on redox. A higher proportion of students (49%) indicated that the salt bridge was introduced in the fifth stage of the seven concepts proposed. There were also some students who answered that the function of the salt bridge was to act as a medium for ions (sulfate and zinc) to move between each half-cell. This indicates that the students contextualised the salt bridge's function to the purpose of a physical bridge, in terms of mediating the transfer of an object from one side to the other. When the students were questioned why the half-oxidation process ultimately stops, there was definite gender split from the responses. Very few male students could articulate a reason for this, whilst the female students deduced that the copper electrode had been covered with newly formed copper. When this point was explored with the female students, there was a realisation that the 'new' copper would react exactly the same as the 'old' copper and that their response was indeed not plausible.

The movement of ions contained in the salt bridge ensured that there was a continuous flow of electrons between the two half-cells. The negative ions of the salt bridge (such as iodide or nitrate ions) will migrate to the aqueous half-cell which is dominated by the positive charge due to the electrostatic attraction of oppositely charged ions i.e. the  $Zn^{2+}$  ions. In contrast the positive potassium ions will migrate to the audeous half-cell which is dominated by the negatively charged species, the sulfate ions. In the Zn half-cell, which was initially dominated by aqueous  $Zn^{2+}$  ions, further electrons will now be produced ensuring a constant flow of electrons through the external wire to the copper electrode. With the presence of an electron flow it would mean that the Daniell cells' half-reactions will be continuous once more.

## CONCLUSIONS

Diagnostic test instruments using illustrations of chemical processes have detected misconceptions amongst first-year mathematics and science students in sequencing the mechanism stages occurring in the Daniell cell and the molten NaCl cell. For the Daniell cell, the half-reduction reaction is considered as the most problematic misconception amongst the students, whilst ion migration in the electrolyte, is the most common concept detected as a misconception in the molten NaCl cell. Before a student can fully understand the seven stages identified for each electrolytic cell discussed in this paper, there needs to be a clear foundation of knowledge and understanding built upon the key prior principles of electrolysis. This needs addressing with the students before their transition to University to ensure they make the required progress with this subject and, to as much as possible, eradicate the misconceptions identified here.

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