New electrochemical Sensor device, based on Arduino, for Measurements of Residue Charge of Primary Alkaline Batteries

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Abstract

As is well known, although so-called secondary batteries, i.e., chemical-physical devices that can be returned to a 'charged' state by appropriate charging methods, are readily available on the market; but, given their low cost, <u>the most widely used</u> and widespread batteries on the market <u>are the so-called "disposable", or non-rechargeable batteries, or alkaline batteries, or,</u> more properly, "<u>primary alkaline batteries</u>".
On 2024 European Portable Battery Association reports 295,000 tonnes, 570 g per capita in 2021. In unit terms, around 23 portable batteries per capita were placed on the market in 2020 [1]. According to a recent Eurostat report, Recycling of batteries and accumulators, around 244,000 tonnes (or an estimated 12 billion units) of portable batteries were placed on the market in the EEA (European Environment Agency) plus Switzerland in 2022 [2].
Given the amount of non-rechargeable batteries on the market, a tool is needed to measure the residual charge and then, if possible, define a re-charging method. Arduino has all the features to a data acquisition instrument, some our previous work use Arduino to build electrochemistry instrument [3] as well as the circuit presented here.

Introduction

Of the various primary batteries that have gradually appeared on the market, alkaline Zn-Mn dioxide batteries are the most commonly used for portable equipment. These latter devices, as is well known, convert chemical energy produced by internal <u>(irreversible) redox reactions</u> into a flow of electrons in the external circuit. In fact, when an alkaline battery of this type discharges, the electrolytic water decomposes into H^+ and OH^- ions. The H^+ ion reacts with the contained MnO_2, forming an interstitial compound, simultaneously transferring an electron. In fact, in the reduction process:

$MnO_2 + xH^+ + xe^- <=> H_xMnO_2$ (being x = 2).

In this reduction process, manganese goes from an oxidation number of +4 to +2. At the same time, the hydroxyl ion OH^- oxidizes the metal zinc, which changes to zinc hydroxide, $Zn(OH)_2$, that is, the metallic zinc loses two electrons (2 e^-), i.e.,:

$Zn + 2OH^- <=> Zn(OH)_2 + 2e^-$ (Zn passes from Oxide Number = 0, to O.N.= +2)

At the beginning of the discharge, when less than 40% has reacted (x < 0.4), the intermediate component H_xMnO_2 has the same structure (ramsdellite) as MnO_2. As the discharge continues, a new compound appears, MnOOH (groutite) (where the O.N. of manganese is +3). This new compound has a very different structure and cannot be transformed back into ramsdellite, even by changing the pH, i.e., by removing H^+ from the solution. This is why, during the discharge (i.e., when becomes x < 0.5, the reaction is no longer reversible), i.e., <u>the battery cannot be recharged.</u>
Attempts to recharge an alkaline battery may cause an imbalance within the cell, leading to gassing and possibly explosion on either charge or discharge cycles [4], *However, if an attempt is made to reverse the chemical reactions of a primary battery,* <u>first off all a careful measurement of the remaining capacity is required to determine whether the battery can be recharged.</u>
<u>The simple circuit described here, based on the Arduino UNO R3, allows the residual charge of an alkaline battery to be measured and plotted.</u>

Aim of the project

<u>The aim of this work is to construct a simple instrument, as shown in Figure 1, which estimate the state of charge of an alkaline battery</u>, here of the AA/LR06 type (i.e. “stilo” battery), <u>to be estimated in three steps.</u> The IEC 60086-1 to IEC 60086-6 regulations should be used as a guide, as well as the manufacturers' data sheets and bibliography.
The first step is to measure the voltage with a high impedance voltmeter (Atmel declare >100Mohm) with 10 steps of 1sec simulating no-load. The second step involves a relay connecting the battery to a 100 Ohm resistive load [4], i.e., double the value of blue curve of Figure 2 from [4], and the voltage is measured in 10 steps of 1sec. The third step includes a relaxation period of 10s to allow the battery to recovery, after which the voltage is measured again in 10 steps of 1s at no load. Therefore, the accurate measurement of residual charge is a complex task <u>[5].</u>

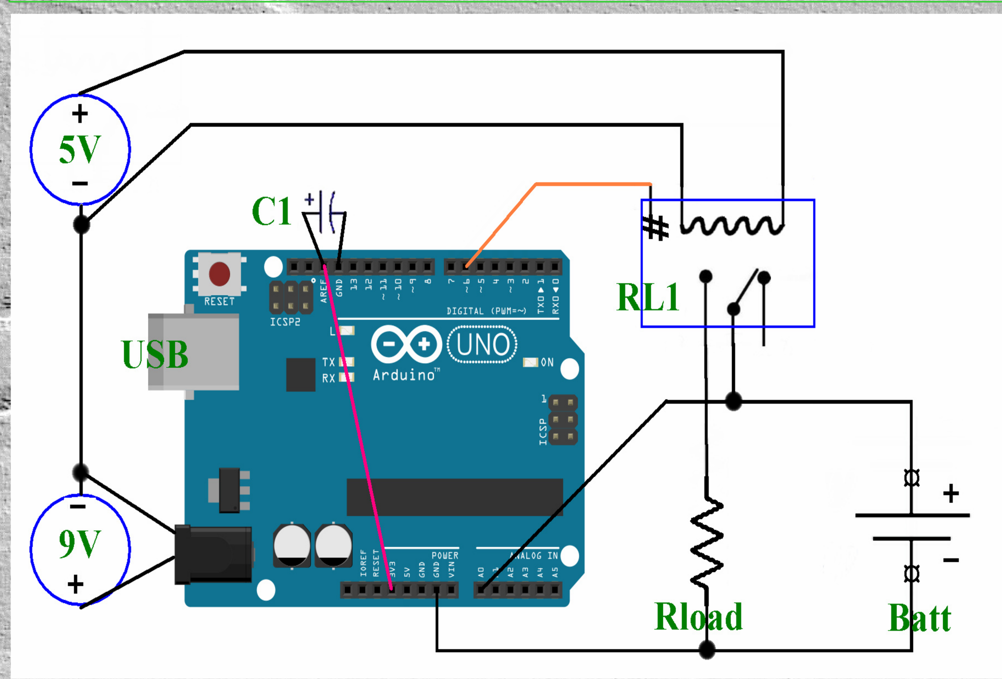

Figure 1. Schematic of the instrument. From the left the 2 power supply; the Arduino UNO R3 with purple bridge to reduce AREF (Analog Reference); the relay to connect the battery (DUT i.e. Device Under Test) to the load; in orange the digital signal to switch on-off the relay. The DUT is connect to ground and to analog pin of Arduino for measure voltage with/without load.

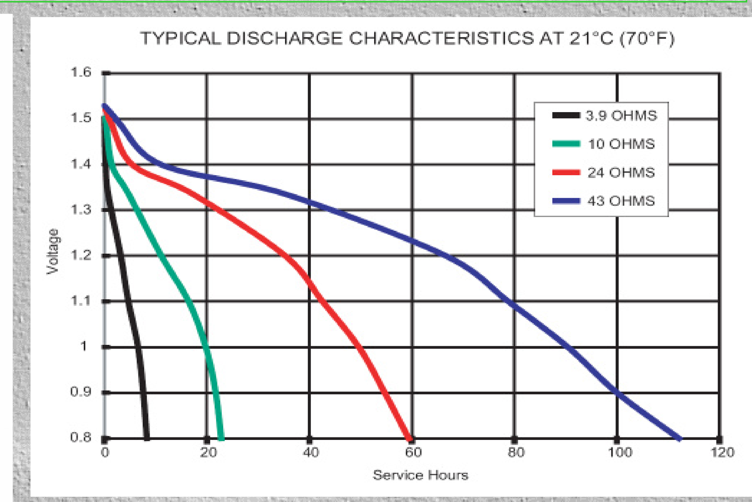

Figure 2. Discharge curve with constante load, see ohm, from this we select the Rload (i.e. load resistance) [4].

Material & Methods

Exhausted batteries were collected using a representative availability sampling method (convenience sampling), selecting those that were easily accessible in collection containers found in many electronics stores and shopping centres. Approximately 20 batteries were taken from each store.
An initial selection was then made in the laboratory to eliminate those that were clearly or partially damaged, such as those shown in Figure 3. This resulted in a final selection of 158 batteries in perfect aesthetic condition, some of which looked brand new.
Also the instrument was built in accordance with the 3R paradigm (i.e. reuse, recycling and recovery) using parts that were already available in the laboratory; only the Arduino and the relay were purchased.
The software (sketch) was written from scratch with comments on each line of code with educational use in an electrochemistry laboratory in mind. No external libraries not included in the Arduino IDE 1.8.9 were used.
The <u>device</u> produces text on the <u>IDE (</u>(Integrated Drive Electronics) serial monitor, which must be copied into a .txt file. This file is structured so that it can easily be read by any Excel program to produce tables (see an example in Figure 4) and graphs (see Figure 5). At the end of the study, all batteries were disposed of at the municipal recycling centre.

Figure 3. Disposed battery not suitable to check the remaining charge … to waste for recycle metals.

Running version:	v. 1.2		
Compiled at:	Dec 20 2024		
Compiled at:	22:37		
Battery name:	Conad Alcaline Plus 12-24 A		
Rload to measure Vbat	100		
	Volt		
sec	V0	Vload	Vafter
0	1.03	0.96	0.84
1	0.99	0.92	0.85
2	0.99	0.9	0.85
3	0.99	0.88	0.86
4	0.99	0.86	0.86
5	0.99	0.84	0.86
6	0.99	0.82	0.86
7	0.99	0.8	0.87
8	0.99	0.78	0.87
9	0.99	0.77	0.87
10	0.99	0.75	0.88

Figure 4. The output text from our device, from which the graphs in figure 5 and figure 6 derive.

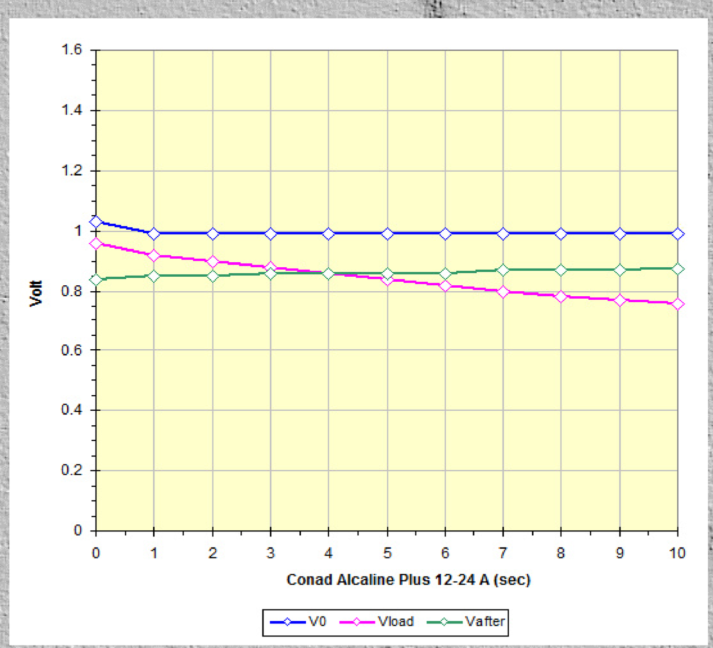

Figure 5. Curves obtained using instrument of Figure 1; first the blue show voltage with no-load, 5s of delay, the violet with 100 ohm load, 10s of delay, the green with no-load. The last point of violet curve, produce the values represented also in Figure 7.

Results

The graph in <u>Figure 6</u> shows typical, expected trends for a batteries with different residual charges:
-the blue curve shows the battery voltage measured every 1 second at high impedance, which in this case remains constant at about 1V;
-the violet curve shows the battery voltage when connected to an R-load of 100 ohms, again in 1 sec. increments;
-in green, is shown the voltage produced by the battery still at high impedance after the recovery period.
The kinetics of the internal redox reactions, also demonstrated in other studies, causes the voltage of the battery not connected to a load to rise, which is why there is a delay of 5 seconds after each series of measurements.
Of all the possible curves, Figure 5 is "typical", a constant voltage at no load, a slow discharge when current is requested, recovery and the green curve, perhaps left for a long time, would reach the blue curve.
Each battery behaves differently, maintaining a pattern as in Figure 5, but with different slopes and values, perhaps related to the different chemical composition and the different discharge process undergone.
The five batteries in Figure 6 show a sample of the 158 batteries measured: a) a new but (unfortunately) discarded battery, b) a used battery but with a lot of residual charge, c) almost discharged but with a typical trend, d) a battery that appears to be still charged from the blue curve but collapses as soon as you ask it for current, e) a battery with a very low residual charge.
For completeness, there are several batteries that show a blue curve close to zero.

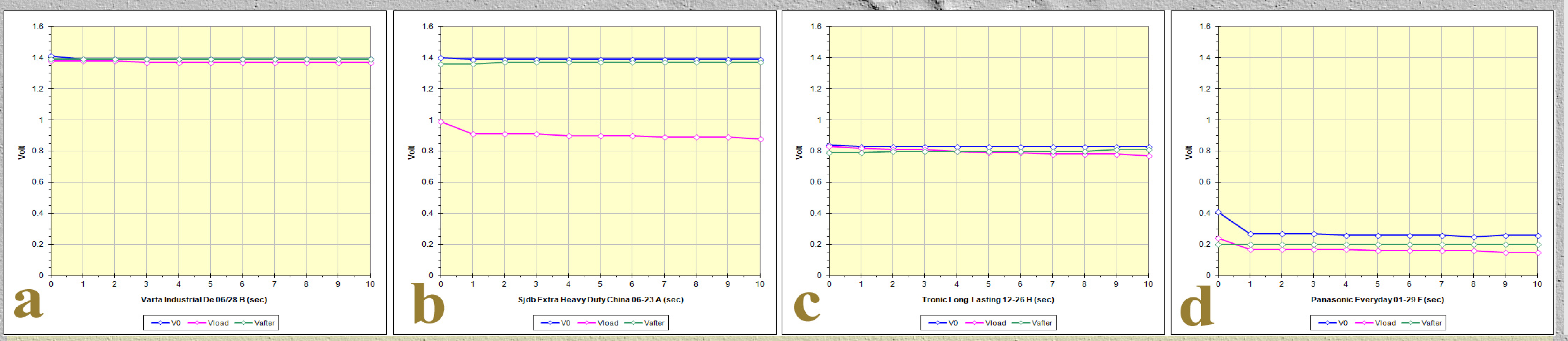

Figure 6. Typical, expected trends for batteries with different residual charges. Four different AA alkaline battery (find in a waste-thank ready for dismantle) measured with instrument of Fig.1. The a) is like new whit a few use; the b) is a perfect example of quality of our measure method, with no-load the voltage is like new but under load the battery fall; the c) is under the limit of discharge for IEC standard 0.9V; the d) is a battery near empty. More battery show 0V when measured.

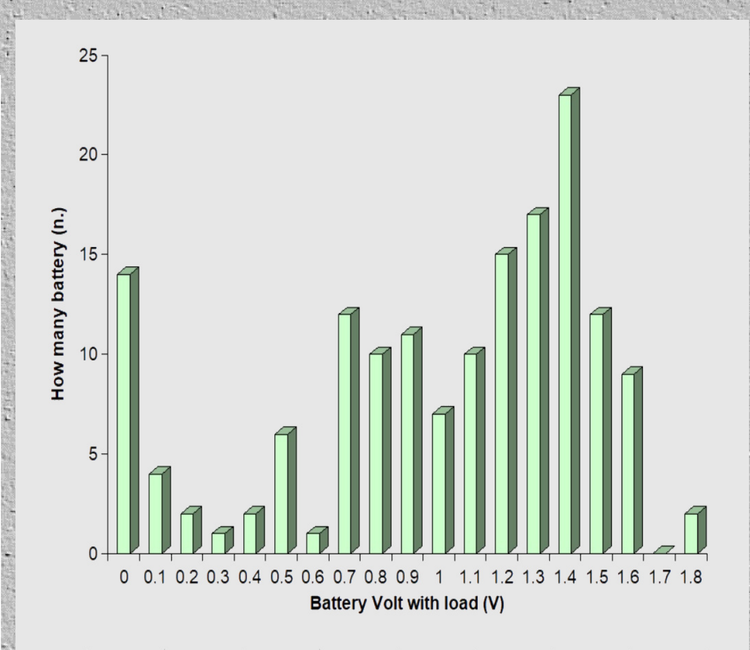

Figure 7. After measure 158 disposed AA battery we obtain the above histogram using the last point of violet curve of Figure 5. Counting, 48% of the measured batteries show a voltage from 1.2 to 1.6V. Accounting the IEC (International Electrotechnical Commission) 60086 norms stated 0.9V as lower limit, 65.8% of our battery stay from 0.9 to 1.6V.

Conclusions

Bearing in mind that standards and manufacturers define an alkaline battery as discharged when it drops to 0.9V [6], let us make some observations about the results.
The number of batteries is still too small for statistics and the study is still in progress, but from the data obtained, shown in Figure 7, we can already see several practically new batteries at 1.6V, a group of batteries with a lot of residual charge with voltages between 1.5 and 1.2V.
Then there is a group with a voltage between 1.1 and 0.9V.
The instrument probably disconnects the battery when it drops below 0.9V, which would explain the small number of batteries between 0.6 and 0.1V, and finally a large number of batteries with no voltage.
A recharging test, which will be the subject of a later paper, could use this graph to identify the batteries that are the best candidates for regeneration.
<u>In the light of these data, a word of advice to users is in order: buy a passive battery tester</u>, such as the (BT-168, the IBT-Tester4 or the BAT-393) commercial models which will cost you a few euros but will allow you to recycle 40% of the batteries you would otherwise throw away, for example in a wall clock or a mouse.

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