ANALYSIS OF INDUCTIVE CURRENT PULSE DYNAMICS IN WATER ELECTROLYSES CELL

Martins Vanags, Janis Kleperis, Gunars Bajars, Andrejs Lusis

Institute of Solid State Physics of University of Latvia, Riga, LV-10050, Latvia

ABSTRACT

We used inductive discharge voltage pulses to power the electrolysis cell with water and very weak water solutions as electrolyte. Results showed that individual voltage pulse characterize by rapidly growing first front that stays unchanged by changing the concentration of electrolyte. The current pulse changes direction from negative to positive direction with increasing concentration of electrolyte. Explanation is proposed that during appearing the high voltage pulse to interface cathode metal/electrolyte, the electrons are emitted in electrolyte and immediately solvated in the shell formed from six water molecules. Three discharge mechanisms of electrons in solvated shells (discharge with hydroxonium, reaction with neutral water molecule to split it and diffusion back into the metal) can explain the change of polarity of current pulse.

INTRODUCTION

Well-established and commercialized is water electrolysis technologies for hydrogen production, but high energy requirements of about 4–5 kWh per 1 Nm^3 hydrogen is a limiting factor for the use of this method on a large scale, except in countries where cheap electricity is available. There were various attempts to improve an efficiency of water electrolysis process, like high temperature and pressure water-alkali cells, zero-gap cell geometry, development of new proton exchange membranes, search for new electrodes with electrocatalytic activity, using ionic activators in water solution etc. Little studied is pulse power supply to electrolysis cell [1,2]. Shimizu et all [2] described method of hydrogen generation by water electrolysis using an ultra-short-pulse power supply. They concluded that efficiency of electrolysis stays constant with increasing supplied power, contrary to DC electrolysis were efficiency decreases increasing power due increasing losses in heat. Twenty years ago Stanley Mayer [3] patented efficient water fuel cell based on two co-axial steel tubes and high voltage pulses (generated by back induced electromotive force) to charge them. Shimizu et al. [2] have inferred that when an active voltage pulse is applied to the water electrolysis cell, the charging takes up too much of the pulse-time tracking. It does not happen if the reactive pulse electrolysis is used. In this case the mentioned disadvantage is transformed into an advantage, because after such a short charge period the discharge tail appears to be several times longer than that of the pulse length measured to infinite resistance. In our previous research [4] we reported about applying the high inductive kickback voltage pulses to electrolysis cell with platinum and tungsten electrodes. In this work, we studied the dynamics of current and voltage during application of inductive high voltage pulse to electrolysis cell with different concentrations of electrolytes.

EXPERIMENT

Electrolysis cell was made from glass and two stainless steel electrodes (grade 316 L, wires with diameter 2 mm and length 10 cm) using deionised water and week solutions of KOH, NaOH, LiOH and H2SO4 as electrolytes. We used dilution step 0,0007M to make very week electrolyte solutions, because the character of current was very sensitive to the concentration of ions in an electrolyte. The maximal amplitude of applied inductive voltage pulse was for electrolysis cell with deionised water only (Figure 1).
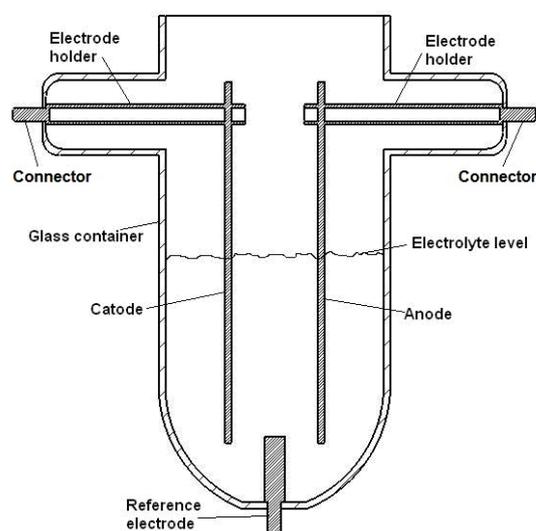

Figure 1: Water electrolysis cell in experiments

The inductive voltage pulses were generated in the electric circuit (Figure 2) consisting of a pulse generator, a DC power source, a field transistor BUZ350, and a blocking diode. A special broad-band transformer was bifilarly wound using two wires twisted together. Square pulses from the generator (pulse repetition time 50 μs and the direct pulse amplitude 1 V) was applied to the field

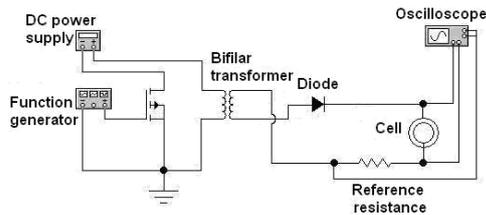transistor connected in series with the DC power source.

Figure 2: Water electrolysis cell in experiments

The duty cycle of pulses was kept constant (50%). To obtain inductive reverse voltage pulses, the primary winding of the transformer are powered with low amplitude square voltage pulses. In the secondary winding (winding ratio1:1) due to collapse of the magnetic field induced in the coil very sharp inductive pulse with high amplitude and opposite polarity with respect to applied voltage appears. Pulse of induced reverse voltage is passed through the blocking diode, and the resulting ~1 μs wide high-voltage pulse is applied to the electrolytic cell. A four-beam oscilloscope GWinstek GDS-2204 is used to record the voltage on the cell and current (calculated from voltage drop on a reference resistance) in the circuit.

RESULTS

The front growth of voltage pulse is equal in all concentrations, an amplitude of pulse is maximal in deionised water, while the discharge tile after voltage pulse is different at different electrolyte concentrations and lasts 15 microseconds in deionised water (Figure 3).
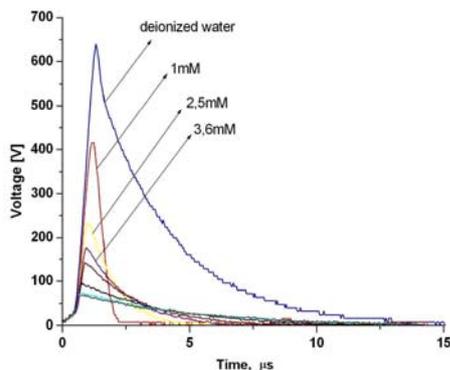

Figure 3: Inductive discharge voltage pulses on cell with different concentrations of KOH

Increasing the concentration of electrolyte to one mM, the amplitude of voltage pulse decreases and the discharge tile reduces. Pulse dynamics in cell with electrolyte concentration 1 mM is exactly what it is in case of the open circuit, only the amplitude is smaller. Continuing to increase the concentration of electrolyte in cell, the value of voltage pulse amplitude continues decrease, while the discharge tail will increase.

Current changes the direction from negative to positive with increasing concentration of electrolyte passing through the point where the current pulse has not descending a long tail (Figure 4).
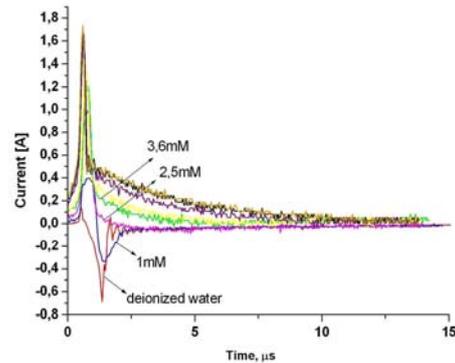

Figure 4: Current pulses initiated by inductive voltage pulses on cell with different concentrations of KOH solution in water

Current pulse in deionised water most of the momentum is negative. Increasing the concentration of solution up to 1 mM, current pulse appears in both positive and immediately following a negative pulse, while discharge tail almost disappears. Continuing to increase the concentration of electrolyte the negative values of current pulse disappear and the discharge tail remains positive and increasing, which indicates that the charge injected in the cell during pulse increases. More increase of concentration does not change the view of current pulse and it remains like from the previous concentrations.

Plotting the voltage and current pulses in the same time scale at different electrolyte solution concentrations (Figure 5) can be estimated phase shift between voltage and current pulses. The first in the cell appears current, which is explained by the fact that the cell is a capacitive element of the very first time (microsecond units) after voltage pulse appearance on cell. Voltage pulse appears little late and is with maximal amplitude in case of deionised water as electrolyte. The phase shift between current and voltage decreases increasing the concentration of electrolyte, as well as the positive momentum of current grows becoming dominant 3.6 mM.
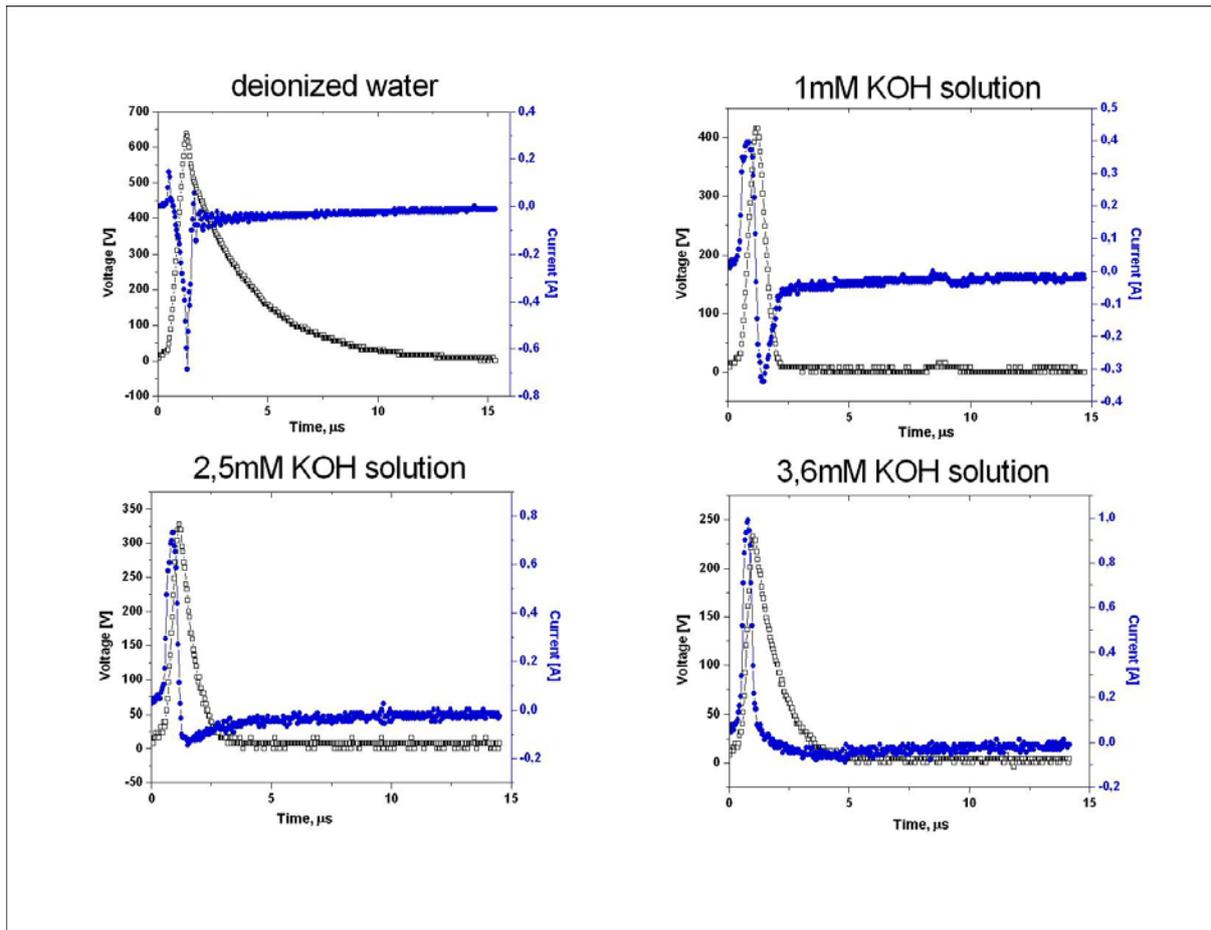
Figure 5: Voltage and current pulses of different concentrations of KOH solutions in the cell

The voltage and current pulses in case of NaOH and LiOH solutions as electrolytes at the same concentration, in principle, are identical to the KOH solution. The phase shift between the pulses is the same as in the KOH solution. But in solution of sulfuric acid the changes are more rapid with increasing the concentration of electrolyte. Figure 6 shows the peak voltage drop when electrolyte concentration increase.

The peak value of voltage pulse is decreasing exponentially, and it stabilizes around the value of 9V for solutions, while in deionized water that value is of 600V. These curves almost coincide in different alkali solutions, while in the sulphuric acid the peak values are falling faster. The dependence of integral of the current pulse (charge) from concentration of electrolyte is presented in Figure 7.
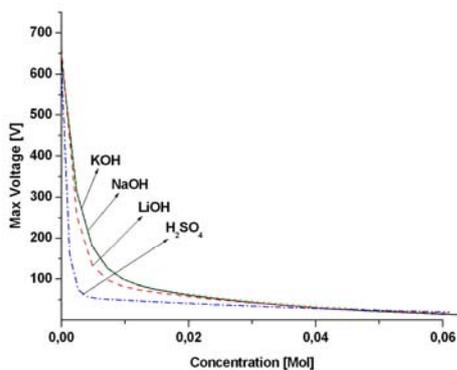

Figure 6: Decrease of voltage pulse amplitude with increasing concentration of electrolyte
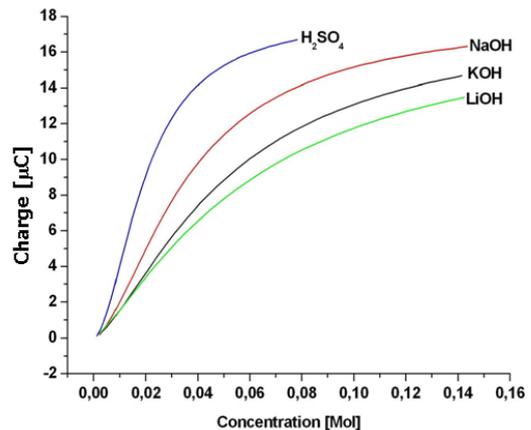

Figure 7: Decrease of charge (integrated current pulse) with increasing concentration of electrolyte

The electric charge (transferred with inductive pulse to electrolysis cell) increases with increase of concentration, and tend saturate at some value. In different alkali solutions, the charge behaviour is nearly identical, while in the cell with sulphuric acid solution increase of charge is more rapid.

From Figures 6 and 7 it can be seen that the voltage drop compensates the increase of charge, therefore pulse energy (multiplying voltage and current) remained constant. This is illustrated in Figure 8, where the pulse energy in electrolysis cell with higher concentrations of alkali and sulphuric acid solutions are nearly constant.
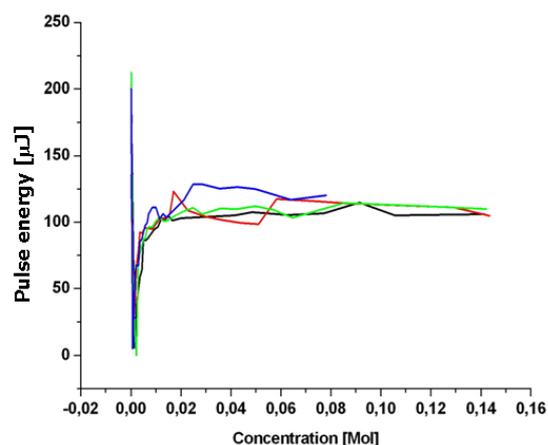

Figure 8: The change of pulse integral power with increasing concentration of electrolyte

The first two measurement points in Figure 8 differ from the most. The first point for deionized water electrolyte is equal to pulse energy 200 μJ, while at the electrolyte with concentration 1mM it falls down to 5 μJ. This is because the discharge tail, which determines the pulse energy, disappears completely. It should be noted that when discharge tail appears, the external power source is disconnected from the cell and energy is used, pumped into the cell during first μs when pulse presented.

DISCUSSION

When the voltage pulse applies to an electrochemical cell, the double layer capacity is charged, and this charging current is registered. In parallel, when the voltage on the double (electrode/solution) layer exceeds the red-ox normal potential, the conditions will be provided for the appearance of a Faradic current, nevertheless the Faraday current has no time to arise within the first microsecond, and thus the amplitude of the reactive pulse is increasing. In other words, in the first microsecond the cell behaves like a capacitor with high Q. The more concentrated the solution is, the higher capacity of the double-layer capacitor; therefore, at the same charge the voltage will be reduced.

Immediately after the application of voltage pulse to the cell the electrons emitted from the cathode into solution. It is considered that electron in water solution is solvated into the centre of octahedral shell made from six water molecules oriented with protons to the centre (Figure 9).
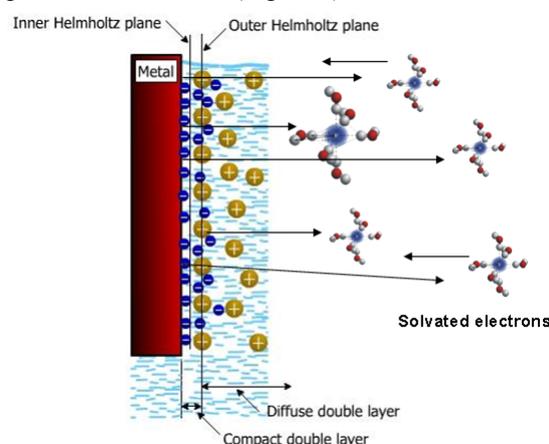

Figure 9: Emission of electrons from etal to electrolyte and next solvatation between polar water molecules (adapted from KeywordPictures)

The radius of solvated electron in aqueous solutions is estimated at about $2-3*10^{-8}$ cm [5], suggesting that it may be regarded as a large ion. Solvation process in water takes less time than $2*10^{-12}$ s, but the time spent by an electron in solvation shell is of the order of millisecond, and in some solutions even for a few seconds. If the solution contains H_3O^+ ions, the lifetime of electron in solvation shell is short (less than 3 μs) because the reaction rate of solvated electron with hydroxonium ion is high (k = $2.2*10^{10}$ $M^{-1}s^{-1}$) [5]. The electrons can escape from solvation shell following the three scenarios: discharging with hydroxonium H_3O^+, reaction with neutral water molecule to split it ($e^-_{aq} + H_2O \rightarrow H + OH^-$) or moving back into the metal. There are small numbers of ions H_3O^+ and OH^- in the deionised water, therefore the first scenario is limited and electrons is likely to move back into the metal and the return flow will be great – therefore current pulse is negative (Figure 5 left top). With increasing the concentration of solution, the point is reached were both flows are equal (Figure 5 right top). Further increasing the concentration of ions in solution, negative current values in pulse disappear and because in electrolyte solution there are many ions, the first scenario of escaping solvated electrons is more realistic.

The voltage and current pulse kinetics changes significantly immediately after charging the double-layer capacitor, switching to a steady discharge tail. The blocking diode does not allow the capacity to discharge in any other way than through the Faraday reaction until the existing potential is unable to activate the electrochemical red-ox process (the existing potential drops below the red-ox normal value). In addition, blocking diode

prevents arising negative current through cell. Therefore behind the diode, parasitic element with the inductive nature exist in the measurement scheme (Figure 2) which allows solvated electrons move back into electrode – arises negative current. Increase of the concentration of electrolyte in the cell changes symmetry factor of cell, parasitic element becomes comparatively small and solvated electrons are discharged by ions in electrolyte, therefore decreasing negative current. Spurious inductive component becomes negligible and the cell takes the upper hand with their capacity.

CONCLUSIONS

When a short high voltage pulse is applied to electrolysis cell, kinetics of the charging does not depend on the electrolyte concentration, whilst the kinetics of long discharge tail depends on the concentration of electrolyte.

Pulse energy is independent of the concentration of the electrolyte when its concentration is greater than 3 mM.

The maximum value of voltage and supplied charge of the pulse is depending on the concentration and tends to a certain value, which depends from the cell configuration.

The change of polarity of current in deionised water is due to the presence of parasitic inductance in the measurement scheme. This indicates that the existence of inductive element in the scheme of pulsed electrolysis power circuit increase the probability of occurring the reverse reaction on the cathode.

REFERENCES

[1] J. Ghoroghchian and J.O'M. Bockris. Use of a homopolar generator in hydrogen production from water. International Journal of Hydrogen Energy, vol. 10 (1985) p. 101-112.

[2] N. Shimizu, S. Hotta, T. Sekiya and O. Oda. A novel method of hydrogen generation by water electrolysis using an ultra-short-pulse power supply, J. of Applied Electrochemistry, vol. 36 (2006) p. 419–423.

[3] S. Meyer, US Patent No. 5149407 (1992):. Process and apparatus for the production of fuel gas and the enhanced release of thermal energy from such gas.

[4] M.Vanags, J.Kleperis, G.Bajars „Electrolyses model development for metal/electrolyte interface: Testing with microrespiration sensors", international journal of hydrogen energy, vol. 1–5, (2010), p.

[5] R. R. Salem, Theory of the electrolysis of water. Protection of Metals, vol. 44 (2008) p. 120-125.