Per-Odd Eggen

Current chemistry

Experiments and Practice in Electrochemistry Education

Thesis for the degree of Philosophiae Doctor

Trondheim, June 2010

Norwegian University of Science and Technology
Faculty of Natural Sciences and Technology
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Preface and acknowledgements

This thesis consists of two parts. The first covers some general aspects of electrochemistry education and provides the background material for the second part. The first part covers only some of the results from the articles in Part 2. Part two contains 4 published articles and 3 manuscripts.

This thesis is a result of a study at Department of Chemistry at the Norwegian University of Science and Technology (NTNU) during the period 2006-2010, and has been carried out under the supervision of Professor Lise Kvittingen.

The doctoral study has been a continuance of my collaboration with Lise Kvittingen and the School Laboratory at NTNU that started in 2001. Before the PhD project started, Lise and I collaborated in developing new laboratory activities for use in school chemistry. During these years many promising experiments have been put to rest, while some have survived and been published. In this collaboration, we have had different roles, and my role has included testing some of these activities in my classroom as a teacher in grades 11-13 and in university courses for chemistry teacher students. Together, Lise, myself and other good colleagues also held courses for chemistry and general science teachers in Norway, and we participated in conferences and projects in Turkey, Mexico, Lesotho, Ethiopia, Germany and South Africa. Our daily arena, however, has been the offices and the laboratories at NTNU (and for parts of the afternoons, in the coffee bar two floors down, enjoying breaks together with colleagues at our own and our neighbouring departments). These experiences have been fruitful both for my work and in personal respect.

Being 51 years old, I am also involved in activities outside my daytime job. Living almost 200 km from the university, having four children and being involved in the society around me in many ways, compromises have been necessary. I could not have managed this without the exceptional ability and willingness to cooperate that I have experienced from my colleagues and the management at the Department of Chemistry, at the Programme for Teacher Education (both at NTNU) and at my school Grong Videregående skole. I will also thank Inger Mari, Kjersti, Gjermund and Sigvart for patience and understanding during these years, despite my own lack of patience in some cases; and Berit and John, who have supported me with a pleasant (and free) "hotel".

Many colleagues and friends should be mentioned in these acknowledgements, but I am in particular grateful for all the help and support from Lise Kvittingen. In addition to superb supervision, she has involved her family in providing me with linguistic and practical support, accommodation in their house in Simonstown (South Africa) for Sigvart and myself, and enjoyable company when visiting places in Trondheim as well as abroad. I know that I could never have published internationally or finished my degree without this support, and I know I am a lucky man, having had this opportunity. Unfortunately, Lise's attempts to raise me have been the least successful part of our joint projects (this last place may, however, be shared with our struggles with the bureaucracy).

While working on my PhD project, I have been involved in chemistry teaching in upper secondary school and at the university. This connection to teaching has absolutely influenced my studies, and my experiences make me confident that research in this field is worthwhile. I look forward to continue!
Snåsa, April 2010, Per-Odd Eggen

Declaration of co-authors:

Paper 1: Both authors have contributed equally
Papers 2 and 3: All authors have contributed equally
Paper 5: My contribution lies mainly within the experimental part.
Paper 7: All authors have contributed equally.

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Current chemistry

Experiments and practice in electrochemistry education

1 Introduction

This thesis is concerned with experiments, models and concepts employed in electrochemistry teaching, when this is a part of a general chemistry course in upper secondary school or an introductory university course. The manuscripts and articles in part 2 present and discuss laboratory activities and models? in electrochemistry. In part 1, my intention is to have a brief look at the electrochemistry section of chemistry textbooks used in general chemistry courses at Norwegian universities[1] because textbooks and experiments are two important and interrelated parts of electrochemistry education. The textbooks referred to are international editions of English and American textbooks for university use[2] or Scandinavian upper secondary school textbooks.

It appears that the textbook is often the main source for concepts and understanding in electrochemistry, and that experiments provide additional understanding and training. I will concentrate on the use of terms, models and selection of practical experiments to see if these can be associated with the many problems reported concerning the understanding of concepts in electrochemistry (Ringnes 1993; Sanger and Greenbowe 1997; Sanger and Greenbowe 1999; De Jong and Treagust 2002; Özkaya 2002; Özkaya 2003; Ceyhun 2005; Schmidt *et al.* 2007). The papers included in this dissertation either discuss traditional educational electrochemistry experiments or propose alternative ones. The overall objective of my work is to explore possibilities to improve knowledge and understanding in electrochemistry in general and practical experiments in particular.

In Norway, chemistry up to school grade 11 is a part of the general science course, together with physics and biology. In grade 12 and 13chemistry is a subject in its own right, chosen by few, but often clever[3], students. For many of them the purpose

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[1] The books referred to includes supplementary literature available at the library, such as textbooks for upper secondary level.

[2] Among them, the textbooks in use at Norwegian universities in 2009

[3] About 7,5% each year study chemistry in secondary school (Norwegian “Videregående skole”). Based on statistics for students studying chemistry, physics, biology and/or mathematics (Hægeland *et al.* 2007)

is to apply for further studies to which there is limited access, such as medicine (Hægeland *et al.* 2007) . In contrast to medical studies for which chemistry in grade 13 is a requirement, chemistry is, at present, not compulsory for general chemistry studies at the university. The general chemistry curriculum at Norwegian universities therefore overlaps with the curriculum for grade 12 and 13. Nevertheless at Norwegian universities international editions of general chemistry textbooks[4] are used, indicating that topics and degree of challenges to some extent correspond with university studies in other countries. I therefore hope that my findings may have some relevance abroad, even though this dissertation is embedded in a Norwegian context.

Both in upper secondary school and in Norwegian universities, knowledge in chemistry traditionally means both theoretical knowledge and practical skills. Norwegian students must pass both a theoretical exam and a practical laboratory course. The study of chemistry also involves different working methods; central are textbooks together with contributions from a teacher/lecturer, discussions among the students, laboratory work and subsequent reporting. This dissertation does not discuss all these aspects, but mainly concentrates on elements in electrochemistry education connected to experiments and related textbook sections. In addition, some brief comments on related aspects, such as context and how the choices of topics in electrochemistry can be legitimated are included.

Having taught chemistry for about 20 years in secondary school, this dissertation will inescapably also be tainted by my own views and experiences, although I hope to have built my arguments on a sound academic basis.

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[4] The textbooks used in general chemistry courses at Norwegian universities in 2009 were all international editions: (Chang 2008; Zuhmdahl 2000; Tro 2008; Brady 2000)

2 A short presentation of electrochemistry education in the past

When Volta invented his "Voltaic pile" in 1799, the mutual effects of electricity and matter was already an established research area. The discovery of the "Baghdad battery"[5] may indicate an even older history, but electrochemistry, as we know it today, had its birth and period of major development in the 19th Century (Usselman 1989). In the same period electrochemistry became a part of chemistry education, influenced by the research done by many well-known scientists such as Michael Faraday together with e.g. Svante Arrhenius, John Frederic Daniell, Humphry Davy, Rudolph Clausius, William Robert Grove, Wilhelm Oswald, Walther Nernst and Gaston Planté. In electrochemistry education, Daniell's inventions and publications had, and still have a great influence. Batteries commemorating his name are still commonly used as examples in general chemistry textbooks (Grønneberg *et al.* 2002; Housecroft and Constable 2006; Chang 2008), even though they scarcely resemble modern batteries (Boulabiar *et al.* 2004).

During the 19th century a number of inventions were made which have had extensive impact on technological development. A variety of primary batteries and some accumulators were constructed and produced for sale. In the chemistry textbooks by Daniell (Daniell 1839) and Arrhenius (Arrhenius 1902) several galvanic cells were presented as examples of contemporary research and technology. While primary batteries made by e.g. Daniell, Bunsen, Groves and Lechlanché were still in commercial sale in the beginning of the 20th century (Schallenberg 1978) models of similar cells were offered to teaching institutions in equipment catalogues (Jacobsen 1903; Kohl 1905/1906)[6]. Reversible gas fuelled cells[7] made by William R. Grove and the lead accumulator constructed by Planté in 1859 are examples of contemporary technology described in Arrhenius' book (Arrhenius 1902).

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[5] The "Baghdad battery" is a device assumed to be about 2000 years old. It consists of a clay jar containing a copper cylinder and an iron rod that is isolated from copper with bitumen. It is speculated that this could act as a battery if filled with e.g. lemon juice.

[6] These batteries were produced the second half of the century, but it is not clear when the use culminated. Models are found in catalogues from before 1910.

[7] resembling e.g. hydrogen-oxygen fuel cells

With the invention and development of galvanic cells, possibilities to study and utilize electricity for many purposes emerged. Electrolysis of water had already been performed prior to 1800 (Nicholson 1800; Faraday 1849). Few years later, | electrolysis was central as a method in the discovery of many elements, such as aluminium, sodium and potassium (Davy 1808). Thus galvanic and electrolytic cells have been important in science since their invention, and this is reflected in chemistry education.

3 Teaching and learning electrochemistry

3.1 Why learn electrochemistry?

Why do we teach chemistry in general and electrochemistry in particular? When developing the curriculum content, this question is an essential consideration. As with all chemistry topics, both basic knowledge and specific examples must be included. Understanding redox reactions in general is an example of a topic that is essential for at least two reasons; to understand phenomena in every day life such as combustion and batteries, and: to obtain basic knowledge for further studies. Advanced topics in electrochemistry are normally only of interest for those who intend to study chemistry at a higher level.

Public authorities within education may have various reasons for including electrochemistry in the curriculum. Through history, inventions involving electrochemistry have contributed to production of goods; and research within electrochemistry is continually developing (Weppner 2003). Both scientific institutions and industry rely on a yearly supply of graduate students. It is therefore reasonable that politicians provide for this "production" of skilled labour (National-Resarch-Council 1998). There is a continuous discussion on how to adapt education to current, or even future, requirements. However the process from research to the school curriculum is long, and school curricula naturally lag behind. One may say that electrochemistry students are prepared to meet the challenges of yesterday.

Hence, in electrochemistry education, there is a challenge to adapt the subject to the current situation.

3.2 Electrochemistry in general chemistry textbooks

Even though the development of curricula is a national and not an international endeavour, there that curricula are regularly revised, there appears to be a certain consensus amongst many countries about the essential content of electrochemistry as a school and college/university subject. The international editions of American textbooks used at Norwegian universities are sold in other European and in Asian countries[8], and the same topics are also part of Ethiopian and South-African curricula (Department of Education 2003; Institute for curriculum development and research 2004). The electrochemistry curricula situation in Norway may therefore have relevance abroad.

In Norway students first encounter electrochemistry as a part of a chemistry course in grade 13.[9] Laboratory work is included as a compulsory activity, and, though it is not explicitly stated in the curriculum, experiments with e.g. galvanic and electrolytic cells are implicitly required[10]. Galvanic and electrolytic cells are apparently also ”compulsory” parts of electrochemistry chapters in all general chemistry textbooks. In addition, topics such as potentials and battery types, including fuel cells, are normally discussed (Brandt *et al.* 1998; Reistad *et al.* 1998; Pilstrøm *et al.* 2000; Zumdahl 2000; Grønneberg *et al.* 2002; Chang 2008; Tro 2008).

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[8] For example, Pearson Education have offices in London, Sydney, Singapore, Hong Kong, Toronto, Mexico, Tokyo, Malaysia and New Jersey.

[9] Electrochemistry is also a part of the compulsory natural science course in grade 11, but this part of the curriculum will not be discussed.

[10] Three goals in the curriculum involve electrochemistry and state that students “shall be able to: conduct experiments on corrosion and explain how corrosion may be prevented; conduct experiments using electro-chemical cells and explain spontaneous and non-spontaneous redox reactions; calculate the capacity and cell potential of a battery and the yield in an electrolysis” (My translation) Utdanningsdirektoratet (2006). Kjemi - Programfag studiespesialiserende utdanningsprogram.

Metallurgy and corrosion are also included in some books (Zumdahl 2000; Chang 2008).

In contrast to the "compulsory" parts of electrochemistry chapters, topics such as semiconductors, electrochemical probes and electrochemistry in biological systems are generally not part of the curricula at this level (John 2005) although they are probably just as familiar to many pupils and students as the traditional topics. Examples are photosynthesis, blood glucose measurements (Wang 2006) and solar cells. Relevant teaching activities on alternative topics in electrochemistry exist (Ibanez 2001; Ibanez *et al.* 2004; Ibanez *et al.* 2005), thus there is no obvious reason to neglect these topics.

The various textbooks' presentations of electrochemistry topics share some common features. Normally there is one part covering the basic chemistry relevant to the topic. This is often accompanied by some historical examples and a description of electrochemical devices for domestic use or industrial methods today. Typically current batteries or metal production are mentioned, although it is not always easy to distinguish between the historical and current technological examples. The subject matter presented is normally related to specific examples and figures, and is therefore not "context-free", even though the context may be unclear. It appears that the textbook authors have looked for examples that will be easily grasped, emphasising context and cotemporary examples less.

3.3 Students' motives to learn electrochemistry

"Most exciting chemistry experience I have ever had! The goal oriented structure of this class in which experiments were performed for a reason (i.e. steps to reach an ultimate goal) gave unprecedented interest to a chemistry course"[11] (Ram 1999).

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[11] —Comments by student in fall '96, Chem. 291L (Ram 1999)

The quote above illustrates that students are unfortunately seldom able to relate chemistry experiments to something outside the school subject, and that the choice of working methods, also in chemistry education, is important, at least as a motivating factor.

Students' motives for choosing chemistry as a school subject rely on more than the subject itself. In Norway, chemistry is a requirement for medicine, veterinary medicine and dentistry (Opptakssentralen_Medisin 2010). These studies are regarded as prestigious, and provide a common motive to study chemistry. Furthermore students receive extra credits[12] in upper secondary schools for choosing science subjects in general, and thereby increase their access to popular studies where the number of applicants exceeds the number of places. The awarding policy is meant to direct students' choices in order to meet society's need for science graduates for industry, research and related businesses (Kunnskapsdepartementet 2010). Despite the fact that chemistry as a subject is associated with popular studies, only a few students will actually continue to study chemistry after secondary school.

The need of the incentive of extra credits to attract students is a bit surprising considering that many youths voluntarily "study" science programs on TV and in other media, without additional reward. Such programs often address complex scientific issues, and it is therefore not unlikely that by watching these programs some learning and understanding takes place. A recent investigation of 15-year-old students' interest in and motivation for science topics does not reveal any wide-ranging interest for science in general. Instead interests vary according to subject, within subject and with gender, as well as being culturally influenced. Both the ROSE- and SAS- investigations (Sjøberg 2002; Schreriner and Sjøberg 2004; Kunnskapsdepartementet 2010), indicate that increased wealth tends to give a

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[12] The extra points given to students who has passed science classes is an advantage when they apply for further studies

decreased interest in science, and the opposite, that education in general, and science in particular, is regarded as a way out of poverty. Many youths are put off science due to its reputation of being difficult as well as irrelevant (Kruckenberg 2006). Thus motives for studying chemistry at school seem to depend on other factors than if the students find the topic interesting. Such factors may be the subject's relevance to contemporary job situation or that chemistry can meet some of society's challenges.

Knowing which motives drive students' choices, public authorities could influence these by incitements that direct students into subjects supposedly required in the future. The same knowledge could ideally also be utilized to change the subject content to spur more interest. The idea of changing teaching in order to increase motivation is of course not new. Numerous articles and books exist in which improvements with regard to both motivation and subject content are suggested, emphasizing different ways to the goal, but all with the intention to obtain "good teaching" for chemistry education (Johnstone 1997; Garratt 2002; Hofstein 2004; Hodson 2005).

3.4 Reported problems /challenges in electrochemistry education

"Electrochemistry is ranked by teachers and students as one of the most difficult curriculum domains taught and learnt in secondary school chemistry" (De Jong and Treagust 2002).

In electrochemistry, students often have to deal with complicated reactions and experimental setups. In several textbooks a galvanic cell is used as an introduction to electrochemistry. To get an overview of this cell, students must deal with concepts such as reduction and oxidation, half reactions, electron transfer, current, ion transport, salt bridge, electrode, pole and electrolyte, amongst others (De Jong and Treagust 2002). Each of these concepts may cause problems, and combining them in a single chapter is particularly challenging.

In addition to concepts to explain redox reactions, such as reduction and oxidation, De Jong and Treagust have listed electrolyte, electrode, electrode reaction and potential difference as crucial to understanding electrochemistry (De Jong and Treagust 2002). Other studies suggest electric current (Garnett and Treagust 1992; Marohn 2004) and standard potential (De Jong and Acampo 1996; Sanger and Greenbowe 1997) to be particularly difficult. There are many investigations demonstrating that students, pupils and even teachers have misconceptions in electrochemistry (Sawrey 1990; Ringnes 1993; Sanger and Greenbowe 1999; Chou 2002; Vitz 2002; Özkaya 2002; Özkaya 2003; Ceyhun 2005; Schmidt *et al.* 2007), and that these problems are experienced in various countries and educational systems (Özkaya 2002). Acknowledging these problems, textbook authors are in the position to actually prevent misconceptions and thereby also counteract them (Ogude 1994; Chou 2002; Özkaya 2006).

When learning electrochemistry concepts are difficult to trace to experiences outside school. The teacher, the textbook and experiences from experiments are therefore often the main sources of knowledge. Together these may ideally "promote the evolution of students naïve views into the more sophisticated scientists views" (Duschl and Hamilton 1990). When references are few, each one becomes a more crucial a basis for understanding a phenomenon. A study from rural schools in India indicates that students who had participated in, or watched, repair of electrical equipment found learning electricity in science classes easier (Sharma 2007). Also theoretical science topics related to every day experiences increase the students' participation in the learning process (Gilbert 2006). However practical electrochemistry is hardly present in everyday life of most students or teachers, thus experiences and concepts will most likely come from school activities, but these activities, if not well founded, may also be the very origin of misconceptions (Leite 1999; Chou 2002; Boulabiar *et al.* 2004).

Completely avoiding misconceptions is of course unrealistic. Instead one will have to deal with them as a normal process of learning. One option is to give students time to reason and discuss in their encounter with a practical problem. An illustration of this is documented in a Swedish study, where students were recorded during a practical on an electrochemical cell (Hamza and Wickman 2007). Misconceptions were sometimes described as “generative of the students’ reasoning”, and accordingly could not automatically be assumed to interfere with learning. This study also illustrated how practical challenges, as conducting experiments in electrochemistry, could give new experiences and an alternative approach to learn concepts compared to theoretical sources.

4 Terminology and concepts in electrochemistry

The many concepts in electrochemistry are major obstacles for learning. Words like “electrolyte” or “charge” have distinct meanings, which need to be understood. Such concepts can be learned through words and models in textbooks as well as through practical activities, which can give additional understanding. Often the same concept is explained differently in different textbooks, both with regards to the choice of terms and the way they are explained, and in the following I will discuss some examples.

4.1 Oxidation-reduction reactions

Oxidation-reduction reactions (redox reactions) do not necessarily belong to electrochemistry although the understanding of redox reactions is a prerequisite for learning electrochemistry. As with electrochemistry, redox reactions in general are reported to be troublesome to learn (Markic and Eilks 2005). The explanations of a redox concept are often a compromise between being understandable and being comprehensive. A statement such as “**Oxidation-reduction reactions** or **redox reactions** are reactions in which electrons are transferred from one reactant to the other” (Tro 2008) has a certain range of applicability (Vitz 2002), while a more complete definition such as “An increase in the oxidation number of any atom within any substrate" and "Gain of oxygen and/or loss of hydrogen of an organic substrate" (McNaught 1997), is sometimes necessary.

According to Sanger chemistry textbooks contain both misleading and erroneous examples and statements (Sanger and Greenbowe 1999; Boulabiar *et al.* 2004), and students tend to misunderstand; though not necessarily because the statements are wrong. Often difficulties arise from the uncertainty of whether a statement is general, or simply refers to a specific example. A comprehensive statement may be useful for teachers and students at a higher level, but the shorter, incomplete version, may be a good alternative for beginners and can be built on in future learning. (Leach and Scott 2003)

Students may have problems combining the different models of redox reactions when solving problems, and the oxidation number model is sometimes recommended as an "overall" model. However, De Jong and Treagust recommend altogether *avoiding* the term oxidation number at secondary school level (De Jong and Treagust 2002). In their opinion, oxidation numbers should be used only at higher levels, allowing students at lower levels to start with easier notions. In many textbooks the use of oxidation numbers dominates in examples and exercises (Brandt *et al.* 1998; Zumdahl 2000; Gilbert *et al.* 2004; Chang 2008), although other definitions of oxidation and reduction are also mentioned (Housecroft and Constable 2006; Ringnes and Hannisdal 2006; Grønneberg *et al.* 2008; Tro 2008).

4.2 Potentials

An electrical potential is an abstract term, and is often referred to as that which gives rise to an electric current (Andersson *et al.* 2000; Gilbert *et al.* 2004; Chang 2008). There are also more elaborate explanations such as: "Potential difference is a measure of the difference in potential energy (usually in joules) per unit of charge (coulombs) (Tro 2008)." or "A galvanic cell consists of an oxidizing agent in one compartment that pulls electrons through a wire from a reducing agent in the other compartment. The "pull", or driving force, on the electrons is called the **cell potential** " (Zumdahl 1998). In the latter example the driving force is called "pull", which is then changed to "cell potential". It is possible to explain the driving force of reactions by discussing atomic properties (Martins 1990), or by entropy analysis (Bindel 2000), but this is seldom done for electrochemical cells. The nature of the "pull", or nobleness (von Moser 2001) of oxidizing agents in galvanic cells is rarely explained, but it is quantified in terms of *standard reduction potential,* where the zero-point by convention is the reduction potential of $2H^+ + 2\ e^- \rightarrow H_2$ (Smolinsky *et al.* 1989) . Why electric potentials exist at all is seldom explained, probably because it is reckoned to be too complicated at the general chemistry level, but a lack of tradition may also contribute.

To get an idea of what "electric potential" means, students can conduct experiments where different half-cells are connected and the resulting potentials measured, as suggested in many textbooks. Standard potentials can be obtained by connecting a half-cell to a hydrogen electrode, but more often secondary electrodes such as Ag/AgCl or a calomel-electrode are used against different metal/metal ion pairs (Tanis 1990; Eggen *et al.* 2006; Eggen 2009). In such an experiment, students must also deal with alternative voltage scales whilst tackling new concepts. The hydrogen electrode is mostly present as an illustration or a description (Zumdahl 2000; Chang 2008) and rarely recommended for use in experiments.

To many students, the concept of standard reduction potential is not straightforward (De Jong and Treagust 2002; Özkaya 2002). Amongst the problems reported are the nature of the scale and the use of different half-cells than H^+/H_2. Another problem is failure to understand that e.g. a pair of half reactions, both having a negative standard electrode potential (such as Fe/Fe2+, E^o = -0,44V and Zn/Zn2+, E^o = -0,76 V), can result in a positive potential (De Jong and Acampo 1996).

4.3 The driving force of the reaction

Galvanic cells are sources of electrical energy. In order to understand how galvanic cells work, the challenge is often to grasp the driving force of the reaction or to "discover the factors that relate to the cell potential" (Bindel 2000). The concept of energy is in itself problematic (Lutz 2007), in particular when combined with electrochemistry. Descriptions of the driving force vary. Some are based on atomic/compound properties, such as: "Zinc metal has considerable electron-donating power, and Cu^{2+} ions tend to be willing acceptors of donated electrons" (Gilbert *et al.* 2004), while other explanations are grounded in the activity series: "From the activity series, we know that zinc atoms have a greater tendency to produce ions than do copper atoms" (Schmidt *et al.* 2007). Grønneberg et al. (Grønneberg *et al.* 2002) explain the driving force by a difference in the ability to produce positive ions in water.

The atomic properties that account for a higher reduction potential of e.g. $Cu^{2+} \rightarrow Cu$ relative to $Zn^{2+} \rightarrow Zn$ are not obvious. The quotation above on metals with electron donating power (Gilbert *et al.* 2004) could mislead the reader to believe that zinc atoms actively donate electrons. The German expression "Elektronendruck" (electron pressure) (Rauh 1998; Grønneberg *et al.* 2008) also indicates the same. Such statements and phrases do not support an understanding that the "electron-donation" is in fact endothermic. On the other hand some authors emphasize that e.g. "The electromotive force is a measure for the difference in the ability to attract electrons in the two metals" (Brandt *et al.* 1998) indicating an attraction of electrons in contrast to the ability to repel electrons as one might believe from the former explanations.

Georg Martins proposes thinking of the electrode reactions in a Daniell cell in terms of three processes: "(1) the endothermic separation of the atoms from the solid metal, the heat of atomization or sublimation can be used for this process; (2) the endothermic ionization of the gaseous atom to form the doubly positive ion; (3) the exothermic hydration of water molecules around the ion, represented by the heat of hydration" (Martins 1990). The sum of these energies would provide an explanation on the atomic level for the drive of chemical change in a galvanic cell. These energies could be related to bonding properties and diameters of neutral atoms and ions. Which of the processes that contributes most to a potential difference in a pair of half reactions may vary, but according to Martins in a zinc-copper cell the crucial process is the hydration of the metal ions.

Instead of explaining the driving force of the reaction in galvanic cells through atomic properties, thermodynamics may provide a valuable approach. This approach is both recommended (Melle 1993; Bindel 2000; Lutz 2007) and used in some textbooks (Pilstrøm *et al.* 2000; Housecroft and Constable 2006). Bindel reports how first year high school students approached the driving force of galvanic cells through entropy analysis, though it should be stressed that both thermodynamics and the function and structure of galvanic cells are prerequisite knowledge (Bindel 2000). An approach relating the driving force of electrochemical reactions to atomic or bonding properties will of course require familiarity with these topics.

4.4 Electrodes, poles, terminals…

An aspect of interest in understanding electrochemistry is the apparently numerous names and descriptions of an electrode. Students, as well as inexperienced teachers, often struggle with concepts such as positive and negative electrodes, anodes and cathodes (Özkaya 2003; Markic and Eilks 2005; Tro 2008). Even within the same textbook, names such as zinc and copper bar/foil/strip, positive and negative electrode, positive and negative pole, anode and cathode and even more terms exist side by side to describe what appears to be the same (Brandt *et al.* 1998; Grønneberg *et al.* 2002; Grønneberg *et al.* 2008; Tro 2008). The problem becomes even more pronounced if a student reads in more than one book, or the teacher shifts between the various terms. Furthermore, terms such as terminals, poles, + or - , are often not explained, although explanations and definitions are normally given for the terms anode and cathode. In some cases the term electrode is also explained (Zumdahl 2000; Grønneberg *et al.* 2002; Gilbert *et al.* 2004; Grønneberg *et al.* 2008). Roughly speaking, the definitions given for anode and cathode are identical, and normally include the word electrode, even when this term is only vaguely explained or not at all (Brady 2000).

Apparently authors are aware of the problems with the multitude of terms and the possible resulting confusion. Some seem to avoid using more than one or two terms, (Zumdahl 2000; Housecroft and Constable 2006; Chang 2008) while others use many (Brandt *et al.* 1998; Grønneberg *et al.* 2002; Tro 2008). One option could be to use anode and cathode as terms for an electrode in all types of electrochemical cells, but this will have unfortunate consequences, and supplementary terms are essential to explain e.g. the + and – signs which label battery and equipment terminals. A student reading Chang's General Chemistry may have problems understanding electric devices if the terminals are not labelled "anode" and "cathode", since these are the only terms used in this book.

The terms anode and cathode were, together with e.g. electrode, ion, anion, cation and electrolyte, introduced by Michael Faraday[13] to avoid conceptual problems:

> ".....these terms may at any time be applied, there seems no reason to expect that they will lead to confusion, or tend in any way to support false views." [14]
> (Faraday 1834)

Unfortunately, it seems that Faradays intentions were rather optimistic.

4.5 The term electrode

One example of a definition of an electrode is that it is an object that "provides an interface at which electrons can be transferred" (Housecroft and Constable 2006).

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[13] Faraday recommends new terms in electrochemistry after having "considered the subject with two friends"

[14] Quotation from Faraday when introducing the terms anode and cathode

This explanation, as well as being a definition, may counteract the common misconception that electrodes themselves are charged (Faraday 1834; Sanger and Greenbowe 1999). Even though the definition gives a reasonable explanation of the function of the electrode, it is limited in extent and fails to include the use of the term for complete half-cells as well as being unclear for reacting electrodes such as the zinc electrode in the zinc/copper cell. Reference electrodes, such as the hydrogen electrode and the silver/silver chloride electrode, are not just metal pieces or graphite rods; they are, on the contrary, complete half-cells, and should be described as such.

Definitions of the term electrode vary, even within the same book, as do also the descriptions. An example is the statement, …"electrode is a conductor in a circuit that carries electrons to or from a substance other than a metal" (Wilbraham 2000). Reading this, one may think that the wire connected to a graphite electrode is an electrode, while the glass electrode is not. Explanations are sometimes presented so that they appear universally valid, although they might just refer to a specific example. One such statement is "At the plus pole, there is a reduction, i.e. an uptake of electrons"[15] (Pilstrøm *et al.* 2000)(p 178). Applied to a galvanic cell, this description is helpful. However, this may also be read as a universal statement, thus making it more difficult to understand the functioning of electrolytic cells.

In some textbooks the terms for the electrodes depend on whether they are parts of a galvanic or an electrolytic cell. The terms Anode and cathode may be used only for electrolysis (Brandt *et al.* 1998; Reistad *et al.* 1998; Borén *et al.* 2005; Housecroft and Constable 2006) or for electrodes in electrochemical cells in general (Zumdahl 2000; Gilbert *et al.* 2004; Chang 2008; Tro 2008). Even in ordinary galvanic cells and fuel cells electrodes may have different names. The many terms combined with unclear applicability are likely to increase confusion.

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[15] Original text: "Vid pluspolen sker reduktionen,dvs elektroner tas upp.". My translation.

Definitions in a textbook’s glossaries and their use in the main text are not always consistent.. In the glossary of *Chemical Principles* (Zumdahl 2000), a cathode is defined as “the electrode in a galvanic cell at which reduction occurs” and vice versa for the anode, of which both indicate that these terms are reserved for galvanic cells. In the main text, however, cathode and anode are used for electrochemical cells in general.

Troublesome annotations in electrochemistry are not a recent phenomenon. More than a century ago authors commented on this, such as Cooper in *Primary Batteries, Their Theory, Construction and Use* (Cooper 1901) where he writes: “The junctions of the external circuit with the battery plates are generally called the **poles** of the battery; and, as we are most generally concerned with the flow of current in the external circuit, the platinum pole, or upper end of the platinum plate (i.e., the plate by which the current leaves the cell) is called the **positive pole**, and the zinc pole, or upper end of the zinc plate, is called the **negative pole**. But the zinc plate of a battery is, nevertheless, often spoken of as the **positive plate**, apparently because zinc in contact with copper in air becomes positively charged.”

Michael Faraday introduced the term electrode for an object at which the reaction in an electrochemical cell occurs. The term “pole” was replaced with “electrode” to avoid an implication of polarity or attraction (Faraday 1834; Daniell 1839; De Jong and Treagust 2002). This period was almost a century before the discovery of the electron, so of course reaction mechanisms involving electrons had not been conceived. The new terms, which were meant to replace older ones in order to improve the terminology, have not led to the desired simplification.

The confusing terminology in electrochemistry is discussed in a number of papers, and de Jong reports that: “…we have indicated that one of the major origins of the reported difficulties in teaching electrochemistry consists of the inappropriate and nonchalant use of contexts in which electrochemical concepts have specific meanings” (De Jong and Treagust 2002). In secondary school textbooks the topic of electrochemical cells is introduced, after redox reactions in general, by the presentation of a galvanic cell, very often a zinc-copper cell (often named Daniell cell). Although teachers are familiar with this example, most students are overwhelmed by it, as this cell inherently demands many new concepts and at the same time has no similarity in appearance with an ordinary battery (De Jong and Treagust 2002). Thus the complexity of galvanic cells is strengthened by the diversity in terms and definitions. The use of different terminologies in chemistry and physics, (such as the term electric field used in physics, but not in chemistry) is also not helpful (Markic and Eilks 2005). To a student who reads more than one textbook, the inconsistencies in terminology are disadvantageous. In "IUPAC Gold Book" (Mc Naught 2008), just two of the discussed terms, namely anode and cathode, are defined, and the use of these as preferred names for all types of electrochemical cells seems to be quite widespread (Brady 2000; Zumdahl 2000; Gilbert *et al.* 2004; Chang 2008; Tro 2008).

4.6 Models for transport of electrons and ions

Charge transport by electrons or ions is another obstacle for learning and a source of misunderstanding (Marohn 2004; Markic and Eilks 2005)According to Sanger and Greenbowe vague or even misleading terminology is often the problem (Sanger and Greenbowe 1999). Common perceptions are that electrons flow through the electrolyte of a galvanic cell, that a salt bridge can be exchanged with a metal wire and that only anions move in the solution to contribute to the current (Sanger and Greenbowe 1999; Huddle and White 2000; Özkaya 2003; Marohn 2004; Ceyhun 2005). Problems associated with the salt bridge, such as high resistance and thereby limited amperage and energy loss when charging rechargeable batteries, are seldom mentioned in textbooks. When learning electrochemistry, some basic understanding of electric current as well as relations between current, resistance and voltage are needed. In textbooks the nature of electric current and the characteristic division of the electrical circuit in a galvanic cell[16] that is crucial for exploiting the chemical energy of the reaction to electrical energy is seldom emphasised[17].

The necessity of the salt bridge for the functioning of the cell is, however, explained in several ways. One is to avoid an opposing voltage: "To compensate for an increasing positive charge, SO_4^{2-} ions move through the salt bridge and into the zinc solution." [18] (Grønneberg *et al.* 2002) is one example. Another way is to stress the necessity of a closed circuit: "The salt bridge just provides for a closed electric circuit."[19] (Brandt *et al.* 1998) or "The bridge provides an electrical connection between the two chambers even though the reactants and products of the two half-reactions are physically separated." (Gilbert *et al.* 2004) A third alternative is to give no explanation at all, but simply state that ions transport charge in the electrolyte (Pilstrøm *et al.* 2000; Housecroft and Constable 2006). Where the function of the salt bridge is not discussed or hardly explained, the reader will have problems getting a grasp of the reactions taking place in the cell. Statements such as "The salt bridge contains a solution that conducts current (an electrolyte),…"[20] also exist (Brandt *et al.* 1998), and may, according to Sanger (Sanger and Greenbowe 1999), make the students believe that the current in the salt bridge consists of electrons. Nevertheless, figures of the salt bridge are often clearer. Altogether, text and figures give relevant information and are only to a minor degree misleading. The most common problem, however, is that explanations are omitted.

4.7 Descriptions of galvanic/voltaic cells

The well documented problems of understanding galvanic cells (Ogude 1994; Ogude and Bradley 1996; Sanger and Greenbowe 1997; Yuruk 2007) arise to some extent from textbook presentations (Sanger and Greenbowe 1999; Lin *et al.* 2002).

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[16] One part where only electrons flow (normally through an energy demanding device) and in the other part where no electrons can flow, but where there is a transport of ions instead.

[17] Brady's textbook is an exception. (Brady 2000)

[18] Original text: "*For å oppveie en økende positiv ladning går SO_4^{2-}-ioner gjennom saltbroen og ut i sinkløsningen*." My translation.

[19] Original text: "*Saltbroen sørger bare for at strømkretsen er sluttet.*" My translation.

[20] Original text: "*Saltbroen inneholder en løsning som leder strøm (en elektrolytt),…*" My translation.

Typically, a general discussion of redox reactions is given, followed by a presentation of a galvanic cell as a way to arrange spontaneous redox reactions in order to utilize the energy available as electric current or as a voltage source. Normally, the sequence of topics in the electrochemistry chapter is; galvanic cells, commercially available batteries, fuel cells (when discussed) and, lastly, electrolytic cells. Ample use of figures supports the text. Although the choice of illustrations varies, the zinc-copper cell is common[21], together with other combinations of half-cells, often connected with a U-shaped glass tube filled with an electrolyte (Zumdahl 2000; Eggen *et al.* 2006; Chang 2008; Grønneberg *et al.* 2008; Tro 2008). This is further discussed in papers 6 and 7.

Depending on the interpretation of the figures, they may become a source of understanding, or of misunderstanding. The galvanic cells do not resemble commercial batteries, but rather school laboratory constructions. Two beakers connected with a U-tube and an electric connection between the electrodes is the most common, reappearing figure. To use this figure to illustrate a current source is inappropriate, since a U-tube containing an electrolyte has a small cross section and a long length, and thus has very low conductance. Even figures showing a zinc-copper cell with a glowing light bulb are displayed, suggesting that this cell creates the necessary current for this purpose, as shown in Figure 1. Such cells cannot provide the current and voltage necessary to power a light bulb, or even a LED[22], so the figures are misleading. (See papers 6 and 7.) If these cells are built in the laboratory, confusion and frustration are produced since the illustrated results are impossible to obtain.

Even though the order of the topics in electrochemistry chapters in general chemistry textbooks is similar, they use different representation and terminology.

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[21] Zinc-copper cells are often called Daniell cells in textbooks, even though they are constructed differently from the original Daniell cells.

[22] LEDs which are commonly available often need more than 1,5V to glow

Variation in use of concepts has already been discussed, but also the choice of figures and models representing galvanic cells vary, as shown in Figure 1.

Figure 1

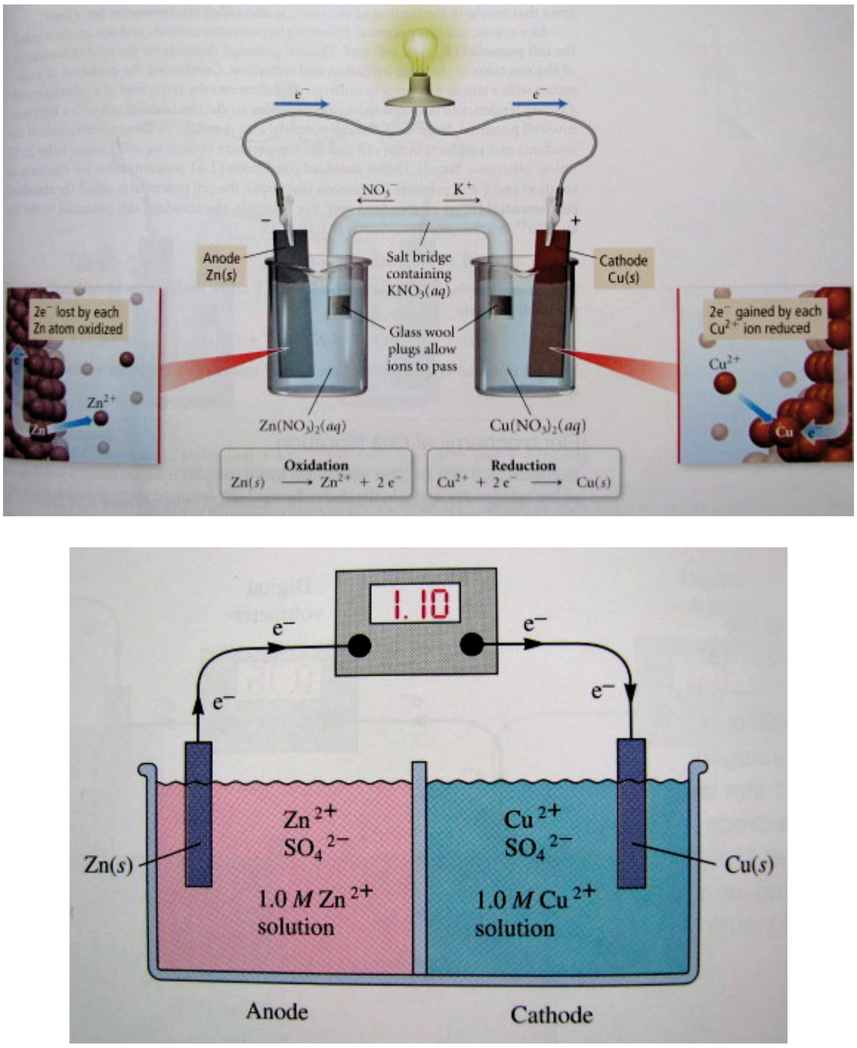

Figure 1. Galvanic cells in *Chemistry, a molecular approach* (Tro 2008) (top), and *Chemical Principles* (Zumdahl 1998) (bottom).

Both figures in Figure 1 are referred to as galvanic/voltaic cells, and can be easily built, although, as mentioned, the light bulb in Tro's figure (top) will not glow. In

Zumdahl's version (below) ion concentrations are given, which is irrelevant information for galvanic cells but meaningful when this cell is designed to measure standard reduction potentials.

There are reports of electrochemical cells that both illustrate the chemical reactions and give sufficient current to run a LED or a small propeller (Eggen *et al.* 2006; Modesto and Yu 2007). Some are even characterized as high capacity batteries (Muske *et al.* 2007). The U-tube cells as in Figure 1 (top) are poor current sources, but can be used to illustrate potential differences between half-cells, and this is the context in which they are sometimes used (Chang 2008; Tro 2008). The U-tube cell was sold as a teaching device in the first part of the 20th century (Kohl 1905/1906). Already in the 1880s such cells were reported as instruments for potential measurements, and not as a part of a battery (Kittler 1882; Kohl 1905/1906).

The galvanic cells in most textbooks have in general little relevance to present technology and challenges. Even though the electrochemical processes discussed are relevant to all galvanic cells, the models used are uniquely teaching artefacts, and do not resemble any galvanic cell outside school. It might be considered doubtful to use 19th century models when teaching electrochemistry in the 21st century. Historical experiments, for example reconstructions of the Voltaic pile or the Daniell cell, can be used with success in education, but then preferably in a historical context (Gooday *et al.* 2008; Pandora and Rader 2008).

4.8 Description of commercial batteries

Galvanic cells have relevance to daily life, as these are closely related to e.g. batteries and corrosion. A variety of both primary and secondary batteries have been in common use some for decades, such as the lead accumulator, whilst other batteries, such as the now common lithium ion battery, have been introduced more recently. Nevertheless most textbooks do not dwell on lithium-ion batteries. Instead frequently less common commercial batteries dominate (Markic and Eilks 2005) such as ”dry cells” (both the Leclanché-type and alkaline batteries), Ni-Metal hydride, the mercury battery, silver oxide battery, lead accumulator and Ni-Cd accumulator.

There are few examples where the function of the lithium-ion battery is explained (Chang 2008), although brief descriptions without any explanations are not uncommon. One reason for not explaining thoroughly the lithium-ion batteries may be that they deviate significantly from the examples in the general discussion of galvanic cells as they for example lack an aqueous electrolyte. Still, their use in both cell-phones and laptops should justify their inspection and explanation., Chang exemplifies how lithium-ion cells easily can be related to other and simpler galvanic cells (Chang 2008).

Molten salt batteries are normally not mentioned in chemistry textbooks at all, even though they have been frequently used since the World War 2, e.g. in electric cars and for military purposes (although not in domestic apparatuses). Molten salt batteries are rechargeable cells where the charging is electrolysis of a molten salt, while the reverse reaction gives power. These cells might therefore be convenient examples of electrochemical cells in general.

The batteries described in textbooks are normally brief presentations that include the chemical reactions taking place. But, as already mentioned, most of these batteries are of old technology, and have associated disadvantages such as rapid power loss, high weight to power ratio or high content of poisonous heavy metals. Sometimes a discussion of the disadvantages is appropriate, but it is often missing e.g. “These qualities make the mercury battery ideal for use in pacemakers, hearing aids, electric watches, and light meters” (Chang 2008). The environmentally friendlier zinc-air battery (a common hearing aid battery) is not discussed in this textbook.

In contrast to the lithium-ion battery, which is almost always poorly explained, the Leclanché cell (Cooper 1901) is normally the first example described (Brady 2000; Gilbert *et al.* 2004; Chang 2008; Grønneberg *et al.* 2008; Tro 2008), even though this cell is hardly found, at least in many Western countries[23], where alkaline batteries dominate as commercial primary (not rechargeable) batteries.

4.9 Fuel cells:

Fuel cells, which still have limited use, are often mentioned as interesting power suppliers for the future (Brady 2000; Gilbert *et al.* 2004; Chang 2008; Tro 2008). They are described as galvanic/voltaic cells which are continually fuelled as e.g. "A fuel cell is a voltaic device in which there is a flow of reactants to the anode and cathode" (Gilbert *et al.* 2004). The main example is always the hydrogen-oxygen cell, even though other examples, such as the methanol fuel cell, are mentioned. The salt bridge or membranes in these examples are KOH-containing gel or PEM (proton-exchange membrane or polymer electrolyte membrane). For fuel cells, the terminology of the electrodes sometimes differs from that of other galvanic cells, and the discrepancy is not necessarily explained (Brandt *et al.* 1998).

With fuel cells (and also lithium-ion batteries) one could give an alternative explanation of the relation between ion transport and electron transport. In the classical salt bridges the ions involved do not participate in the cell reactions. In contrast, the PEM cell illustrates the need for both ion transport and a flow of electrons in a construction where both participate in the fuel cell reaction. Two examples are shown in Figure 2.

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[23] In 2010, I have not been able to find Leclanché batteries in Norwegian shops, but I was able to buy them in Ethiopia.

Figure 2

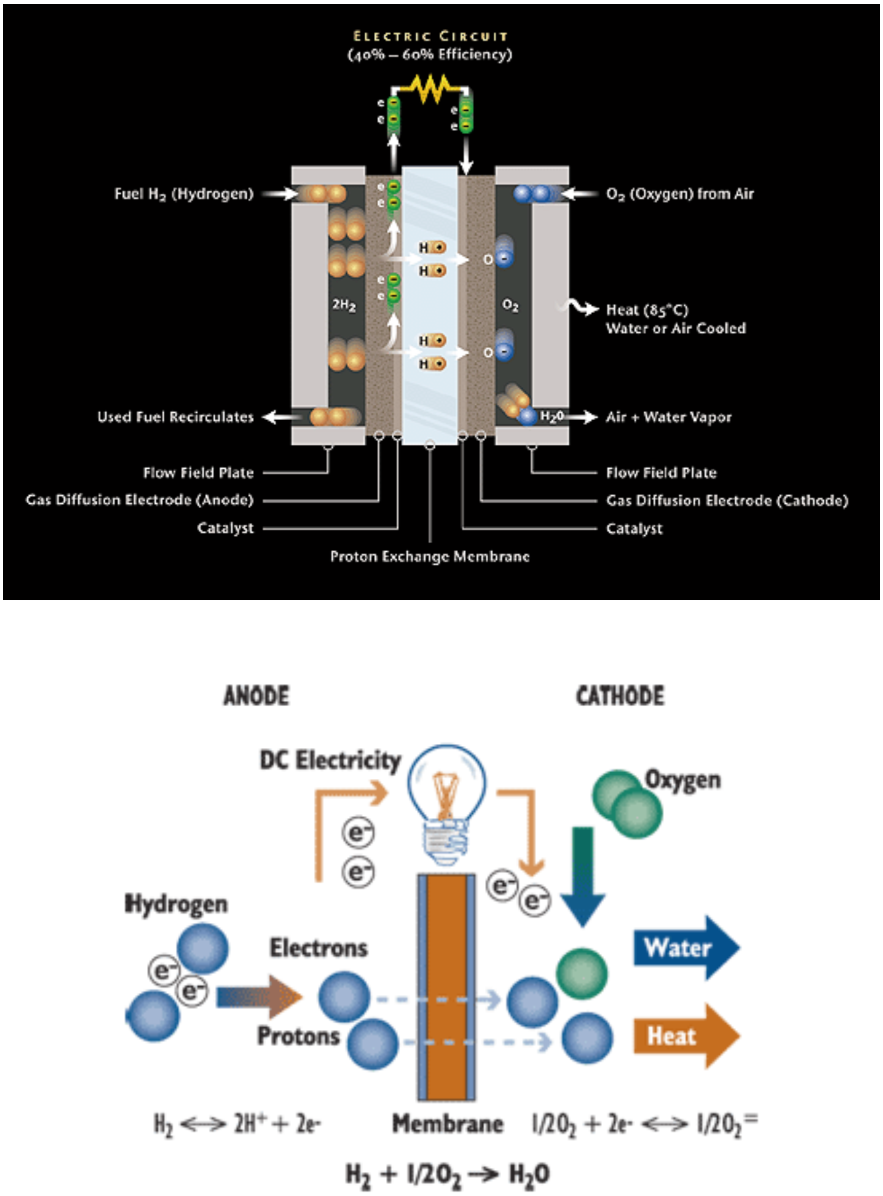

Figure 2. Figures of fuel cells from the web pages of the Australian Antarctic Division (Ballard_Power_Systems 2010) (top) and Rensselaer Polytechnic Institute (Nason 2010) (bottom)

In addition to being an alternative model for galvanic cells, fuel cells are examples of contemporary technology (Zenner 2005). They also illustrate how rechargeable batteries function, since some hydrogen oxygen fuel cells can be charged by electrolysis.

4.10 Electrolysis

Electrolysis and galvanic cells as topics share many concepts, thus the challenges encountered in the galvanic cell also apply to electrolysis, for example the understanding of electron and ion transport (Huddle and White 2000; Marohn 2004) as well as the polarity of the anode and cathode (Schmidt *et al.* 2007). To figure out whether water participates in the reaction can also be a problem (Ringnes 1993). The driving force, which causes problems in galvanic cells, is on the other hand easier to explain and understand in electrolysis, since the reaction is driven by an external power. Further advantages of electrolysis with respect to understanding is the presence of only one salt solution and the absence of a salt bridge (Marohn 2004).

Examples used to describe electrolysis in textbooks are diverse, but seem to be in four categories: One is the reverse reaction of a rechargeable battery, such as the zinc-copper cell or the lead accumulator. Another is electrolysis of a molten salt; a third is electrolysis of water and the last is electrolysis of a salt solution. One of the attached papers describes an alternative experimental setup for the electrolysis of water (Eggen and Kvittingen 2004) which is cost-effective and simple.

As with galvanic cells, experimental set-ups for electrolysis are mainly illustrated by laboratory experiments, although some industrial processes such as electrolysis of molten NaCl are also often presented. The lack of current technology and challenges is noticeable also within this part of the electrochemistry chapters.

Figure 3

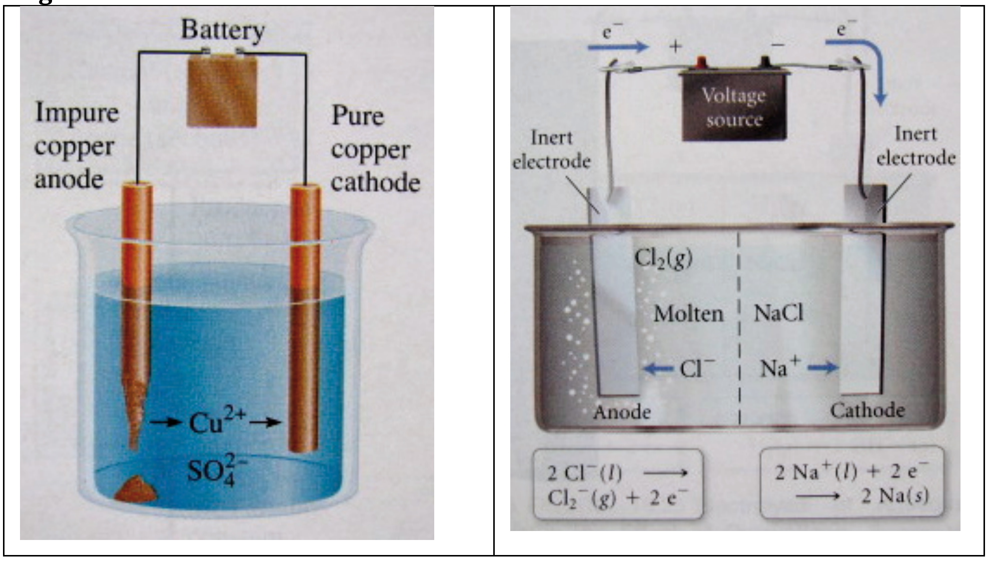

Figure 3. Example of two electrolytic cells from general chemistry textbooks by Chang (Chang 2008) (left) and by Tro (Tro 2008) (right).

4.11 Topics not included

I have in the previous sections argued that several examples, which are in frequent use in electrochemistry education, are outdated as well as not being ideal for understanding. This does not only apply to the examples but also to the topics presented. One such topic is electrochemical sensors, of which the glucose measurement devices are familiar to many students[24]. Different electrochemical probes can be used as examples of contemporary technology (Wang 2006)[25]. Other topics which are not included in electrochemistry chapters, but for which there exist classroom activities, are semi-conductor technology, exploration of biological systems (John 2005) and environmental chemistry (Ibanez *et al.* 2005).

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[24] In one type of glucose sensors, electrolysis is a central part of the analysis

[25] “Indeed, electrochemical probes are receiving a major share of the attention in the development of chemical sensors.” (Wang 2006)

5 Laboratory experiments

Experiments are an essential and natural part of chemistry education (Knight 1992)(Chapters 7 and 11), although critical views on laboratory activities for learning also exist. In my experience experimental work, together with the textbook's explanations, is pivotal to students' understanding of concepts in chemistry, and especially in electrochemistry. However learning from experiments depend on how, and in which context, the experiments are conducted[26] (Sere 2001; Gilbert *et al.* 2002; Hofstein 2004; Hodson 2005; Gilbert 2006; Schmidt *et al.* 2007).

The experiments presented in part 2 of this dissertation illustrate historical and contemporary electrochemical cells (and cell reactions) for educational purposes. The reconstructions of Volta's pile with the splitting of water (paper 5) and the Daniell cell (article) are examples of historically important electrochemical experiments. Article xxx presents how experiments that illustrate basic electrochemistry can be made with few components and simple construction. The purpose in these articles is to contribute to the diversity of experiments, especially for use in non-sophisticated laboratories. These experiments are presented as prescriptive; they can however easily be included in open-ended teaching methods. Low cost has been an additional goal.

Traditional experiments with predetermined outcome and typically recipe procedure do not encourage exploration and curiosity. Many teachers who recognise the value of experimental work also try alternative methods, some with success compared to traditional experimenting (Huddle and White 2000; Hofstein 2004; Markic and Eilks 2005; Mc Donnel *et al.* 2007). More openness is often well received, and can be achieved by emphasizing a problem-based experimental style (Domin 1999).

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[26] For an overview, see Schmidt *et al.* 2007 pp 261-262.

Experimental work is both a meaningful activity in itself and a means to understand the subject matter; issues that are emphasised in chemistry curricula including the Norwegian one for grade 12 and 13. Here it is stated that "The development of chemical knowledge occurs as an interaction between experiments and theory"[27] (Utdanningsdirektoratet 2006). At university laboratory activities are also a compulsory part of the general chemistry courses, but these course activities do not necessarily include a practical in electrochemistry, at least not in Norway. In 2009 only two of the five universities giving general chemistry courses, had electrochemistry experiments in their practicals[28]. At the Norwegian University for Science and Technology in Trondheim (NTNU) the students construct and test a Cu/Zn cell and at the University of Bergen, they conduct a potentiometric titration.

5.1 Why experiments?

Practical work in science classes may have many aims. Some (Beatty and Woolnough 1982; Hodson 1993) are to: motivate by stimulating interest and enjoyment; teach/learn practical skills; promote logical reasoning; enhance the learning of scientific knowledge; give insight into scientific method and to develop expertise in using it; make phenomena more real through experience and developing "scientific attitudes" such as open-mindedness, objectivity and willingness to suspend judgement. Additionally, experiments can initiate discussions and learner-teacher interactions (Hofstein 2004). Practical experiments may result in better learning of concepts or for example the confirmation of a mathematical relation such as the Nernst equation. But experiments also simply enhance knowledge and skills on how to conduct experiments.

Instead of regarding experiments as means to understand theory, conducting experiments can also be a goal for which theory is a means. In electrochemistry

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[27] Original text: "*Utviklingen av kjemisk viten skjer i en vekselvirkning mellom eksperimenter og teori.*" My translation.

[28] All universities were contacted by phone or e-mail in January 2010.

products such as better batteries can be the goal, while the understanding of the subject is a prerequisite to achieve it. Science learning can, according to David Layton, be a two-step process: first to proceed from everyday knowledge to scientific knowledge by the process of science education, and second to develop “knowledge for practical action in specific situations” from this scientific knowledge by a “process of translation or reworking” (Layton 1991). Layton claims that the educational system mainly favours the first of these two steps, namely the acquiring of scientific knowledge. Creative activities, entrepreneurship and willingness to go through trials and failures are seldom explicitly stated in the curriculum, although these are valuable skills. “When technology plays this role in education, it may be classified as educational technology, as distinct from technology education” (Bungum 2003). This also applies to electrochemistry (Belt *et al.* 2005).

The role of practical experiments in chemical education is not always applauded, but questioned from at least two perspectives: conducting experiments at school is time consuming and expensive, and the learning effect is unsure (Sjøberg 1998; Hodson 2005). The latter statement harbours the view that experiments are only a means to achieve knowledge and understanding of theory, and not that experimental work is a discipline in itself. According to Kind (Kind 1996), some teachers solely see practical work as a way of teaching and learning “subject matter knowledge”, whilst others also consider practical work as an independent part of the syllabus*. “*This gives very different signals for what will be the learning outcome of practical work, and therefore indicates various views about what it means to be good at “doing science*” (Kind 1996).* One may question if conducting experiments contributes to the process of understanding, but it is unquestionable that doing experiments contributes to learning how to conduct experiments.

Throughout history chemistry has been a practical skill just as much as a theoretical subject (Knight 1992). Reading books and reports by e.g. Volta (Volta 1800), Faraday (Faraday 1834; Faraday 1844), Daniell (Daniell 1837; Daniell 1839; Daniell 1839; Faraday 1844) and Mendeleev (Mendeleeff 1891) the impression is that mastering the experiments was almost a goal in itself and that theory was a means to achieve this, just as much as the opposite. Mendeleev expresses this in his chemistry textbook: *"*Chemistry, like every other science, is at once a means and an end. It is a means of attaining certain practicable aspirations. Thus, by its assistance, the obtaining of matter in its various forms is facilitated; it shows new possibilities of availing ourselves of the forces of nature, indicates the methods of preparing many substances, points out their properties, etc. In this sense chemistry is closely connected with the work of the manufacturer and the artisan, its sphere is active, and is a means of promoting general welfare.*"* (Mendeleeff 1891) This quote also reveals that the purpose of chemistry to a great extent is to create new materials or processes, and not only to reveal the secrets of the unknown. In chemistry, when learning the "work of the manufacturer and the artisan", practical training is of course necessary. The critics of the "cookbook" experiments in school (Johnstone *et al.* 1994; Garratt 2002; Domin 2006) do not necessarily mean that this type of experiment should be banned, rather that traditional methods should be supplemented by more open-ended working methods. Following a recipe is a well-known method to gain both experience and learning, and many chemists through history, and today, have acquired knowledge using this "distrusted" method.

In school time is often a limitation to proper learning and understanding. Over the years as the subject develops the curriculum also becomes overloaded (Gilbert 2006). As the textbooks incorporate more new topics and increase the number of chapters and pages, time allocation limitations become pronounced, and identifying central topics of the curriculum becomes important. Open-ended and context-based teaching methods can be more time-consuming than traditional ones, which is not the same as less efficient), and this is one factor to consider when prioritising topics and methods (Hofstein 2004; Gilbert 2006).

5.2 What kind of experiments?

An argument against the traditional school system is that students mainly learn to "walk along known paths" and therefore do not learn to tackle new problems or to question “truths”. Einstein, amongst many others, had a critical view of the school system and said that "It is almost a miracle that modern teaching methods have not yet entirely strangled the holy curiosity of inquiry; for what this delicate little plant needs more than anything, besides stimulation, is freedom" (Einstein, 1879). This want for a bit of freedom should not be ignored when conducting practical experiments. There has been, and still is, a debate on the advantages of prescriptive versus open-ended experiments and to what extent traditional experiments and working methods should be altered accordingly (Markic and Eilks 2005; Zenner 2005). The current debate often favours open-ended activities. Nevertheless the traditional prescriptive working methods hold their ground in the everyday life of the school, and science teachers are therefore accused of being conservative with respect to their teaching methods (Quale 2003).

There are many experiments to choose from when electrochemistry is to be taught. For galvanic cells, there are at least four categories of traditional experiments: one is to construct a cell designed for use in the school laboratory, such as the “school version” of the Daniell cell; a second is to measure potentials of various metals/metal ion pairs; a third is to reconstruct historical models such as the voltaic pile; and lastly, to build models of batteries used in daily life, for example the lead accumulator.

As discussed in paper 2 and 6, the galvanic zinc-copper cell with a U-tube salt bridge is common as a model in chemistry textbooks. The alternative galvanic cell presented in paper 2 is made of few and cost-effective components and makes a LED glow. This alternative presents a hands-on activity, which can support the understanding of galvanic cells. Using graphite instead of copper as electrode material enables the students to see the copper metal deposited and may reduce the confusion about the role of the copper electrode. The LED (replacing a voltmeter or an ampere meter) visualizes the electric power produced without requiring that the learners understand concepts such as current and voltage. These cells can be built in different ways, by varying the size or the electrode materials, and by exchanging the floral foam with e.g. a salty gel. The proposed construction can be a starting point for more open-ended activities.

The voltaic pile is mainly of historical importance, and it is for this reason its reconstruction is justified (Høttecke 2000). The straightforward and apparently simple construction deceives the complex chemistry behind it, which should not be underestimated. The relevance of the pile for understanding galvanic cells in general, and modern batteries in particular, is limited. Still, its significance as an icon in the history of science may legitimate spending some time on its use and construction. Reconstructing experiments in a historical context is reported as useful for students' understanding of concepts and insight into the history of science (Sichau 2000; Binnie 2001). If students are allowed to explore the advantages and disadvantages of the Voltaic pile, this may also shed light on later contributions in electrochemistry, such as the Daniell cell. Compared to the Voltaic pile the Daniell cell had less impact on electrochemistry, nevertheless the descendant school version of the Daniell cell exists in abundance in general chemistry textbooks today (paper 6, 7????). Papers 5 and 6 discuss the reconstructions of the Voltaic pile and the Daniell cell as illustrating historical batteries. These reconstructions may also help to understand the significance of different chemical theories behind the two inventions (paper 6).

The two papers on reference electrodes (3 and 4) show how to construct cheap and robust alternatives to traditional commercial reference electrodes. One is a secondary (copper) electrode and is particularly cheap and at the same time simple to use. The other is a hydrogen electrode, thus making it possible to measure standard reduction potentials in school experiments. This electrode has a tiny piece of platinum metal as the electrode material, which increases the cost, and it is also slightly more complicated to construct compared to the copper electrode. The advantage, however, is that standard reduction potentials can be obtained directly, and thus the problems of using secondary scales are avoided.

An example of an experiment on batteries in current use is the investigation of the lead accumulator, invented in the 1850s (Garche 1990), and which, for example, still dominates the car battery market. Building a model is fairly simple (Grønneberg *et al.* 2002) and makes sense both from the perspective that the chemical reactions involved are presented in most chemistry textbooks, usually after the introduction of some simpler cells, and that the lead accumulator is a galvanic cell in common use. This last fact is, as mentioned before, in contrast to many of the other obsolete batteries described in textbooks, (Markic and Eilks 2005).

An alternative to the conventional experiments on galvanic cells is a functioning model of the PEM fuel cell. Activities in electrochemistry generally rely on knowledge and experiments distant from current research, but fuel cells appear to be an exception. The PEM cell is commonly available in schools, despite not being available in everyday life. Several reports describe school experiments where fuel cells have been used with success (Dittmer 2003; Zenner 2005; Kamiya 2007). Some fuel cells designed for simple experiments are also suitable for demonstrating the function of rechargeable batteries, as they work well in electrolysis. Experimenting with "future technology" may be motivating as well as revealing that chemistry is a science still in progress.

Access to new materials, equipment and knowledge makes it possible to develop experiments that address novel issues and methods in electrochemistry education. Such experiments are not often accessible in textbooks, but instead e.g. in journals (Ibanez *et al.* 2004; Ibanez *et al.* 2005; Kamata and Paku 2007). However, there is a gap between these two sources of knowledge, which chemistry educators should aim to bridge.

6 General discussion of papers presented in part 2

This chapter summarizes, for the convenience of the reader, the results presented in Part 2 and discussed so far in Part 1.

A small scale and low cost apparatus for the electrolysis of water (paper 1)

This paper describes how to construct a simple and very cheap apparatus for the electrolysis of water made by disposable pipettes and iron wires. Two set-ups are presented, one with a separate collection of hydrogen and oxygen, and another in which the two gases are collected together. These experiments can be conducted without any laboratory facilities, as the chemicals used are not harmful. The small size make both consumption and waste of chemicals little.

Small-scale and low-cost galvanic cells (paper 2)

This paper describes the construction of two small, simple, and illustrative galvanic cells that can be made with modest laboratory facilities. The first is a cell made of a Mg ribbon, a neutral salt solution held in place by floral foam, a graphite rod and a copper salt solution. The second construction is a small battery consisting of zinc rods, graphite rods, thin silver wire, a neutral salt solution and a copper salt solution. A LED is used to visualize the energy produced. These constructions and experiments demand modest laboratory facilities.

Small-scale and low-cost electrodes for standard reduction potential measurements (paper 3)

This paper describes the construction of a copper electrode that can be used as a secondary reference electrode. A hydrogen electrode and a chlorine electrode are made in order to calibrate the copper electrode. The copper electrode is made of a disposable pipette, copper wire and 1,0 M copper salt solution and a gel containing salt. The advantage of these electrodes is that they are low-cost and simple to make.

By being small, the amount of chemicals used is reduced, thus there is both a cost and environmental benefit.

Hydrogen electrode (paper 4)

This paper describes the construction of a hydrogen electrode for direct measurements of "standard" reduction potentials. The electrode is made from a disposable pipette, 1,0 M HCl, a piece of platinum wire and a gel containing salt. The advantage of this electrode is the possibility to measure "standard" reduction potentials directly.

Reconstructing iconic experiments in electrochemistry – experiences from a history of science course (paper 5, manuscript)

This paper explores in a contextual frame the experiences of reconstructing the electrolysis of water with an instrument from the historical collection at NTNU. A Voltaic pile was built to provide the electric energy. The paper also describes the use of these instruments in a teaching setting, and the benefit and entertainment that followed.

Daniell cell (paper 6, manuscript)

This paper describes the reconstructions of the Daniell cell and cells resembling Volta's "Crown of cups". The results from my reconstructions are collated with Daniell's original papers. An attempt to explain why a galvanic cell with U-tube as salt bridge is a common model in chemistry textbooks is also included.

Laying the Daniell cell to rest (paper 7, manuscript)

In this paper we argue that the so-called Daniell cell as depicted in textbooks should be laid to rest as a model for a galvanic cell in the teaching of electrochemistry at an introductory level. This is based on historical, chemical and pedagogical arguments. By this paper we hope to stimulate to further discussion and hopefully to improved models.

7 Concluding remarks

In this thesis, I have discussed experiments in electrochemistry education and the relation between text, figures, concepts and experimental setups. As shown, the electrochemistry in general chemistry textbooks has little emphasis on current aspects of electrochemistry. In some cases (as with U-tube galvanic cells) these set-ups are hardly seen outside the educational system. The examples given in textbooks are not referred to as historical, even though they resemble historical examples more than contemporary ones.

The difficulties students experience when learning electrochemistry is enhanced by the multitude of concepts involved. Some of these concepts are vaguely explained, if at all, in the textbooks, and the use of different terms for the same phenomena is also abundant.

The educational system contributes to both general knowledge and to the education of future scientists. To accomplish these tasks, the emphasis on methods from the 19th century is questionable. Alternatives exist to address basic electrochemistry and at the same time direct the subject more towards today's situation and challenges. This could include the introduction of new models and alternative working methods as well as a change in context. I have questioned the current terminology and argued for alternative educational methods in electrochemistry; and in the papers attached there are descriptions of new experiments for electrochemistry education as well as reconstructions of some historically important inventions.

My desire is that current learning and understanding of "current chemistry" should soon become less confusing and more inspiring!

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Paper I

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Paper II

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Paper V

Reconstructing iconic experiments in electrochemistry – experiences from a history of science course

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Introduction

This is a story describing the challenge and entertainment of restaging the experiment to decompose water with electric energy from a voltaic pile in a history of science course. The instrument used for the decomposition of water was a demonstration instrument from the historical collection at the Department of Physics of the Norwegian University of Science and Technology. The voltaic pile we made was inspired by Volta's description from 1800.

A course and historical collections

At the Departments of Physics and Chemistry at the Norwegian University of Science and Technology[1] we have within the last ten years managed to collect historical scientific instruments and other objects, as well as archive material from the former institution, the Norwegian Institute of Technology, which was established in 1910. In 2006 we started a course in the History of Science in which we decided to reproduce some classical experiments with instruments from these collections. Our motivation was mixed and at least four aspects were compelling. The first was that by displaying instruments and experiments in a history of science course we would illustrate the material cultures and contexts which otherwise are "illegible to those who know how to read only writing" (Quote: Lubar & Kingery 1993, p.viii; Rentetzi 2007, pp.xiii-xiv; Wittje 2003). Through restaging of historical experiments past challenges and confusions could also be reopened and reflected on (Cavicchi 2006). Second we needed to activate our collections as they compete with modern instruments for space in the science departments. Third we were curious about our collections and reconstructing experiments is one way to obtain more intimate knowledge. Last, but not least, we would enjoy ourselves and reconstructing some experiments. We acknowledge that professionals from museums might feel discomfort on behalf of our objects, but we believe that our collections should be activated into teaching and research, nevertheless preservation is also our concern.

A modest instrument, a classical experiment, an icon?

We had decided to air one of our instruments, but which one? From the historical physical cabinet there were beauties to choose between, such as the polariometer, goniometer, spectrophotometer, electrometer, torsion balance or refractometer used in teaching and research at our institution. After some pondering we chose a modest little instrument used in teaching, which was appropriate as our course is mainly aimed at prospective science teachers, namely an instrument for demonstrating the decomposition of water using electric energy. We could think of several reasons for choosing this experiment. The electrical decomposition is a classical experiment with a unique history. It is an iconic experiment in both physics and chemistry teaching, although both the purpose and conclusions vary between these disciplines. For chemists, the experiment is closely related to the constitution of chemical substances and the quantitative relation of hydrogen and oxygen in water. It would be an exaggeration to claim that physicists whole-heartedly share this view. For the physicists the canonical role of the experiment in their teaching is rather related to the chemical effect of electricity and thereby the very nature of electricity itself. Another use of the decomposition apparatus is as a voltameter. In a voltameter, the decomposition is no longer the object of investigation or the epistemic thing (Rheinberger 1997); it becomes a measurement principle to measure current.

A long history

Electrolysis of water has a history of more than 200 years. Our instrument, dating from 1910, is nicely set in the middle of that period. At the beginning of the nineteenth century electricians often performed this experiment after Paets van Troostwyk and Deiman (1789), Pearson (cited in Faraday 1849, p.92), Carlisle and Nicholson (Nicholson 1800) and Hildebrand (1805) had pioneered the work. The experiment was part of the important debate on the very nature of water and its composition. In the course of the 19th century it became widely disseminated and a remarkable example can be found in *Les Merveilles de la Science* of Louis Figuier (1868). After the establishment of the Norwegian Institute of Technology in 1910, electrolysis of water soon became part of the regular teaching (figure 1). It continued to enjoy a prominent place in Norwegian chemistry textbooks from the first decades of the twentieth century (Bruun 1920, pp.17-18)[2] and still figures in today's textbooks on general chemistry (Chang 1994; Zumdahl 2003, p.857) as well as in the Journal of Chemical Education (Eggen & Kvittingen 2004; Heideman & Wollaston 1986; Zhou 1996). Although less common in physics textbooks today, the experiment appeared regularly in textbooks between 1920 and 1970 (Arnljot 1968, pp.165-166; Bruun & Devik 1965, p.126; Holmsen & Strøm 1942, p.77; Holtsmark 1925, pp.116-117; Jansen & Eskeland 1946, pp.170-171; Lubar & Kingery 1993). The purpose of decomposition of water has changed over time, from being part of the evidence that water consists of hydrogen and oxygen (Pearson as cited in Faraday 1849; Hildebrand 1805; Troostwyk & Deiman 1789), to a proof, in Norwegian textbooks, of the law of definite proportions 1940, (Bruun 1920, pp.17-18; Holmsen & Strøm 1942, p.77; Jansen & Eskeland 1940, pp.101-102; Kåsa & Strøm 1939, pp.111-112) and finally as part of general electrolysis (Chang 1994, pp.793-794; Zumdahl 2003, p.857). For the physicist, the voltameter represents a quantitative method to measure current. Judging from the catalogues of Max Kohl (Kohl, pp.615-617)[3] and Leybold (1913, pp.702-707), which included 10-15 examples of the voltameter, the decomposing of water was a popular activity around 1900. Even a Norwegian school supplier had seven varieties in its catalogue (Jacobsen 1903, pp.66-68).

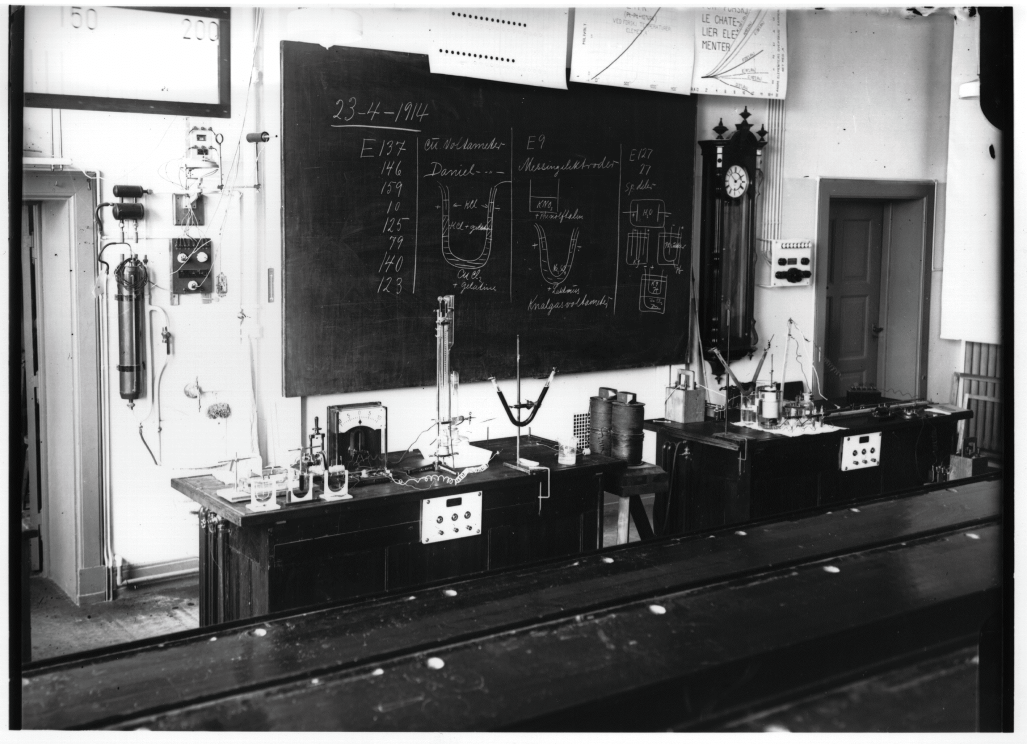

FIGURE 1. Demonstration experiments in the physics lecture, 23. 4. 1914, at the Norwegian Institute of Technology. The topic is electrolysis. Courtesy of the State Archive in Trondheim (Statsarkivet i Trondheim), Archive for the Norwegian Institute of Technology, Department of Physics, Ua:1 and Uc:1.

A Norwegian context

Our apparatus, although not particularly beautiful, was made by the Norwegian instrument maker Ole Georg Gjøsteen (1854-1936) (NBL 1929). Gjøsteen, a man of considerable initiative, combined political aspirations, in particular on school issues in the Labour party, with a life-time job as an instrument maker and janitor at the University of Oslo. To add to his income he started a company to supply educational equipment to schools as the university sector was a meagre market with only one in the whole of Norway at the time. Gjøsteen's life is an interesting story in itself, linking our institution at the fringe not only of Europe, but also of Norway, to the central institutions, theories and experiments within science and chemistry, as well as to a life at the so-called lower end of the social ladder at the university. In the context of our reconstruction of electrolysis of water, he is our national as well as local anchor, through the presence of his apparatus in our collection.

Everybody knows it

Electrolysis of water is an experiment that 'everybody' has conducted and 'everybody' apparently knows will work, from Primo Levi, in his beautiful book *The Periodic Table*, where he describes the experiment as "an experiment with a guaranteed result" (Levi 1989, pp.21-28) to a relatively recent description in *Journal of Chemical Education* in which the author claims that only a truly sheltered student has not seen this as a classroom demonstration at least once. He further says that we (teachers) know that "exactly 2 moles of hydrogen gas (H_2) evolve at the cathode for every mole of oxygen (O_2) produced at the anode" (a statement which we also found in textbooks) and that "the measured volumes of evolved gas nicely illustrate several important relationships: stoichiometry, combining volumes (Gay-Lussac), the Avogadro hypothesis, Faraday's laws, etc" (Kelsh 1985). So, this is apparently a simple experiment with a predictable outcome and therefore it was a good candidate for our reconstruction and the airing of an object from our collection. Wealso had some previous personal experience with the electrolysis of water, we thus were relatively confident that we would succeed in reconstructing the experiment using Gjøsteen's apparatus. Retrospectively, we are amazed we were that ignorant, considering that some of us are relatively seasoned experimentalists with enough experience to know that no experiment is straightforward, without surprises and will work immediately.

In order to conduct the electrolysis we needed an electric source. The batteries used with Gjøsteen's instrument were gone and dry cells seemed awfully out of place and, as the reader can probably guess, electrolysis of water is so closely connected to the voltaic pile that we decided to reconstruct one. Thus at this point we were expanding our historical collection with a new replica of a historical object. One might well argue that it is anachronistic to use a voltaic pile, dating from the early 1800s, together with our decomposition apparatus from 1910. A quick look in our instrument catalogues, however, reveals that voltaic piles were still common instruments for teaching purposes in the early twentieth century, even though they had disappeared from research and other technical applications long before (Kohl).

An electric source - another icon

The voltaic pile, similarly to the splitting of water by electric current, is an icon in the history of experimental chemistry and physics. They are often also combined. Volta's paper (Volta 1800), dated 20th March 1800 to Sir Joseph Banks at the Royal Society, in which he describes the construction of the pile, was read by Carlisle, who shared it with

Nicholson (Pancaldi 2003, pp.212-221), even before it was announced to the Royal Society on 26th July 1800. Within months the construction of the pile was disseminated to different milieus and to various European cities. This was very much associated with the pile as a powerful machine for chemical purposes, initially important in the discussion of the composition of water, and soon also in the isolation of new elements (Figuier 1868; Pancaldi 2003, pp.212-221). In the July number of Nicholson's Journal[4] parts of Volta's paper were cited together with a multitude of experiments already made by a variety of scientists who had obtained the description of the pile (Figuier 1868, p.400; Pancaldi 2003, pp.212-221).

The importance of the pile can probably not be overestimated, and several authorities have emphasized this; from Heilbron (1999, p.494), who described the pile as a discovery that "opened up limitless fields", to Tom Tit (alias Arthur Good) a century previously, who reckoned the pile to be one of the three most precious apparatuses in any curiosity cabinet (Good 1898, p.64), as well as Louis Figuier some decades before, who described the implication of the pile for the decomposition of water as: "It is by the means of this instrument, with an elementary simplicity and a quite mediocre puissance, that Carlisle decomposed water, that is to say accomplished the most fecund of the discoveries which have been made with the pile of Volta, as it revealed equally to physics and to chemistry a horizon without limits" (Figuier 1868, p.400, our translation).

Experimenting, re-reading, rehearsal and re-rehearsal

At this point our primary aim was to decompose water with an electric current using Gjøsteen's apparatus. The use of the voltaic pile to achieve this was initially merely subsidiary. So what happened? As the pile is so well known, we set off, to be perfectly honest, without reading Volta's paper at all. The pile is depicted in so many places; anybody knows it is sufficient to shuffle two types of metal plates and some humid layer in between, which we did. About 30 plates were assembled and nothing happened, not a single little bubble could be detected at the electrodes, even with a magnifying glass. We live in the twenty-first century so a voltmeter was obtained and plainly displayed 0.0 V. A good laboratory advice states 'if everything fails, read the manual' so we did. In Volta's letter the 'artificial electric organ', that is the pile (Volta 1800), was meticulously described and clearly we had made mistakes, when unintentionally applying today's view of electrolytic cells and placed an electrolyte in between each metal disc.

We started rebuilding, and soon found ourselves entangled in the field of experimenting, where a series of decisions might determine the outcome of the experiment. In between the pairs of copper and zinc plates a solution of imbibed materials was to be used. Which material? Pieces of skin? Carton? Which type? Possibly filter paper? The size, did that matter? What about the liquid? Were we to use pure water, salt water, soapy water; and what about the concentration? There were some answers in Volta's text, yet choices and compromises were necessary.

We ended up using filter paper as this was of a suitable size, and table salt (sodium chloride) of unknown concentration, as well as an imbibition of unknown amount. According to Volta, the electric energy came from the contact between the metal plates, so these needed to be in contact, which we tried to achieve by pressing the column together with appropriate, that is unknown, force. When we connected this pile to our apparatus, bubbles indeed appeared, minute, unmistakably, but so slowly. The temptation to use the dry cells lying around was hard to resist as we struggled to adapt to the new time scale, but we did not waiver – initially. As it took hours and hours, we eventually went away, got distracted and forgot the whole experiment and returned the next day. What did we find? Gas had been evolved, in both test tubes, but clearly there was no 1:2 ratio between the oxygen and hydrogen gas, as can be seen in Figure 2. For the next period we repeated the experiment again and again, varying electrode material, electrolyte, voltage, saturating the solution with the gases, etc. However we never reached a precise 1:2 ratio, which is said to be easy to obtain, although, with some practice, we approached this ratio.[5] Then other duties called. The pile was left for some weeks before we returned. To dismantle it, we found that the most useful utensils were a hammer and chisel. The whole column had become as hard as concrete. Rereading Volta was of no help, the only problem he mentions is that of a too dry column, which he kindly suggests should be re-humidified. Our pile was put to swim in various solutions without much effect. Somehow Volta never mentions dismantling the pile, and we now understand why[6]. But we wanted our students to build the column, so the metal plates had to be presented in a recognisable state. That meant, after the struggle of dismantling the pile, we had to scrape and clean the plates for days and still they were far from good-looking. This experience, however, clearly indicated one of several problems with the Volta pile. We were therefore pleased when we discovered that also Cruickshank (1801) complained about the maintenance of the pile. He then turned it on its side to form the so-called trough battery, one of the first steps in the improvement of voltaic cells (Cruickshank 1801).

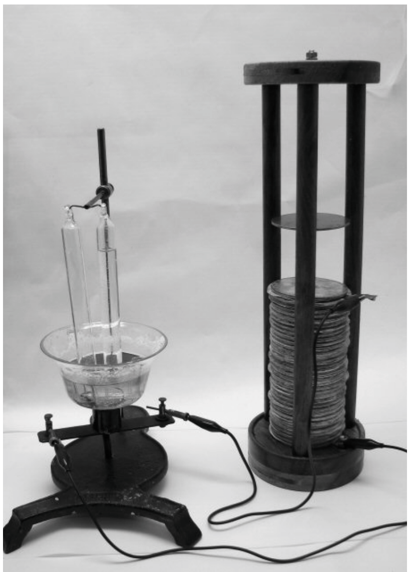

FIGURE 2. Ole Georg Gjøsteen's apparatus for the decomposition of water connected to a voltaic pile. Note that the left hand test-tube is full of hydrogen, whilst the right hand test-tube is approximately 1/5 full of oxygen.

Premiere

During the premiere the students were urged to build the pile. The repetitive action, of putting 60 roundels each of zinc, copper and ox skin (filter paper having been abandoned long before) on top of each other, lasted for some time, creating a kind of monotonous ambience. The students had no expectations and were politely interested. When finally completed, we decided to verify the power of the pile before connecting it to Gjøsteen's water splitting apparatus. Around 1800, a prime instrument for analyzing the effect of the pile was the human body. We were again inspired by Volta, who had applied the terminals from the pile to various parts of his body, from hands to eyes, tongue and ears. Volta reported that he could feel the incremental increase in power as new pairs of plates were added. The effect being noticeable already from 4 to 5 pairs (Volta 1800), which we were entirely unable to discern. Again, not able to deny ourselves a voltmeter, we felt its readings almost confirmed our lack of senses. Were Volta's experimental results thus theory-laden? One should not underestimate Volta and his contemporary experimentalists' excellent senses and knowledge, and our lack of such.

Nevertheless, after completing a pile of 60 units we made a ring, held hands (salt wetted) and electrocuted both the students and ourselves. The peaceful atmosphere evaporated immediately as we received shocks, which seemed to be an unevenly distributed experience.

Afterthoughts

During the period of experimenting, there was ample time to question statements, descriptions and phrasing in Volta's text, but also of the contextual framework. Some fairly obvious ones were: Why did he construct it in the way he did? Which inspirations, struggles, previous work and other scientists were he inspired by or relied on? As we did not have much time at our disposition we restricted ourselves to one of his comments about the electric fish (the torpedo fish) and the electric eel, both extraordinary animals on several counts. Volta actually calls his pile 'an artificial electric organ' directly inspired from 'the natural electric organ' of the electric fish or eel (Picccolino 2005; Walsh & Seignette 1773-1774) Developing this theme, Volta actually suggested that one could enclose the whole pile with a material/skin and make a well-configured head at one end and a tail at the other. Then, Volta wrote, the 'artificial electric organ' would not only resemble the electric eel internally, but also externally (Volta 1800). This seemed an attractive idea to us, but we decided the other way round, that is to investigate a 'natural electric organ'. At the local fish market we purchased an 'arctic electric eel', brought it back and started laparoscopy at an appropriate place, the flank. By enlarging the hole a bit, we got a glimpse of the inside and apparently there was something resembling pictures of 'the natural electric organ'. At that moment, we felt that chemistry, biology and history were wonderfully united; indeed we experienced a temporary moment of eureka. Such transient moments are well worth cherishing, a fact any experimentalist knows, as we were soon to realise that something was wrong. Evidently our eel was not electric, and the place of our dissection was less than accurate as the electric organ is to be found close to the tail, plainly revealing our lack of biological knowledge. So one more lesson, after struggling and enjoying ourselves when trying to reconstruct two iconic experiments in the history of chemistry, was that we had to agree with the Mayor of la Rochelle, who attended experiments with the electric fish performed by Mr Welsh in 1773, on which he reported: "That indeed all yet done was little more than opening the door to inquiry" (Walsh & Seignette 1773-1774, p.468).

Epilogue

There were several objectives at the outset of our reconstruction of these historical experiments using one of the modest objects in our collection, but a major one was to incorporate an experiment with a live performance for the students in our history of science course. As we had struggled and enjoyed ourselves to a far greater extent than we had anticipated through the whole process, an ownership and deeper interest had developed, which gave momentum to adapt our new knowledge for further dissemination to a broader audience. An unforeseen result is that this experiment has become a good "candidate" when receiving visiting school children. And in the enthused meeting with the youths our reconstructed experiment has corroborated its own existence.

Acknowledgement

Our thanks are due to instrument-maker Egil Thorsetnes, NTNU, for making parts for our pile, to Berit Bungum for lending us her collection of physics textbooks.

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Endnotes

[1] NTNU was established in 1996 as a further development of the University of Trondheim (UNiT). UNiT was established as a result of a merger between the Norwegian Institute of Technology (NTH), The College of Arts and Sciences (AVH) and the Museum of Natural History and Archaeology. For a perspective on the founding of NTH, see Wittje (2006).

[2] Bruun authored textbooks for gymnasiums both in chemistry and physics; both held large market shares. Bruun's chemistry text appeared regularly from 1914 until the end of the 1970s (see *Sverre Bruun og Olaf Devik - et lærebokjubileum* 1964).

[3] The year is unknown, however, the catalogue probably originates from the period 1926-1936.

[4] The *Journal of Natural Philosophy, Chemistry and Arts*, edited by W. Nicholson was commonly called the Nicholson's Journal or Nicholson's Philosophical Journal

[5] Some authors mention deviations from the 1:2 ratio explaining these as current density/voltage, absorption of hydrogen onto the Pt-electrodes, production of ozone when electric current is passing through oxygen and unequal solubility of the two gases in the aqueous solution (e.g.Kelsh 1985; Poyser 1889; Zhou 1996).

[6] On the other hand W. Nicholson, when reporting on Volta's invention, mentions chemical reactions taking place within/on the pile and problems of recovering the plates. See Nicholson (Nicholson 1800).

Paper VI

The Daniell cell, a source of constant current, confusion and understanding

An attempt to reveal the reasons for its long life as model in chemistry education

Introduction

It is claimed that the Daniell cell for many years has been the "prominent and dominant (if not the only) cell" used as a model for galvanic cells in chemistry textbooks (Boulabiar 2004). This galvanic cell was constructed by John Frederic Daniell (1790-1845) in the middle of the 18th century under the name "The constant battery" (Daniell 1836), and the invention contributed considerably to battery technology at the time. Its use as a current source ceased more than hundred years ago, but despite this, it is still abundant in electrochemistry teaching. In this paper, the invention of the Daniell cell as a major step forward in battery technology, and as a common model in education will be discussed. Looking back, we can see "Daniell cell" used as name for many different types of zinc-copper cells. The relevance of some of these versions for teaching purposes is questionable, and so is the sometimes-odd disparity between use and construction. It will be argued that the selection of different models carrying the same name shows that the "Daniell cell" is not only a historical construction but has developed to a concept with its own meaning.

The Daniell cell's status as an icon in chemistry education is in many ways a paradox. None of the batteries normally available for sale today are zinc-copper cells, and the original Daniell cell has not been used to any extent since the 19th century, except from as a model in chemistry education. The most noticeable paradox is however, that chemistry textbook authors have held on this model to such an extent. Since it is no longer used as a source of electricity, and does not resemble batteries familiar to students from everyday life, it is hard to explain why it seems to hold its position as the first choice when describing galvanic cells.

To understand the improvements entailed by the Daniell cell, an exemplar of the cell from a historical collection was tested in our laboratory and compared with reconstructed galvanic cells resembling pre-Daniell batteries. This gave the chance to experience what challenges the users faced and the improvements they experienced with the Daniell cell. The results from this testing is held together with descriptions of 19th century batteries from other sources, and with Daniell's own descriptions of his work, to give insight into the problems the Daniell cell contributed to resolve. In the last part of the paper examples of so-called Daniell cells are provided. These examples show an evolution of the Daniell cell as textbook model from the first appearance in 1836 and until today (2010), and possible reasons for its status in education are discussed.

Batteries before Daniell's time

When Volta presented the voltaic pile in 1800 (Volta 1800), scientists (and others) got a source of electricity that opened many new opportunities, and it was immediately put to use by a number of European researchers (Pancaldi 2003). This had great impact on chemical science as well as studies of magnetism and electricity, with Davy's discoveries of e.g. sodium, potassium and aluminium as famous examples. Before 1840, batteries were not to a large degree applied in practical matters apart from in science. One exception from this was the first telegraph stations that depended on batteries, but did not require high currents. The "Crown of cups", another variant of Volta's battery inventions, was sometimes used for this purpose (Schallenberg 1977).[1] This variant consisted of the same elements as the voltaic pile, but arranged as a chain of cups filled with ionic solution linked together in a circuit (Figure 1).

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[1] According to Niaudet, Volta created the Crown of cups before he constructed the pile (Niaudet 1880)

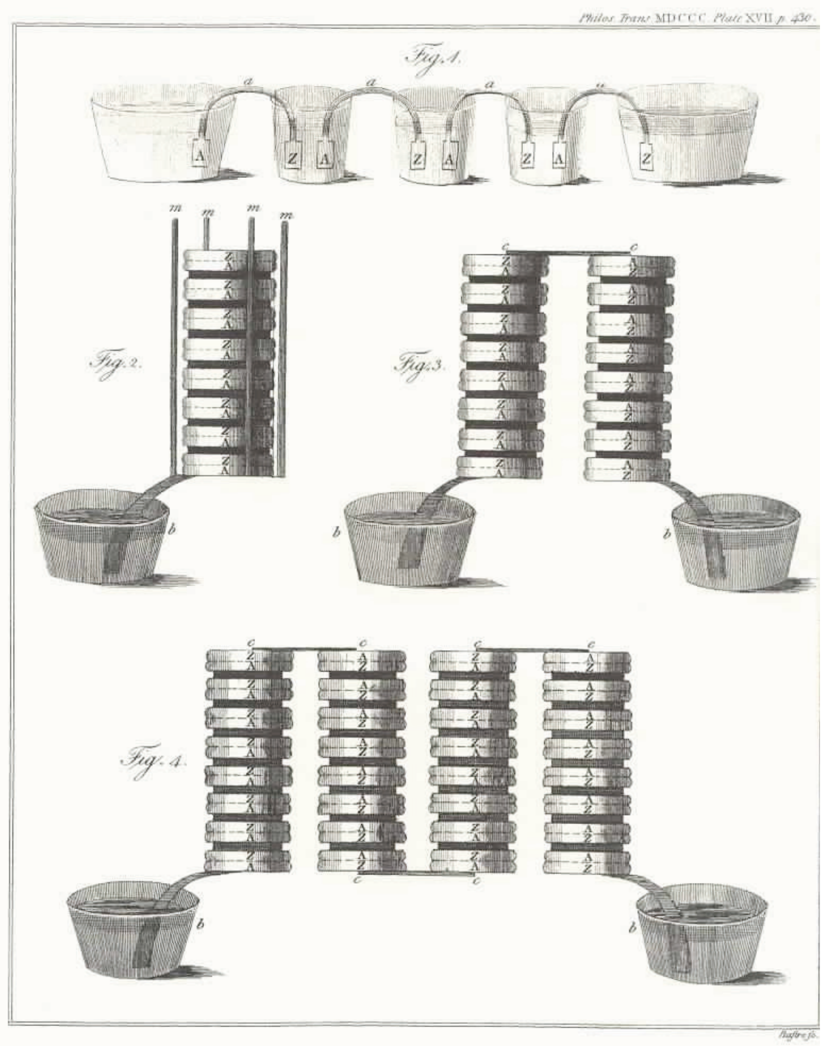

Figure 1
Voltas own figures showing the Crown of cups (on top) and different setups of the Voltaic pile (Volta 1800).

The Voltaic pile was an upraised pile of zinc and copper discs paired together. Each metal pair was separated by pieces of paper, leather or cloth soaked in electrolyte solution. Both the Voltaic pile and the Crown of cups had disadvantages that limited their use. One was the quickly decreasing effect. The pile was also puzzling to put together, and the construction was heavy, causing the electrolyte solution to be squeezed out from the bottom discs. The disc components reacted to each other even when the pile was disconnected and hence did not create electricity (Niaudet 1880). These reactions caused a “cementing” of the pile, and made it complicated to disassemble and clean. The crown of cups to some degree had the same disadvantages as the voltaic pile, and also took up more space. The descriptions of these disadvantages were to some extent confirmed in the reconstructions described later in this paper, but also in our reconstruction of the Voltaic pile. (Eggen *et al.* 2010)

All the batteries between 1800 and 1836 were according to Niaudet, who wrote a contemporary treatise on electric batteries, variants of the Voltaic pile (Niaudet 1880), having single elements in which two different metals were directly connected. Instead of standing piles one could put the piles (horizontally) in a wooden trough filled with electrolyte solution. Hence, lifting the piles out of the trough could turn the battery off. Cruickshank’s battery was a version of a ”trough battery” published in 1801 (Cruickshank 1801; Dobson 1970). In Daniell’s textbook from 1839 he mentioned two batteries that appear to be forerunners of his own (Daniell 1839), Cruickshank’s being one of them and the other constructed by Wollaston. When describing his own “constant battery” he compared it with “the common batteries” which were Wollaston’s batteries, indicating that these were the most commonly used batteries at the beginning of the 1830’s (Daniell 1836 a; Goodman 1970). These “voltaic” batteries could provide high voltage and current shortly after they were put together, but the effect decreased rapidly (Schallenberg 1977).

Several factors complicated the use of batteries. Daniell mentioned these problems in the introduction of his article where he described “the constant battery” (Daniell 1836 a) as well as in his textbook (Daniell 1839). He describes the electrolyte as a mixture of sulphuric and nitric acids. In traditional batteries this would lead to corrosion of the zinc electrodes. This corrosion was an important reason for the development of batteries where the electrode could be removed from the electrolyte when the battery was not used. In addition to corrosion, “deoxidation of zinc oxide” on the copper discs led to a rapid decrease in effect. (Daniell 1839, page 438). Deoxidation of zinc oxide is explained as the reduction of zinc ions to metallic zinc on the surface of the copper or platinum electrode (Daniell 1836 a; Owen 2001). This will be discussed later, in connection with the reconstruction of pre-Daniell cells. The zinc deposit caused a considerable drop in voltage between the two electrodes. Since both electrodes were placed in the same solution, there could also be a deposit of copper on the zinc electrode. On top of this, the acidic electrolyte[2] created hydrogen gas on both electrodes. The gas bubbles decreased the connection areas between the electrolyte and the metal electrode. (Owen 2001). The reason to use strongly acidic electrolytes was to provide higher current and improved durability[3].

The creation of metal deposit or hydrogen gas on the copper or platinum electrodes was called “polarisation” of the discs. This term is not normally used in contemporary electrochemistry textbooks, but was more common in the 19th century. One example of an explanation of the term is found in the book “Primary Batteries” by W. R. Cooper: ”Polarisation may be defined as a temporary reduction in E.M.F. due to an alteration of the electrolyte, or of the plates, brought about by the voltaic action of the cell.” (Cooper 1901). Polarisation caused decreasing voltage, and was therefore a problem.

Batteries used in the first half of the 19th century required much maintenance, but since the batteries were mostly used for research and in telegraphy, keeping them in good repair, according to Schallenberg, was manageable. This because researchers often hired technicians to take care of the batteries (Schallenberg 1977), and the telegraph stations had full time employees who besides the telegraphing could manage battery maintenance. After some time the need for batteries that were ”capable of withstanding a maximum of mistreatment and neglect” emerged (Ibid). This happened because the need for electricity for telegraphy and electrolysis increased and at the same time, work operations were streamlined. According to Schallenberg the improved labour efficiency with fewer employees combined with higher levels of production, resulted in less time for battery

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[2] Daniell describes different electrolytes. In most cases a solution of sulphuric acid is used and some times nitric acid as well.

[3] Today this can be connected to the reduction of H^+.

maintenance. When science and telegraphy after a while requested more powerful batteries, the Daniell cell represented important progress.

Daniell explained that his main motivation for improving the battery was to make a stabile source of electricity. However, the rather modest need for maintenance turned out to be another great advantage of his invention (Ibid).

The Daniell cell as a tool for understanding electricity

Daniell became a professor of chemistry at Kings College in 1831 (Thackray 1971; Davies 1990). He practiced experiments as a part of lectures, and the development of better laboratory equipment and experiments became an important part of his work (Daniell 1845; Partington 1964; Mertens 1998)[4]. The first battery he invented was the "dissected Battery", made in containers of glass (Daniell 1836). The glass made it easy to see their construction and thus suitable for teaching purposes. Later he made several changes based on both his own work and the research of others. These changes resulted in a battery with substantial advantages compared to the alternatives existing at the time (Day and McNeil 1996; Boulabiar 2004), and was according to Wilhelm Ostwald "The first cell that we can call a constant cell" (Ostwald 1896). Daniell's new battery was presented in an article formulated as a letter to Faraday where he writes: "I have been led to the construction of a voltaic arrangement, which furnishes a constant current of electricity for any length of time which may be required; and have thus been enabled to remove one of the greatest difficulties which have hitherto obstructed those who have endeavoured to measure and compare the different voltaic phenomena, viz. the variableness of the action of the common batteries*."*(Daniell 1836 a)

The purpose of constructing new batteries was apparently not mercantile, but instead scientific. The separation between "useful art" and "philosophy" was important at the time. Daniell emphasized this separation in his lectures (Mertens 1998). The scientific purpose is visualized in the title of his textbook from 1939: *An Introduction to the Study*

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[4] See the obituary printed in "Elements of Meteorology" published after Daniell's death: Daniell, J. F. (1845). Elements of Meterology. London, John W. Parker, West Strand.

of Chemical Philosophy: Being a Preparatory View of the Forces which Concur to the Production of Chemical Phenomena and also in the name of the journal/periodical where his work was published: *Philosophical Transactions of the Royal Society of London*. Electrochemistry at Kings College was thus not considered as “Useful art” with technological and practical purposes, but as a “chemical philosophy” directed towards research and teaching.

Since the goal of Daniell’s work was scientific studies of electrical phenomena (Daniell 1836 a), it can be assumed that the development of the battery was based on his understanding of electricity. At the time he was hired at Kings College, different theories about the source of electricity existed. Already before the construction of the Voltaic Pile there were at least two theories about source of energy. Volta named it ”forza motorice”, in English meaning ”electromotive force”. Volta considered whether electricity was created as a consequence of chemical reactions, but rejected this view and soon defended the theory that *the contact between two different metals* was the source of electric power (Kragh 2002, page 135)[5].

Daniell supported on the other hand the alternative main theory, that the source of electric current was *chemical reactions* (Kragh 2002). As has been shown by Kragh, this theory had a lot of followers already from the end of the 18th century, but it did not reach a breakthrough until Michael Faradays article *On Electro-Chemical Decomposition* appeared in 1834 (Faraday 1834). Daniell cooperated with Faraday through several years, and the explanation of electricity in his own textbook was based on Faradays theory: ”Professor Faraday was the first to prove, by an unambiguous experiment which we have already described (§ 721), that the contact of dissimilar metals is not necessary to the generation of a Voltaic current, and that the force is exactly proportioned to the amount of chemical action.” He completed the chapter by stating: “It is not, of course, denied that electricity is developed by the contact of metals; but it is small in quantity, of high

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[5] Daniell discussed Volta’s theory in his textbook but clearly shows that this is a view he does not share. Daniell described Volta’s theory of contact as ”the source of electricity was the contact of the dissimilar metals” and further on “The interposed liquid was regarded by the inventor of the pile merely in the light of an imperfect conductor, which allowed of the accumulation of the electrical fluids, disengaged by the electro-motive power of the metals, by a species of inductive influence. “ (Daniell 1839, pp 437-438)

intensity, and intermitting in its action; and to generate a current, the contact of a compound liquid with a metal seems to be necessary, as has been before explained." (Daniell 1839, p 438) Here Daniell clearly demonstrates that he does not base his work on Volta's theory, but that the source of electricity in galvanic cells can be found in chemical reactions, like Faraday, as Daniell sees it, proves.

Daniell's development of "the Daniell cell"[6]

Daniell constructed a battery to be applied in at least two different ways: as a useful source of electricity and as a teaching model (Daniell 1836 a; Mertens 1998). To measure what improvements he made compared to "normal" (Wollaston's) batteries, he needed an instrument, and for this purpose he chose to use a "Voltameter" (Daniell 1836 a). A few years earlier, Faraday described an instrument for measuring current in an electronic circuit, a "Volta electrometer", later called a Voltameter. In principle, the Voltameter is an electrolytic cell where the quantity of electricity is proportionate with the volume of the gas produced by electrolytic decomposition of water (Faraday 1834). Using the Voltameter, Daniell could investigate different variables of the battery and managed to make it less complicated and a more stabile source of electricity.

In his presentation of the "dissected battery" Daniell describes an important observation; that the battery would lose effect because of the zinc deposit on the platinum electrode. He used this discovery as part of the explanation for choosing an alternative construction of a zinc copper cell where the battery is divided in two compartments, separated by an ox gullet (Daniell 1836 a). The division into two separate half-cells, where the ox gullet constituted what we today call a salt bridge, prevented the zinc ions from being reduced on the surface of the other electrode (now made of copper instead of platinum).

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[6] According to J. R. Partington, F.W. Mullins (1836) and M. H. Jacobi (1838) made similar batteries independent from Daniell at the approximately same time Partington, J. R. (1964). A History of Chemistry. London, Macmillan & Co Ltd. .

. The French scientist Edmond Becquerel claimed that his father Antoine-Cesar Becquerel was the true inventor Niaudet, A. (1880). Elementary Treatise On Electric Batteries, J. Wiley & sons.

, Gough, J. B. (1970). Becquerel, Alexandre-Edmond. Dictionary of Scientific Biography. C. Gillispie, Coulston. New York, Charles Scribner's sons. **I**.

, Kay, A. S. (1970). Bequerel, Antointe-César. Dictionary of Scientific Biography. C. Gillispie, Coulston. New York, Charles Scribner's sons. **I**.

.[6]

Likewise copper deposit on the zinc electrode was avoided, at least until enough copper ions had diffused through the membrane (Arrhenius 1902). The battery was constructed in a cylindrical copper container, which at the same time functioned as one of the electrodes of the battery. In the centre of this cylinder, the ox gullet divided the cell in two compartments. The inner compartment (the inside of the gullet) was filled with diluted sulphuric acid[7] and equipped with an amalgamated zinc electrode[8] and the same siphoning system as the "Dissected Battery" (Kemp 1829). In the outer room of the copper container, the sulphuric acid solution was replaced with saturated copper sulphate solution. To keep this solution saturated, bags of cloth with copper sulphate crystals were added (Daniell 1836 a).

This construction had many advantages: There were no deposits ("polarization") on the electrodes, neither by metals or by hydrogen gas (Mertens 1998). Since the replacement of sulphuric acid with copper sulphate solution in the outer compartment prevented polarisation of the cell, the copper sulphate solution was called a "depolariser". Other advantages with Daniell's construction were that with two electrolyte solutions, he obtained stable, high electrolyte concentrations compared with the rapidly declining acid solution in earlier versions of the batteries, and it was no longer necessary to use high cost platinum electrodes. Already the same year (1836) Daniell published improvements of this battery where he reduced the size of the electrodes and removed ”the cumbrous addition of the dripping funnels", the siphoning system that kept the zinc electrode sprinkled with sulphuric acid solution (Daniell 1836 b). In this article it also seems like he was close to making another important improvement of the battery, noticing that a zinc sulphate solution functioned as electrolyte when surrounding the zinc electrode and that the battery was still working even when the acid was neutralized. In the years following, more changes were made, and in 1839 the ox gullet membrane was replaced with a porous earthenware container[9] as in Figure 2 (Daniell 1839).

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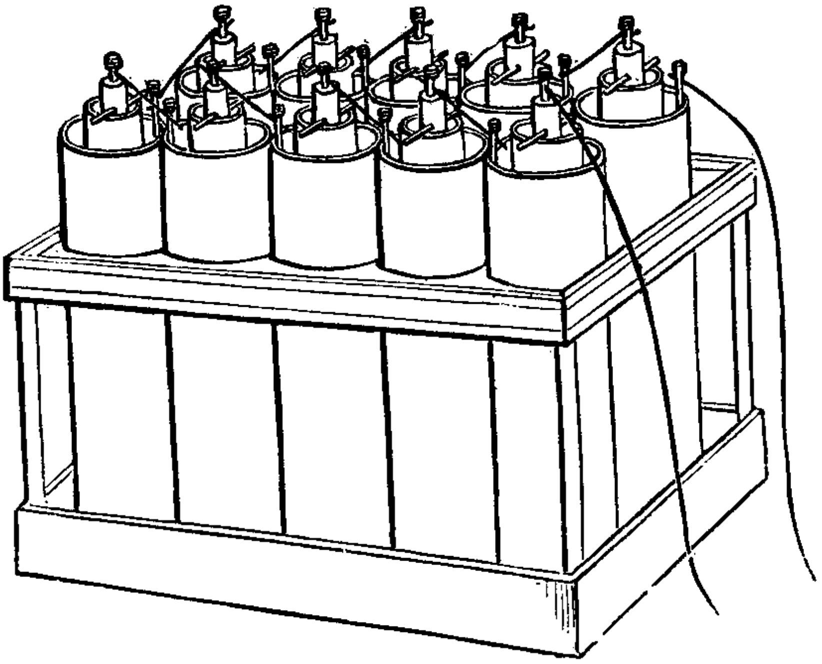
[7] ”8 parts of water and 1 of oil of vitriol" (Daniell, 1839)

[8] The amalgamation of the zinc hindered the oxidation of the electrode without reducing battery performance (Kemp 1829)

[9] Such porous cylinders of burned clay soaked with water were used as wine coolers.

Fig. 397



Daniell's Ten-celled Sustaining Battery.—(Fig. 397.)—

Figure 2
Illustration from Pike's laboratory equipment catalogue, New York (Pike 1856).

After Daniell's death, the Daniell cell was not only used as a battery, but also further developed. The acid solution surrounding the zinc electrode was replaced with a zinc sulphate solution to avoid corrosion of the zinc electrode when the battery was not in use, and this also made amalgamation superfluous. In 1880, Niaudet pointed out the same as Daniell himself insinuated in 1836, that when the sulphuric acid surrounding the zinc electrode was replaced by zinc sulphate solution, the battery still worked well (Niaudet 1880). When this change occurred is not known, but in Arrhenius' textbook from 1902 the Daniell cell is described as a cell with $Zn/ZnSO_4$ and $Cu/CuSO_4$, but the text makes it clear that the zinc sulphate solution is a result of the reaction between the zinc electrode and sulphuric acid (Arrhenius 1902). Later in the 20th century, the cells are described with zinc sulphate solution instead of the sulphuric acid.

In some variants of the cell the clay/earthenware cylinder was removed. This worked since the two solutions of zinc sulphate and copper sulphate have different specific mass, allowing the zinc solution to float on top of the copper sulphate solution without the two being blended. These batteries were called gravity batteries. There were a number of inventors of such cells, like Callaud, Meidinger and Varley (Niaudet 1880).[10] Some named their batteries after themselves, but often batteries with zinc and copper electrodes were called Daniell cells, regardless of the construction, as will be shown later. The Daniell cell was also used as a standard reference cell up until 1872 (Hamer 1978).[11]

The first textbook describing the Daniell cell was, reasonably enough, Daniell's own (Daniell 1839). More than 170 years later, in 2010, the cells emerging in several chemistry textbooks show different types of galvanic cells named "Daniell cell" (Wurtz 1876; Salveson 1975; Nebergall 1976; Lauritzen 1985; Chang 2008; Grønneberg *et al.* 2008). These cells differ from the original Daniell cell both in appearance and components, as will be shown and discussed later.

The discovery of "a beautiful pink layer of pure copper"

The Daniell cell was not only important as a battery but also because of the side effect of electricity production; the creation of what Daniell describes as "a beautiful pink layer of pure copper" on the copper electrode (Daniell 1836 a). According to Mertens, this discovery originated an industry of its own, namely electrolytic metallization (Mertens 1998). The product of the metallization industry was a metal surface layer on different items, and the batteries were the source of electricity that made this product possible. Alfred Smee, one of Daniell's earlier students at Kings College, described the Daniell cell as the source to electrolytic metallization, and Smee continued working with this effect of the electrochemical reactions. By this, the Daniell cell became both a source of

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[10] According to Niaudet Varley was the one who got the patent for the gravitation cell

[11] At the time there was no international agreement about which reference cell should be used, the concentration of the electrolytes was not decided, and the unit of Volt for emf was not introduced.

knowledge and a source of electricity in the establishment of electrolyses as an industry, but as a battery, other cells constructed by for example Robert Bunsen and William Robert Groves soon ousted it. Smee himself published a competing battery in 1840 with two zinc electrodes and one electrode made from platinised silver or copper in a sulphuric acid solution (Mertens 1998).

The Daniell cell compared to other 19th century batteries

Daniell was not the only scientist improving battery technology and electrochemistry at the time. William R. Grove's battery, like Daniell's, consisted of two half cells separated by porous earthenware.[12] It consisted of a zinc electrode in sulphuric acid solution, and the other of a platinum electrode in nitric acid. The advantage compared to the Daniell cell was that it provided a significantly higher voltage (1,8 - 2 V compared to 1,1 V) and also a higher current (Laidler 1993). The drawback was the expensive platinum electrode and the development of nitric gasses. The battery would also experience a drop in voltage as nitric acid concentration decreased. This battery still had some advantages compared to Daniell's. One example of the relevance of Grove's battery is that for a period of time it was the most popular source of electricity in American telegraph stations (Schallenberg 1977). Robert Bunsen constructed a similar version (Niaudet 1880). His battery was very much similar to Grove's, having an electrode made of carbon instead of platinum. This worked well and also lowered the price. Bunsen's battery was mass-produced for electrometallurgy. As new battery types made by Georges Leclanché, Smee, Callaud and Frederik L. W. Hellesen appeared, the Daniell cell was outdone as a source of electricity. According to Mertens these batteries were made after Daniell's battery became known, allowing inventors to use Daniell's work as a starting point (Mertens 1998).

Thus, in the end of the 19th century, many different batteries were available. Equipment catalogues from the beginning of the 20th century clearly shows that Daniell's battery was well known in many countries. (Gjøsteen ; Kohl ; Leybold ; Jacobsen 1903; Kohl 1905/1906; Pye 1926; Gallenkamp 1936). However, it did not dominate, and the selection in the catalogues indicates that the other batteries mentioned above also were

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[12] Robert Grove is also known as the inventor of the first fuel cell, a hydrogen oxygen cell from 1839.

used in teaching. By these catalogues, it is not obvious that the Daniell cell would be the battery most recognized by the posterity. The Bunsen battery and the Lechlanché battery [13]are two other examples that keep reappearing in the catalogues.

Reconstruction of the "Crown of Cups"

To understand the disadvantages of the batteries available before the Daniell cell, and thereby get an impression of the progress made by this new invention, series of simple reconstructions of batteries of the Crown of Cups type were made.

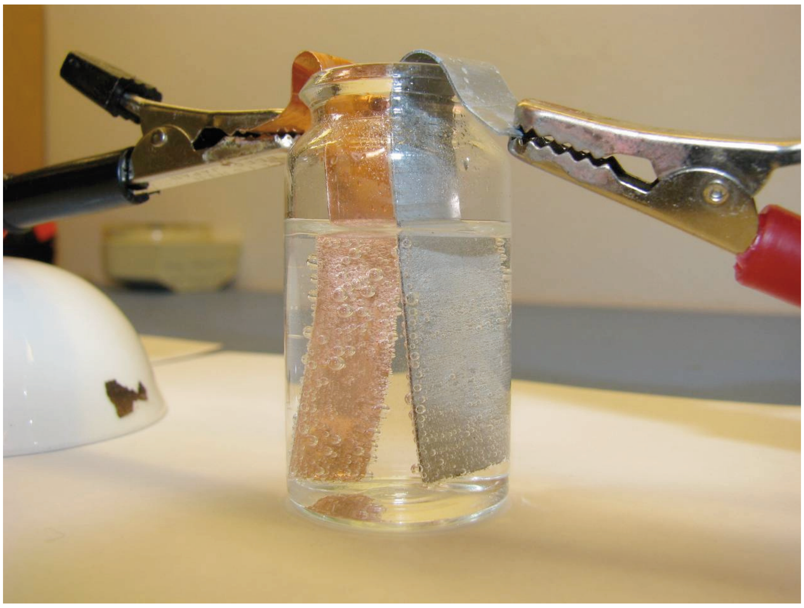

Figure 3
Zinc copper cell with 1/8 diluted sulfuric acid concentration as electrolyte. Two of these cells were connected in a series for the experiment.

In these reconstructions it was easy to see the disadvantages of having two electrodes placed in the same electrolyte. In the first attempt to get familiar with these disadvantages, three miniature versions[14] of the Crown of Cups were built (like the upper

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[13] The Lechlanché cell is commonly mentioned in textbooks, but as an example of a commercial battery, and usually not as a model for explaining concepts and the function of galvanic cells.

[14] In each case two zinc-copper cells were connected in a series and then connected to a volt/ampere meter. The three batteries contained respectively sodium chloride solution, sulfuric acid solution (1 part sulfuric acid + 7 parts water) and a mix of diluted sulfuric acid and nitric acid as electrolytes. These are three electrolytes mentioned used in the first half of the 19th century. The three batteries provided nearly the same voltage, but only the batteries with acidic electrolyte solutions attained a measurable amount of current. In

part of Figure 1). The only cell in the reconstruction that worked for more than two hours was a cell with diluted sulphuric acid. The further descriptions refer to this cell type. When this cell was not connected to an electric circuit, the zinc electrode reacted with the acid solution, creating bubbles of gas on the surface of the zinc electrode, but this did not appear on the copper electrode. After the two electrodes were connected with a metal wire, there was formation of gas bubbles on both electrodes but more on the copper electrode as seen in figure 3. This agrees with Daniell's own descriptions (Daniell 1836 a, page 109-110).

The formation of zinc deposit on the positive electrode (polarization) was one of the problems reported for pre-Daniell batteries, and the reconstruction showed this phenomenon clearly (see figure 4).

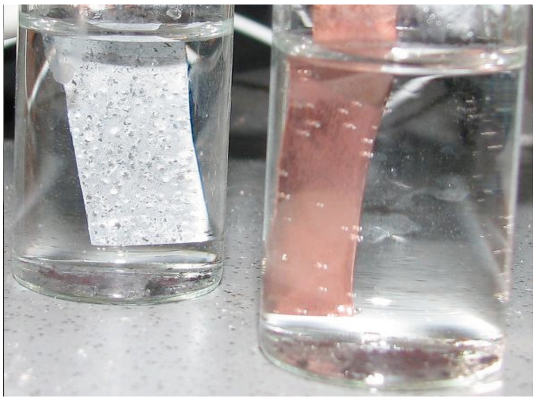

Figure 4
Both electrodes in this figure are copper electrodes from zinc copper cells with sulfuric acid solution as electrolyte (after 15 hours use). The electrode to the left has a deposit; the one to the right is cleaner. Daniell reported the deposit to be metallic zinc. (The zinc electrodes in the two cells are removed to get a better image of the copper electrodes.)

As the copper electrode got a visible zinc deposit, the voltage of the cell simultaneously decreased from about 1 V to about 0.02 V. The development of gas on both electrodes was almost ceased. To test whether the deposit caused the drop in voltage, we replaced the "galvanized" electrode with a new and clean copper electrode. This change

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the battery with nitric acid in the electrolyte, the zinc electrode was completely etched away during a couple of hours, like Daniell himself reported (Daniell 1836 a, page 109).

immediately restored both the voltage and the gas formation, and confirmed Daniell’s description of “deoxidation of zinc oxide”, as described earlier.

The reduction of zinc ions on the surface of the copper electrode (Owen 2001) is difficult to explain from basic redox chemistry. By simply reading the original Daniell article, this information was incomprehensible, but by completing the experiment and observing the deposit and its interference on the function of the cell, the content of Daniell’s article made more sense. Other researchers who reconstruct old experiments share this experience. One example is Elizabeth Cavicchi’s reconstruction of Faradays experiments with induction: ”To see the responsive and creative developments of others, I had to engage with coils deeply enough to become confused and let uncertainties arise” (Cavicchi 2006).

The Crown of Cups type of batteries gives a fairly low maximal amount of current. Daniell’s description indicates that the batteries in reality were short-circuited when used, making the potential difference between the electrodes to approach zero. In the reconstruction, we also short-circuited the batteries during usage, and by this we achieved similar results as those reported by Daniell. When the cells were connected to a resistance to create larger potential difference, no zinc deposit emerged on the copper electrode. This is another circumstance underlining that the reconstruction provided information that could easily have slipped away without it.

Testing the Daniell cell

At the NTNU physics department there is a historical collection including a Daniell cell (Wittje and Nordal 2005). This cell is not constructed precisely according to Daniell’s description (Daniell 1836 a). The difference is mainly that the model from the collection has a copper electrode on the inside of the clay/earthenware container while the zinc electrode is placed on the outside. One possible explanation for this is that the cell was purchased for use in demonstrations, which would make a glass outer wall favourable, so the students easily could observe what happened inside the cell[15]. This design also made it possible to rebuild it into a Bunsen cell. The model used in the reconstruction closely resembles the cells named Daniell cells or Bunsen cells in a 1905 textbook (Weinhold 1905).

To test this “Daniell cell” it was attached into a series of 6 cells (figure 5). The five other cells were ”homemade” from copper plates, zinc plates, porous clay cylinders and beakers. In principle these were similar to the old model from the university collection. Sulphuric acid solution (1part sulphuric acid + 7 parts water) and a saturated solution of copper sulphate were used as electrolytes. This six-cell battery was connected to an apparatus for electrolytic decomposition of water, also from the physics department’s historical collection.

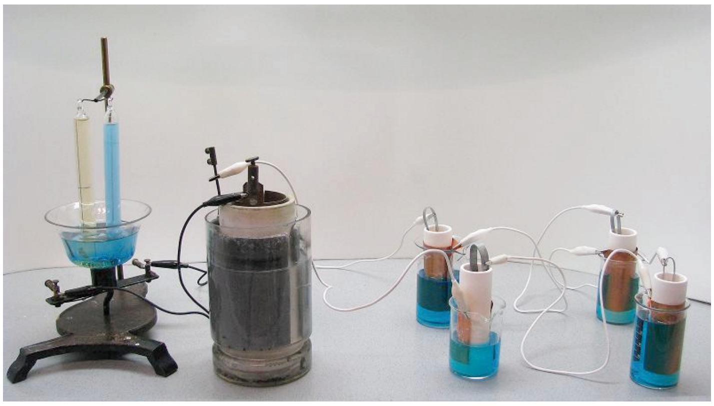

Figure 5
A battery of 6 cells, all in principle similar to the Daniell cell. To the left water splitting apparatus.

The water splitting apparatus used during the experiment was a parallel to the Voltameter used by Daniell in his experiments. The same apparatus was earlier used in a reconstruction of the Voltaic pile (Eggen *et al.* 2010). Trying both the Daniell cell and the Voltaic pile connected to the same apparatus convinced us that the Daniell cell was a

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[15] It is not know whether the battery model from the collection was used in demonstrations at the NTH after it was purchased, but XRF-analyses made by Ph.D. student Kidane Fanta Gebremariam in 2009 showed remainders of sulphate on the electrode, which indicates that it has been used.

great improvement compared to the Voltaic pile. Capacity increase was demonstrated by the fact that the six "Daniell cells" used only a few hours to decompose the same amount of water as the Voltaic pile with 30 cells could manage over night. Another improvement was the possibility to quickly dismantle the battery to stop the corrosion of zinc and "turn it off". Also, the time required cleaning the Daniell cell after use was only a fraction of the time required to clean the Voltaic pile. The combination of increased power, durability and usability made it a major technological step forward.

The Daniell cell as a "philosophic" model in our time

As described earlier the Daniell cell was created for scientific purpose. The reconstructions convinced that the cell represented a significant progress within battery technology. What is left is to comment on, is the role of the Daniell cell in 2010, more than 170 years later. By entering the Google search engine in 2010 and searching for pictures of "the Daniell cell" several hundred hits emerged.[16] None of the first 20 pictures that emerged were of the cell like Daniell constructed it, and 13 of the 20 first images showed a model with two containers next to each other connected with a U-tube or a wick (see Figure 6). In these pictures, the two half-cells consisted of a copper electrode in copper sulphate solution (often 1mol/L) and a zinc electrode in a corresponding zinc sulphate solution. The salt bridge was filled with e.g. a solution of potassium chloride. Many of these so-called "Daniell cells" had a glowing light bulb, a voltmeter or an ampere meter connected to it, as shown in Figure 6.

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[16] By doing a similar search for "Daniell battery" (instead of "Daniell cell"), the same kind of two-chambered cell appears, but this search also results in models of the original Daniell cell and other versions, some pictured in Figure 7.

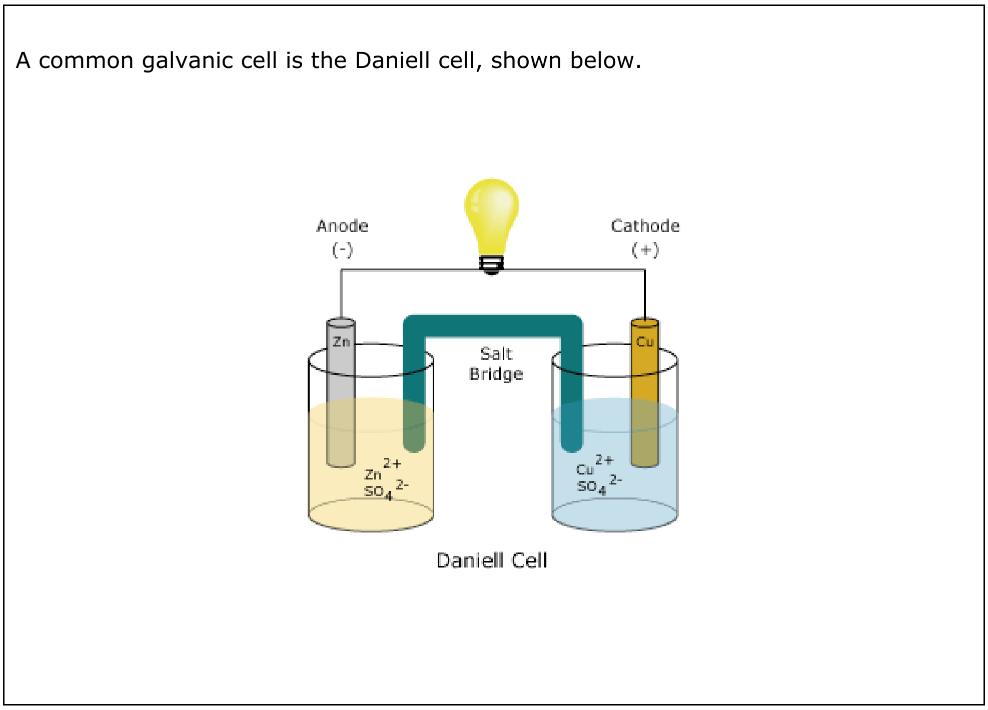
A common galvanic cell is the Daniell cell, shown below.

Figure 6
A figure showing a ”Daniell cell” from the website ”About.com.: Chemistry” (Helmenstine 2009).

The similarities to the original Daniell cells are that the electrodes are made of zinc and copper and that the two electrolyte solutions are separated in two different chambers. The differences are that the electrolyte surrounding the zinc electrode is a solution of zinc sulphate instead of sulphuric acid, the containers are placed next to each other instead of inside each other and the connection between the two electrolyte solutions consists of a U-tube filled with salt solution instead of an earthenware container. These differences are not only relevant for the appearance of the cell, but for the function as well, e.g. by affecting the conductance of the salt bridge.

Zinc copper cells with two containers connected with a U-tube or a wick, and named Daniell cells are repeatedly found in textbooks, but the Daniell cell presents itself in even more versions. A selection of textbooks of general chemistry from the NTNU University Library archives shows that, from Daniell’s time and until today, different galvanic elements are used as examples. The “Daniell cell” is mentioned in several of the books, but often the name refers to other variants of the zinc-copper cell. One of the textbooks says: ”An element as described previously, [Cu |1-molar $CuSO_4$ | 1-molar $ZnSO_4$ | Zn] is the very often used Daniell’s Element;…..” (Biilmann 1914), indicating that all cells with the mentioned components are “Daniell cell”. Figure 7 shows four alternative versions portrayed in other textbooks. All are named after Daniell, even if they differ quite a lot from Daniell’s own construction.

The limited selection of textbook illustrations in Figure 7 shows both that the term Daniell cell can have different meanings and that there have been different attempts to explain how a zinc copper cell functions. Figures a) and c) show models used for other purposes than teaching, while models b) and d) seem to be designed for illustrating the electrochemical function of zinc copper elements. The selection of different models carrying the same name shows that “the Daniell cell” is not only a historical construction but has developed to a concept with its own meaning.

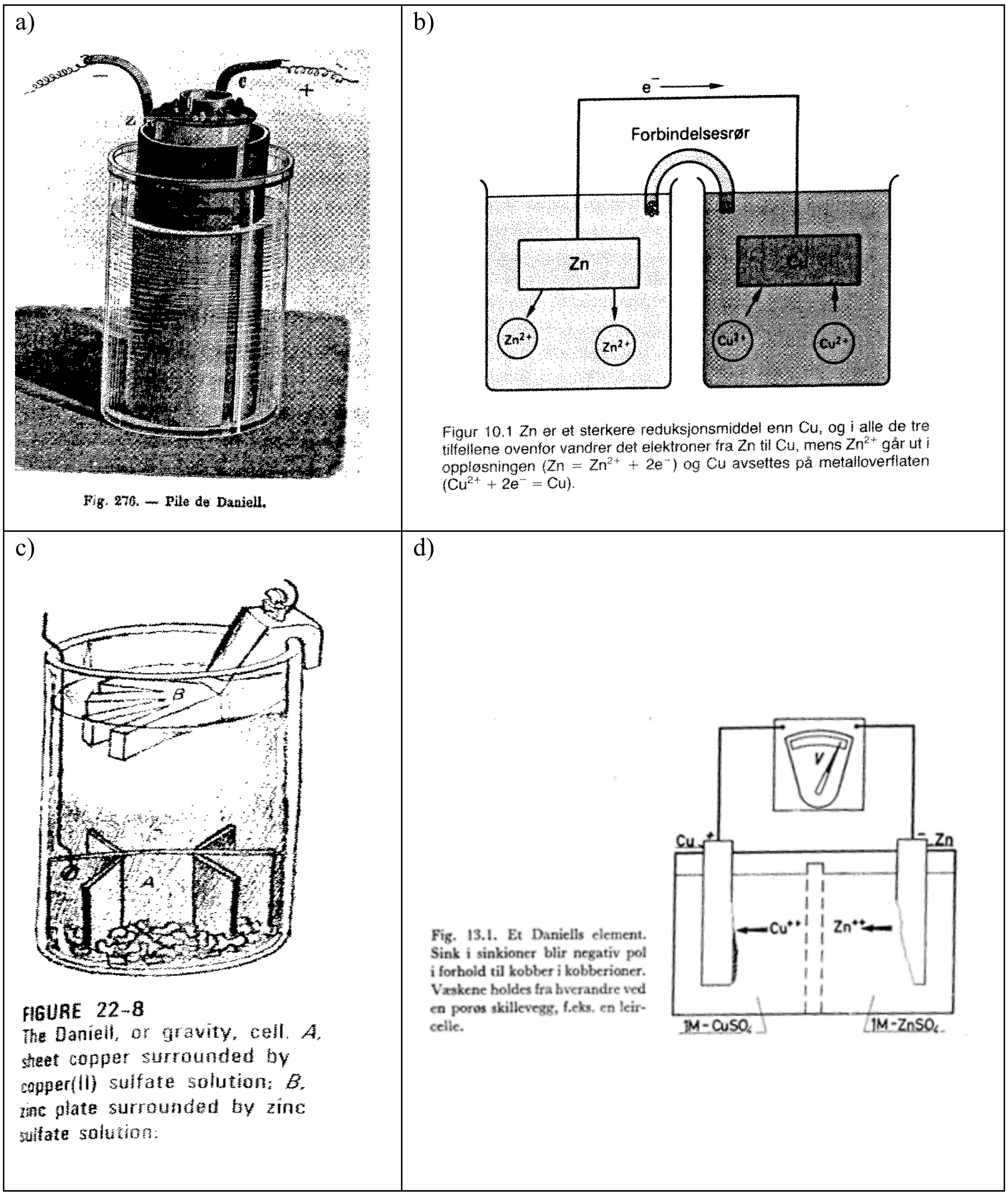

Fig. 276. — Pile de Daniell.

Figur 10.1 Zn er et sterkere reduksjonsmiddel enn Cu, og i alle de tre tilfellene ovenfor vandrer det elektroner fra Zn til Cu, mens Zn^{2+} går ut i oppløsningen ($Zn = Zn^{2+} + 2e^-$) og Cu avsettes på metalloverflaten ($Cu^{2+} + 2e^- = Cu$).

FIGURE 22-8
The Daniell, or gravity, cell. *A*, sheet copper surrounded by copper(II) sulfate solution; *B*, zinc plate surrounded by zinc sulfate solution.

Fig. 13.1. Et Daniells element. Sink i sinkioner blir negativ pol i forhold til kobber i kobberioner. Væskene holdes fra hverandre ved en porøs skillevegg, f.eks. en leircelle.

Figure 7

a) ”Daniell cell” with zinc on the outside and copper in the middle of a glass jar (Wurtz 1876)

b) ”Daniell cell” with a U-tube as salt bridge (Salveson 1975)

c) ”Daniell cell” with two-layer electrolyte solution (Nebergall 1976), a so-called Gravity cell.

d) ”Daniell cell” with a porous separating wall and rod-shaped electrodes (Lauritzen 1985)

Application as teaching model

The reason for using the Daniell cell in chemistry education in the 19th century could have been to understand the principles of chemistry and as an example of (at the time) modern batteries. Today, the Daniell cell is no longer used as a source of electricity, and it does not connect theory to something students see in everyday life. The extensive misunderstandings about how zinc copper cells work (Ogude 1994; Ogude 1996; Sanger 1997; Yuruk 2007) imply that the teaching is not optimal. It is claimed that the “Daniell cell” shown in figure 6 “acts as the principal source of misconceptions about ionic conduction” (Boulabiar 2004).

Still, the “Daniell cell” has both its justification and its disadvantages as a model used in teaching. The U-tube cell is suitable for illustrating differences in standard reduction potential, [17] and resembles a construction made for this purpose by Erasmus Kittler, pictured in the Kohl-catalogue from 1905 or 1906 (Kittler 1882; Kohl 1905/1906). This cell was not a battery, but instead made for cell voltage measurement.

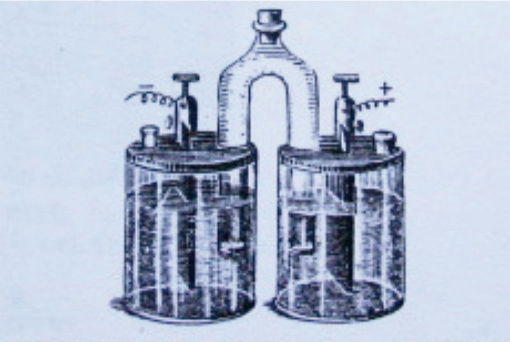

Fig. 2217, No. 25910, 1/6 nat. Größe.

Figure 8
Kittlers cell made to measure ” The Electromotive Forsce of the Daniell cell”, [18] pictured in the Kohl-catalogue

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[17] In the textbooks referred to in this text the zinc copper cells are not primarily used for illustrating standard reduction potential but instead to illustrate the principle of galvanic cells.

[18] Original title of Kittlers paper: ”Die Electromotorische Kraft des Daniell’schen Elements”. My translation.

There are also other obvious advantages with using this zinc copper cells in teaching. The substances used are affordable, stabile, and practically harmless to use. Other substances fit for the purpose like silver, silver oxide; cadmium, mercury and lithium do not have the same advantages. Schools often have in store both the chemicals and the equipment necessary, making it relatively simple to perform experiments with these cells. It is equally simple to find experiment descriptions. The absence of toxic substances, strong acids and unwanted creation of gas could also be important reasons why the Daniell cell won a place in teaching instead of other cells developed in the 19th century.

The disadvantages of using this model for teaching are to a large degree related to the use as a model for power supplying galvanic cells. Two of the cell components, the copper electrode and the zinc sulphate solution, have no special function and can be left out or replaced by other substances. A cell of this type cannot provide sufficient current to make a light bulb glow[19], even if that is commonly appearing in figures like the one in Figure 6. A salt bridge like in figure 6 would create a large resistance in the cell and consequently cause low current, especially compared to Daniell's construction, in which the efficiency of the salt bridge was carefully considered (Daniell 1838).

When Daniell constructed his cell and implemented it in his teaching, these objections were not relevant. The understanding of electrochemical reactions was not the same as today and the light bulb was not yet invented, and Daniell (as the other battery constructors at the time) made salt bridges with a much higher conductance than a U-tube can facilitate (Niaudet 1880).

In 1836, the Daniell cell represented important progress in the efforts of improving battery technology, and the fact that later models of zinc copper cells still are called Daniell cells, even though they were constructed by others,[20] shows Daniell's strong position within his field and implies that the name was regarded as positive. It also seems likely that the terms 'Daniell cell' and 'zinc copper element' in some cases were

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[19] It cannot make a light emitting diode glow, since diodes need about 1,6 V to glow while a copper zinc element provides about 1 V.

[20] See figure 5 for examples

perceived as synonyms (Kittler 1882; Biilmann 1914). According to Boulabiar, the Daniell cell has been the dominating, if not only cell discussed in French and Tunisian textbooks, and equipment catalogues from the 19th and 20th century indicate a similar status in other countries. A quick review of Norwegian textbooks from the last 30 years reveals that the zinc copper cell has held a central position also in Norway, often under the name Daniel cell.[21] Since this model has been used in teaching for such a long period of time, the Daniell cell is familiar to ”everybody” who has studied chemistry, and thereby its tradition in teaching is enhanced. The fact that today’s students are presented to the same cell seems to ensure that the tradition continues, and this also increases the possibility that future teachers and textbook authors will join the tradition.

Closing comment

When Daniell constructed the Daniell cell in 1836, the invention was of great importance. The battery performed much better than its forerunners and, inspired by this construction, many battery types designed for different purposes were developed. The cell is considered as the origin of electrolytic metallization and was used as a battery for this purpose and in telegraph stations for several decades, even though other types of batteries were more common. It has had a central place as a model in teaching, and it still holds its position in chemistry education even though the cells called “Daniel cell” today are clearly different from the original. It is difficult to explain why a model of a battery that has not been in use in more than 150 years has been given such a central place in textbooks. Its suitability as a teaching model is opposed by research showing that students find galvanic cells very confusing. Even if the so-called “Daniell cell” is easily available and relatively simple to construct, one may think that the development within electrochemistry since 1836 should have provided better and more recent models for teaching. Its position within chemistry teaching is a continuation of a long tradition and a confirmation of the significance of the progress obtained by Daniell’s invention.

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[21] In the first part of the 20th century, batteries were part of the physics field, and the descriptions of them are found in physics books instead of chemistry books. This despite that during the 19th century it became clear that the source of current in batteries is chemical reactions.

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Paper VII