Acoustic Methods as a Tool for Management of Electrochemical Process of Energy

Nina KIRCHEVA 1,3, Sylvain TANT 1,3, Benoit LEGROS 2, Sylvie GENIES 3, Sébastien ROSINI 3, Pierre-Xavier THIVEL 1

1Laboratoire d’Electrochimie et de Physico-chimie des Matériaux et des Interfaces, UMR 5279 CNRS – Grenoble INP – UdS - UJF, Saint Martin d’Hères, France
Phone: +33 (0) 476 826 733, Fax: +33 (0) 476 826 777; e-mail: pierre-xavier.thivel@lepmi.grenoble-inp.fr
2Mistras Group S.A., 27 rue Magellan 94370 Sucy-en-Brie, France; blegros@mistrasgroup.eu
3CEA-LITEN, Grenoble France, sylvie.genies@cea.fr, sebastien.rosini@cea.fr

Abstract
In an international context of low-carbon energy development, the electrochemical processes of conversion and storage of energy are a promising way. Indeed, on one hand lithium batteries are hopeful energy storage systems for Hybrid and Electric Vehicles and, on the other hand, Fuel Cells are one of the most attractive energy conversion devices to be used as a power source for stationary power generation. However in spite of significant scientific advances, batteries and fuel cells require improvements in order to increase their reliability, their safety and their industrial application potential. In particular, substantial hazards (e.g. thermal runaway, hydrogen leak, overcharge or unsafe operating conditions, etc.) exist for system integrity, users and environment, and it is important to develop methods and strategies for their prevention. The aim of this research is to evaluate if acoustic methods are appropriate techniques to become an innovative diagnosis tool for battery or fuel cell management systems. Acoustic Emission (AE) and Acousto-Ultrasonic (AU) Techniques were thus investigated through three PhD thesis works, using LiFePO4/graphite or LiAl/LiMnO2 coin cells and Proton Exchange Membrane Fuel Cells systems. Concerning lithium ion cells, for instance, the AE technique shows good sensitivity for the detection of degradation of electrode materials leading to capacity fade. Furthermore, numerous sources of AE were detected and identified: the active materials volume expansion during intercalation process, the modification of composition of the passivation film on the graphite negative electrode, the electrochemical instability of the materials and the possibly degradation of the electrodes. Concerning, PEM Fuel Cells, AE technique was used to detect flooding or other unsafe operating conditions. Using statistical treatment, AE sources linked to identified-physical phenomena permit to diagnose the state of hydration of a single cell. Using single cells and stacks from 2 to 6 cells, AE and AU techniques allow detecting modifications within the stack under various operating conditions (membrane swelling and shrinking, gas pressure variation in channels, etc.). Although researches are still needed, this study has shown that the Acoustic based techniques (AE and AU) are suitable to follow electrochemical cells. Monitoring of battery and fuel cell by AE and AU opens the way to the development of promising diagnosis and management systems.

Keywords: Acoustic Emission, Acousto-ultrasonic, Fuel cell, Lithium-ion, Management System.

1. Introduction

In an international context of low-carbon energy development, the electrochemical processes of conversion and storage of energy are a promising way. Indeed, on one hand lithium batteries are hopeful energy storage systems for Hybrid and Electric Vehicles and, on the other hand, Fuel Cell is one of the most attractive energy conversion devices to be used as a power source for stationary power generation. However in spite of significant scientific advances, batteries and fuel cells require improvements in order to increase their reliability, their safety and their industrial application potential. In particular, substantial hazards (e.g. thermal runaway, hydrogen leak, overcharge or unsafe operating conditions, etc.) exist for system integrity, users and environment, and it is important to develop methods and strategies for their prevention. The aim of this research is to evaluate if acoustic methods are appropriate techniques to become an innovative diagnosis tool for battery or fuel cell management systems. Acoustic Emission (AE) and Acousto-Ulersonic (AU) Techniques were thus investigated through three PhD thesis work, using LFP/graphite coin cells batteries and Proton Exchange Membrane Fuel Cells systems.
2. Acoustic experimental set-up

When undergoing mechanical excitation, even at local level, materials spontaneously generate transient elastic waves, called acoustic emission. These waves propagate into the material and can be recorded as AE signals allowing the detection of active defects within materials. AE can be applied in real time and continuous basis during the test and is used in the industry either for process monitoring, material characterization or damage assessment. Acousto-Ultrasonic (AU) technique is an active technique, sensitive to the variation of the propagation of mechanical waves in materials. AU technique has been successfully applied in the investigation of the gas-evolving electrodes in metal–electrolyte interfacial processes.

The AE and AU systems are provided by Mistras Group SA. Figure 1 show the experimental set-up used in the case of fuel cell investigation. The same experimental set-up was employed in the case of Lithium-ion batteries studies.

![Figure 1 - Schematic of AE and AU system for fuel cell studies](image)

The acousto-ultrasonic system (Mistras Group SA.) is composed of two parts: emission and reception. R15-resonant-piezoelectric sensors (Resonance frequency of 150 kHz) were chosen for both emission and reception. The excitation signal was delivered by an ARB-1410 arbitrary waveform generator card, which provides highly accurate (14-bits) and high-speed (100 MS/s) electrical signals. Using WaveGen 1410 Software, it can provide simple and customized waveforms of all shapes and amplitudes up to +/- 150V. The AU signal received by piezoelectric sensor was amplified by a preamplifier with a 20-1200 kHz bandwidth filters and a 40 dB gain. A PCI-2 AE system was used for data acquisition and digital signal processing. This card was selected for high speed scanning (up to 40 MS/s), the possibility to perform real time sample averaging providing thus best accuracy and for its 18 bit resolution. The bandwidth was set to 1 kHz – 1 MHz (high-pass filter, 4th order Butterworth and low-pass filter, 6th order Butterworth). Finally, the trigger function of ARB card is linked to the 2nd channel of PCI-2 acquisition card to permit the synchronization between cards and thus the calculation of the time delay between emission and reception (Flight Time).

The piezoelectric emitter converts the electrical signal (Figure 2(a)), characterized by a frequency of 150 kHz and an amplitude of 5 V and consisting of 5 periods, into a mechanical vibration in the material. The mechanical vibration received on the piezoelectric sensor is converted into an electrical signal (Figure 2(b)), so called waveform. Waveforms are recorded for each transmitted signal. The Fourier transforms of those waveforms are calculated by the optimized Matlab Fast Fourier Transform algorithm (Figure 2(c)).
Concerning the AE measurement, only the reception part is involved and the data acquisition system also obtained the AE parameters, such as duration, energy, number of events... Fuel Cell system or batteries are connected to dedicated test bench that controls electric circuits and all necessary devices.

3. Fuel cell management system

3.1 Water management

Among the numerous phenomena that occur during fuel cell operation, water behavior is still not completely understood and remains difficult to survey. This is a major issue as water management is well known to be tightly related to both PEMFC reliability and performances. Improving or optimizing water management during the cell operation is thus a subject of crucial point, which is object of continuous and diversified research effort. Water management must take into account processes occurring in gas channels, across the Gas Diffusion Layers (GDL) and inside the Nafion membrane. This simultaneity makes the overall problem quite complex and difficult to handle. This can be illustrated by the fact that whereas Nafion needs to be highly hydrated for best performances, GDL and gas channel must be protected from flooding. Some of the main parameters and phenomena that have to be managed are hence relative humidity (RH) and water droplet formation in gas channel as well as the water level in both the GDL and the Nafion membrane. Water is produced through the electrochemical reaction and the reactant gas can be humidified to help the humidification of the membrane and so to increase its ionic conductivity. On the other hand, water transport in the membrane is led by electro-osmotic drag and back-diffusion. The ideal water level is therefore not easy to determine experimentally and difficult to maintain especially without trustworthy in-situ water level measurements.

For water management, different techniques such as electrochemical impedance spectroscopy, current interruption or pressure drop are proposed in the literature. The aim of our studies...
is to investigate the utilization of acoustic techniques for monitoring PEMFC and, in particular, the water management within the fuel cell.

Studies were undertaken at different scales: firstly the acoustic behavior of the membrane has been studied during drying or humidification, and secondly the acoustic behavior of a single fuel cell was investigated under different experimental conditions.

3.3. Study of the Nafion membrane

A previously study [1] showed that AE could indicate the drying phenomena in Nafion membrane. In particular, it was shown that acoustic phenomena are detected while the electrochemical characteristics of the membrane reached a plateau. Unlike electrochemical parameters, AE activity seems prone to detect the breaking point, beyond which the membrane is submitted to strong internal stresses that can yield to irreversible damage.

The behavior of a membrane has been also investigated using AU method. On figure 3, are shown the evolutions of the electrical resistance and of the ultrasonic energy received on a piezo-electric sensor as a function of the relative humidity of the atmosphere in contact with a Nation membrane.

![Figure 3–Resistance and AU transmitted energy versus relative humidity](image)

As expected, the membrane resistance decreases with the relative humidity indicating a better ionic conductivity. In the same way, a decrease of the transmitted AU energy is observed. This decrease indicates a modification of the mechanical properties of the membrane with the water content. As reported by Roberti and Carlotti [2], the Young’s modulus decreases upon the increasing water content leading to a softening of the membrane. Water acts as a plasticizer, which could explain the decrease of the AU signal. Thus, the both acoustic techniques are able to detect the mechanical changes within the membrane, leading to interesting information for membrane characterization.

3.4 Single fuel cell tests

AE and AU techniques were used to investigate the water flow in the gas channel and the phenomenon appearing in the gas diffusion layer or in the electrode.
A single cell with an active area of 25 cm$^2$, provided by Paxitech®, was used. The bipolar plates are made in graphite and the gas channels are engraved on it (figure 4). The fuel cells are fed with pure hydrogen as fuel and either air or pure oxygen as oxidizer.

Figure 4–Graphite gas distribution plates

On Figure 5 [3], the cumulative acoustic emission activity (number of hits) and the airflow rate have been plotted versus time. For a gas-flow rate less than 0.75 L.min$^{-1}$, which corresponds to a Reynolds number of around 880, the acoustic emission curve is flat indicating that little or no AE events take place. Beyond this threshold, the activity of AE increases sharply even as the overall flow regime remains laminar (Re <2000). However it is necessary to take into account that the localized turbulences (in time or space) occur as singularities in the gas channel.

Figure 5–Time evolution of the cumulated number of AE hits (black solid line) and the controlled profile of the steep increase of feeding cathodic gases flow rate (gray dashed line) at 60°C with humidified gas [2].

This experiment shows that the presence of water droplets in the gas channels is sources of acoustic emission due to localized turbulences such as singularities in the gas channels. Thus AE is able to detect water droplets accumulation in the gas channels.

A statistical post-treatment based upon Noesis® facilities was proposed in [3] to gather qualitative information on the origin of the AE events measured during PEMFC operation in different conditions. More precisely, Principal Component Analysis (PCA) first allowed the discrimination between data coming from distinct origins and hence their classification into
different clusters or classes. Afterwards, a Supervised Pattern Recognition (SPR) algorithm was employed to train the software to recognize signals belonging to those previously established classes of AE events. The AE data treatment and analysis allow the separation, according to their sources, of 3 classes:

- phenomena that take place in the gas channel, i.e. those related to biphasic flow or water droplet circulation in our hydrodynamic conditions (hydrodynamic effects)
- phenomena that take place in both the GDL and the gas channel i.e. those related to water removal from the GDL to the gas channel (so called non-reactive interactions between gas and MEA).
- phenomena related to water uptake and desorption in the catalyst layer (filling of the porosity of the active layer (AL)) and membrane (swelling, shrinking) That include membrane shrinking and swelling due to water level decrease and increase, and water transport into the membrane and the catalyst layer (so called reactive interactions).

3.5 Stack fuel cell tests
Currently studies are underway to validate these acoustic methods on fuel cell stack constituted by two or more individual cells. As example, in order to evaluate the link between the AU and the hydration level of the stack, the hygrometry of the inlet gas has been modified (figure 6). Several relative humidity 3-hours-steps (25, 50 and 80 % of relative humidity) are performed at a constant current density of 0.225A.cm$^{-2}$. On this figure is depicted the average cell voltage (black line) and the AU energy (grey line) as a function of time. As expected, the stack voltage is strongly dependent on the relative humidity in gases. Due to the dependence of the ionic conductivity with the water content of membrane, the best performances are obtained for the higher values of humidity. At the same time, the energy received by the piezoelectric sensor seems to be dependent on the gases relative humidity. The average levels of AU transmitted energy are respectively 40nJ, 35nJ and 23nJ for 25%RH, 50%RH and 80%RH. Using this measurement, it can be possible to link the levels of membrane hydration with the acoustics impedance and then to use ultrasonic methods to diagnose the humidity levels directly inside the stack.

Figure 6 – Variation of membrane hydration Relative Humidity Steps at 0.225A.cm$^{-2}$. (80°C, 1.2bars constant gas flow rate equivalent to 1.5/2 at 0.5A.cm$^{-2}$)
Moreover, as observed on figure 6, an acoustic activity appears at 80% of relative humidity indicating a possible presence of water droplet in the gas flow channel. Our investigations concerning fuel cell show that acoustic methods are able to detect some change within fuel cell. In particular, AE appears with the presence of water droplets in the gas channel indicating a “flooding” of the fuel cell. Concerning AU method, the transmitted energy varies with the water content but other studies are necessary to correlate more precisely the AU modification and the fuel cell behavior.

4. Battery management system

4.1 Lithium-ion/graphite formation study
One of the most important steps for the Li-ion batteries manufacturing based on graphite as negative electrode is the step of formation corresponding to the first charge process. During this process, on the negative side, lithium ions are inserted into the graphite electrode for the first time thanks to two electrochemical reactions: a surface reaction leading to the formation of a passivation film on the surface of the graphite particles by decomposition of the electrolyte, the graphite reduction and lithium insertion inside the host matrix. The passivation film, denoted also as “Solid Electrolyte Interface” (SEI) plays a key role because it protects the lithiated graphite from further reactions with the electrolyte and provides stability to the graphite structure as well as reversibility of the further lithium-ion intercalation. Moreover, during the successive charge and discharge cycles, the structure of graphite is dimensionally stable enough not to damage this passivation layer.

The experiments were carried out on hand-made cells, constituted of various electrode materials: graphite (type chosen: meso carbon micro beads (MCMB)) as working electrode and lithium metal as counter/reference electrode (Li/MCMB), Lithium Iron Phosphate (LiFePO$_4$-LFP) as working electrode and lithium metal as counter/reference electrode (Li/LFP) and finally graphite (MCMB)/LFP cells.

The formation of the coin cell batteries was led at constant current rate Cn/20h (where Cn denotes the theoretical capacity of the lithium iron phosphate electrode) until to reach voltage threshold.

Three types of phenomena were studied:

(i) formation of passivation film on the surface of the graphite particles using Li/MCMB cell;

(ii) modification of the LFP structure during Li-ion intercalation /de-intercalation using Li/LFP cell;

(iii) overall phenomena using MCMB/LFP cell.

The next figures show the voltage profiles during the first formation charge/discharge cycle of the three cells and the coupled AE activity in term of cumulated hits. The most important acoustic activity is observed for the Li/MCMB cell during the formation of the passivation film usually produced mainly between 0.8 and 0.5V vs. Li$^+$/Li and during the subsequent lithium intercalation between the graphene planes (Figure 7a). Concerning the formation of the Li/LFP cell it is surprising to note that the acoustic activity is very weak (Figure 7b). We observe that the structural modification of LFP associated with the desinsertion (charge) and insertion (discharge) is weak enough to not produce detectable acoustic activity above the threshold of 25 dB applied, convenient to a strong reversibility of the insertion/desinsertion of lithium in the crystalline structure of such material. At last, for the MCMB/LFP cell, the AE activity is mainly observed during the first charge at the moment where the passivation film is formed on the graphite electrode in a way similar to the one observed at the Li/MCMB cell (Figure 7c). Thus AE technique seems a promising tool for the detection of the formation of graphite/LFP battery. A fine analysis of this process has been proposed in [4].
Figure 7 - Evolution of the cell voltage and the AE activity during the formation of the (a) Li/MCMB cell, (b) Li/LiFePO4 cell and, (c) MCMB/LiFePO4 battery.
4.1 LiAl/LiMnO$_2$ cycling
Another possibility of using AE technique is to follow accumulators during charge and discharge cycling. As example, figure 8 shows a classical charge/discharge cycle for a commercial LiAl/LiMnO$_2$ secondary cell. The black solid line represents the variation of the voltage, and the dashed line represents the current. The red solid line gives the acoustic activity in term of cumulative hits. The acoustic activity appears during discharge process (potential decrease from 3.2 to 1.5 V). During the charge process, when potential increases from 1.5 to 3.3 V, no acoustic activity is measured. During the floating charge time (constant potential), a weak activity appears. During the second discharge/charge cycle, the same acoustic behavior appears but with a smaller number of events. This acoustic activity could be related to the internal mechanisms occurring inside the cell during the discharge;
- the delithiation of the LiAl electrode,
- the lithiation (insertion of lithium within the MnO$_2$ material) of the LiMnO$_2$ electrode.
Currently, work is underway to correlate the mechanisms at the electrodes with the acoustic activity. Time analysis, frequency analysis and statistical analysis should permit to determine the health status of the battery in operation.

![Figure 8](image)

Figure 8– Evolution of the cell voltage during charge and discharge cycle for LiAl/LiMnO$_2$ cell at C/10 current rate.

5. Conclusions
Acoustic methods for the study of electrochemical processes seem to be very innovative and promising and have the advantage to be non-invasive. The acoustic methods present sensitivity to changes associated with the water in fuel cell or with the internal mechanisms in batteries. Acoustic parameters could be used as interesting parameters for battery management system. Further studies are necessary to confirm this interesting experimental technique and to correlate acoustic signature with internal phenomenon occurring during electrochemical process utilization.
References


