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Original Paper

Modeling of the Electrochemical Reactions at the Electrode-Electrolyte Interface of Nickel/Metal Hydride Batteries by an Equivalent Electrical Circuit

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Abstract

Based on the experimental impedance spectra, the electrochemical reactions that are deposed at the electrode-electrolyte interface can be modeled by equivalent electrical circuits. Each element used in the circuit must have a physical correspondence in the electrochemical system. In this work, a model has been proposed to a NiMH battery electrode to describe, in detail, the electrochemical process at the interface of this electrode. The theoretical impedance of a proposed circuit is a function of several variables. These adjusted variables to reach a good agreement between the theoretical spectra and the experimental spectra in the studied frequency. The Z-simplex software allows refining the experimental results. These results show a good superposition between the experimental spectra and the theoretical spectra corresponding to the proposed electric circuit. This leads to the conclusion that the proposed circuit describes the phenomena that take place at the interface of the hydride electrode.

Keywords

batteries, hydrogen, equivalent electrical circuit, electrochemical impedance spectroscopy, hydrogen diffusion coefficient

1. Introduction

Nowadays, the commercial portable energy storage devices such as lead-acid battery, Lithium Ion Battery (LIB), and nickel-based alkaline battery are frequently used in electric vehicles because of their large energy density. Hydrogen is a resource-rich element and generated by water electrolysis reaction. A typical hydrogen-based energy storage system consists of a water electrolyser. Many metals, alloys and intermetallic compounds of type AB_5 have the property of storing hydrogen with good properties in terms of safety, energy efficiency and long-term storage. However, to be able to respond to applications, they must have a high capacity, a good reversibility and a great reactivity. Besides the utilization for hydrogen storage, these compounds can be use as negative electrode in NiMH batteries. The surface properties of the Metal Hydride (MH) particles in the MH-anode are further very important for a functional electrode. To understand the different phenomena that flow to the electrode-electrolyte interface, different electrochemical method such as Chronopotentiometry, Chronoamperometry and cyclic voltammetry, are techniques in large signals that only inform the slowest step of the electrochemical process. Modeling electrochemical impedance spectroscopy is usually done using equivalent electrical circuits. These circuits have parameters that need to be estimated properly in order to make possible the simulation of impedance data. Electrochemical impedance spectroscopy it used to analyze the electrochemical response of a system subjected to a small amplitude perturbation around a given operating point characterized by the current-potential (I_0, E_0). In this paper, we have we have determined the impedance spectra of the $MmNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.4}Fe_{0.35}$ compound. Basing on experimental spectra, we propose an equivalent electrical circuit and fitting by Zsimplex software to determine certain electrochemical parameters.

2. Theory

This method allows theoretically discerning, according to their time constant, the various processes involved in the electrode. This method, it also used to determine the kinetic parameters such as the exchange current density and the diffusion coefficient of hydrogen in the alloy. These parameters are in direct relation with the mechanisms of insertion and desertion of hydrogen during cycling. The experimental and theoretical values of impedance represented in two distinct types of diagrams:

- Representation of Nyquist: the curve is drawn in the complex plane (-imaginary of Z noted "$-Z_{Im}$" as a function of real of Z noted "Z_{Re}").
- Representation of Bode: this graph, separated in two parts, presents the phase φ of the impedance as well as its modulus, according to the logarithm of the perturbation frequency.

The impedance spectra, in one or other of the representations, reflect the phenomena that take place on the surface of an electrode such as oxidation-reduction reactions and mass transfer phenomena. Their modeling, which forms the essential part of the study of these spectra, requires the use of an equivalent electrical circuit to describe the electrochemical processes at the interface. The theoretical impedance of a proposed circuit is a function of several variables. These adjusted variables to reach a good

agreement between the theoretical spectra and the experimental spectra in the studied frequency domain. Thus, information concerning the electrochemical process can be determined by the interpretation of these variables. For example, the impedance of the electric circuit shown in Figure 1 is given by equation 1:

$$Z = R_1 + \frac{R_2 + R_3 + j\omega R_2 R_3 C_2}{1 + j\omega R_3 (C_1 + C_2) + j\omega R_2 C_1 + (j\omega)^2 R_2 C_1 C_2} \quad (1)$$

This impedance is a function with several variables (R_1, R_2, R_3, C_1, C_2 and ω). Once the parameters of the equivalent circuit are determined, the impedance Z becomes a simple function of the frequency ω and an impedance spectrum is obtained.

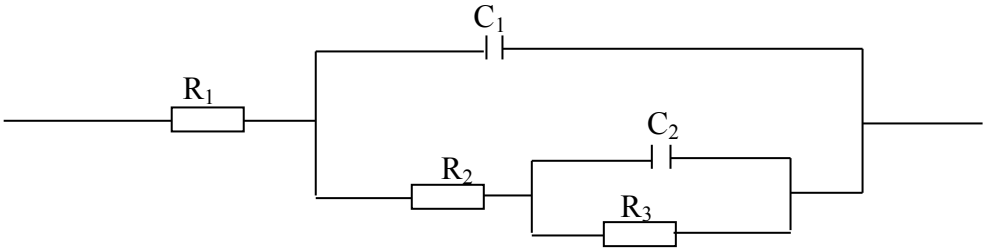


Figure 1. Electrical Circuit with Different Variables

Since the phenomena that take place at the interface are very complicated, modeling requires the use of more complex electrical elements that depend on the frequency. In this case, the CPE (Constant Phase Element) denoted Q, will be used to replace a capacitance C. Indeed, in the case of most of the solid electrodes, a deformation of the impedance diagrams in the complex plane is often observed. This deformation can be attributed to the heterogeneity of the surface in terms of porosity and surface roughness, causing a distribution of the different absorption sites. To explain this behavior of the electrode, the model of the EPC has been proposed. This model predicts a rotation of the capacitive loops in the complex plane. This rotation is at a 90 ° angle (1-n), where n is the fractional parameter (0 < n < 1) representing the degree of depression of the semicircle. In this case, the impedance of this Constant Phase Element (CPE) which replaces the capacity of the double layer is written:

$Z_{CPE} = \frac{1}{T\,(j\,\omega)^n}$, where T is a constant expressed in F Cm^{-2} S^{n-1}

Similarly, the diffusion phenomena is represented by a Warburg impedance which is written by the equation 2:

$$Z(\omega) = \frac{1}{Y_o (j\omega)^{1/2}} = \frac{1}{Y_o \sqrt{2\omega}} [1 - j] \quad (2)$$

where, Yo is determined by smoothing the impedance branch corresponding to that of Warburg.

This impedance appears in the Nyquist plane as a straight line with a slope of 1. It is given by equation 3:

$$Z(\omega) = \frac{1}{\sqrt{2}\,FSC_o\sqrt{D}}\left(\frac{dE}{dx}\right)[1-j] \quad (3)$$

If we make the equality between the two equations (2) and (3) we get the equation 4:

$$Y_o = \frac{FSC_o\sqrt{D}}{\left(\frac{dE}{dx}\right)} \quad (4)$$

This expression allows us to determine the diffusion coefficient of hydrogen in the material. Impedance spectral modeling is performed by the software "Zsimplex".

This software makes it possible to determine the parameters of the proposed circuit. Each element used in the circuit must have a physical correspondence in the electrochemical system. Table 1 gives a list of the elements, their symbols, their transfer functions and the smoothing parameters given by the Zsimplex software.

Table 1. List of Elements, Their Symbols and Their Transfer Functions

Elements	Symbol	Transfert fonction		Fitted parameters
		Admittance (Y)	Impédance (Z)	
Resistance	R	1/R	R	R
Capacitance	C	j C ω	1/(jCω)	C
Warburg	W	$Y_o(j\,\omega)^{1/2}$	$1/Y_o(j\,\omega)^{1/2}$	Y_o
CPE	Q	$T\,(j\,\omega)^n$	$1/T(j\,\omega)^n$	T et n

Before starting the fitting, it is necessary to represent each electrical circuit proposed by a code. The parentheses are used to say that the electrical elements are in parallel. For example, R (RC), to say that R and C denoted by (RC) which are in parallel, are connected in series with a resistance R. The circuit code presented in Figure 1. It is written: R_1 (C_1 (R_2 (R_3C_2))). The procedure for fitting the impedance spectrum using the Zsimplex software is as follows:

i) Draw, by Zsimplex software, the experimental impedance spectrum in the Nyquist or Bode plane,

ii) Propose an electrical circuit, which can describe the various electrochemical phenomena that take place at the electrode,

iii) Transform this circuit into code,

iv) Fitting the experimental data by the software,

v) Evaluate the quality of smoothing (general error),

vi) Repeat steps from (i) to (v) until a good fit.

In general, a well-fitted spectrum has an overall error of less than 10% on all parameters. This error is given by the software as a curve (error as a function of frequency). Similarly, the quality of the smoothing by Zsimplex software is given by the equation 5:

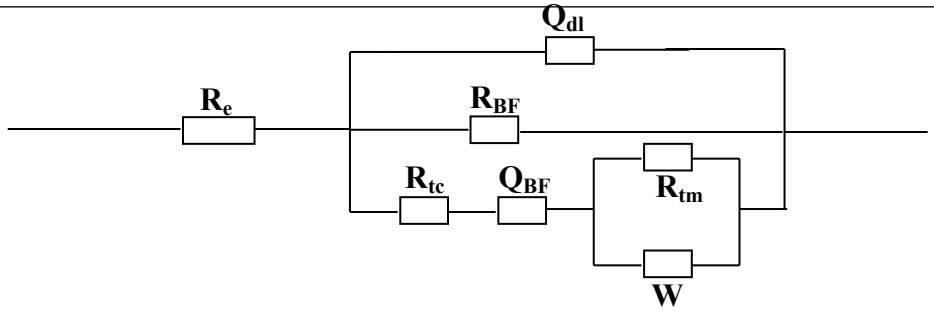
$$\chi^2 = \frac{1}{N}\sum_{i=1}^{N}\left|\frac{Z_e(\omega_i) - Z_p(p,\omega_i)}{Z_e(\omega_i)}\right|^2 \quad (5)$$

Where N is the total number of experimental points, Ze and Zp the values of the experimental and theoretical impedances corresponding to the frequency ωi. For a well-refined spectrum, the value of $\chi^2 < 5\ 10^{-3}$.

3. Equivalent Circuit of a Hydride Electrode

The aims of the electrochemical impedance modeling are 1) the search for an appropriate electrical circuit whose behavior with respect to a low-amplitude perturbation around an operating point is equivalent to the actual behavior of the electrode, and 2) the determination of the values of its different components.

Since the overall current flowing through the surface of the electrode is the sum of a faradic current IF and a capacitive current IC, the interface can be represented in the case of small disturbances by the circuit shown in Figure 2. In the Zsimplex program used, the code assigned to this circuit is Re (RBF (Qdl (RtcQBF (RtmW)))). Determining the values of the components of this circuit makes it possible to calculate the values of the kinetic parameters. Namely the capacity of the double layer, the charge transfer current density, the diffusion coefficient of the hydrogen in the material, the capacitance of the high frequency loop, the charge transfer resistance and the mass transfer resistance, which describe the different electrochemical processes that take place at the electrode surface.



R_e: Electrolyte resistance, Q_{BF} : Capacity of the low frequency loop,

Q_{dl} : Double layer capacity, R_{tm} : mass transfert resistance,

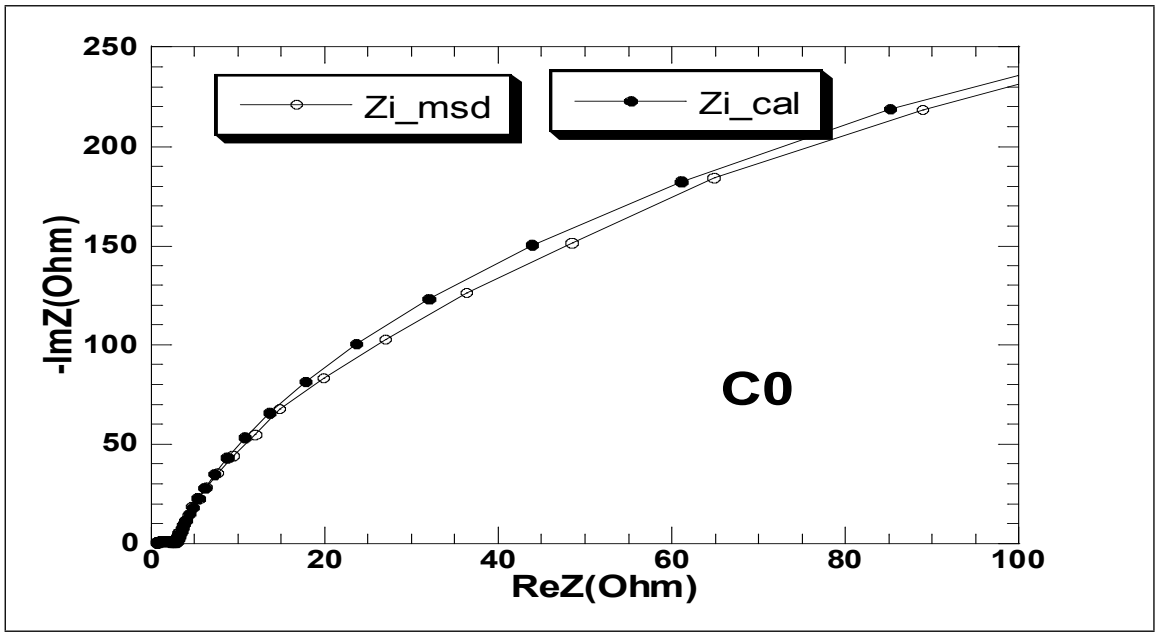
R_{tc} : Charge transfert resistance W: Warburg impedance.

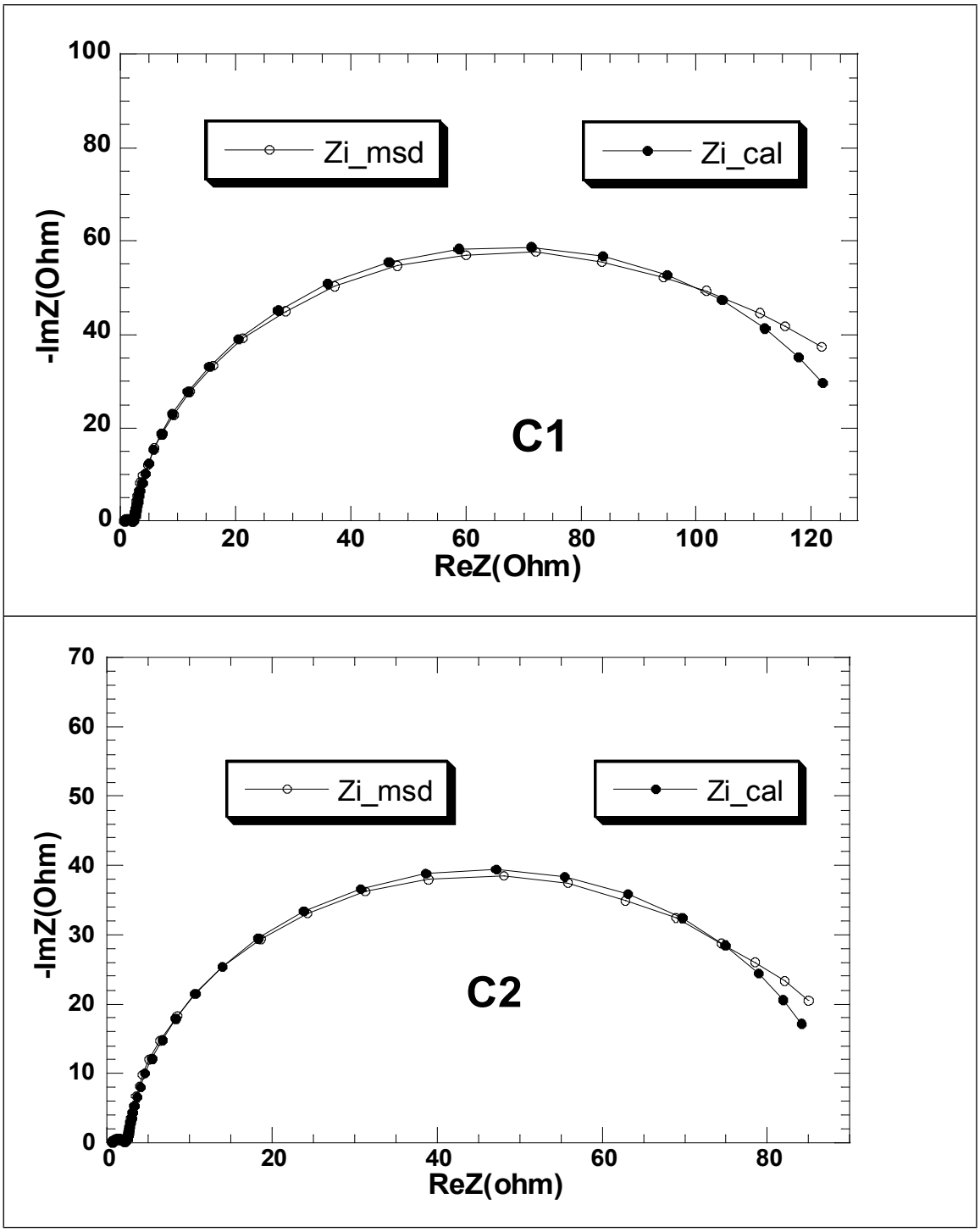
R_{BF} : Resistance of the low frequency loop,

Figure 2. Equivalent Electric Circuit of the Phenomena Occurring at the Interface Hydride Electrode-Electrolyte

4. Results and Discussion

Figure 3 gives the spectra measured after different number of cycles for a state of charge of 10% and calculated using the software Zsimplex and that for respectively the $MmNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.4}Fe_{0.35}$ compound. The Z-simplex software allows refining the experimental results by using the equivalent electrical circuit given in Figure 2. The errors on the phase φ and moduls are represented by the Figure 4. These Figures show a good superposition between the experimental spectra and the theoretical spectra corresponding to the proposed electric circuit. This leads to the conclusion that the proposed circuit shown in Figure 2 describes the phenomena that take place at the interface of the hydride electrode. The parameters of this circuit are and the values of the corresponding kinetic parameters are given in Table 2.




Zi_msd
Zi_cal
C1
-ImZ(Ohm)
ReZ(Ohm)
0
20
40
60
80
100
120
Zi_msd
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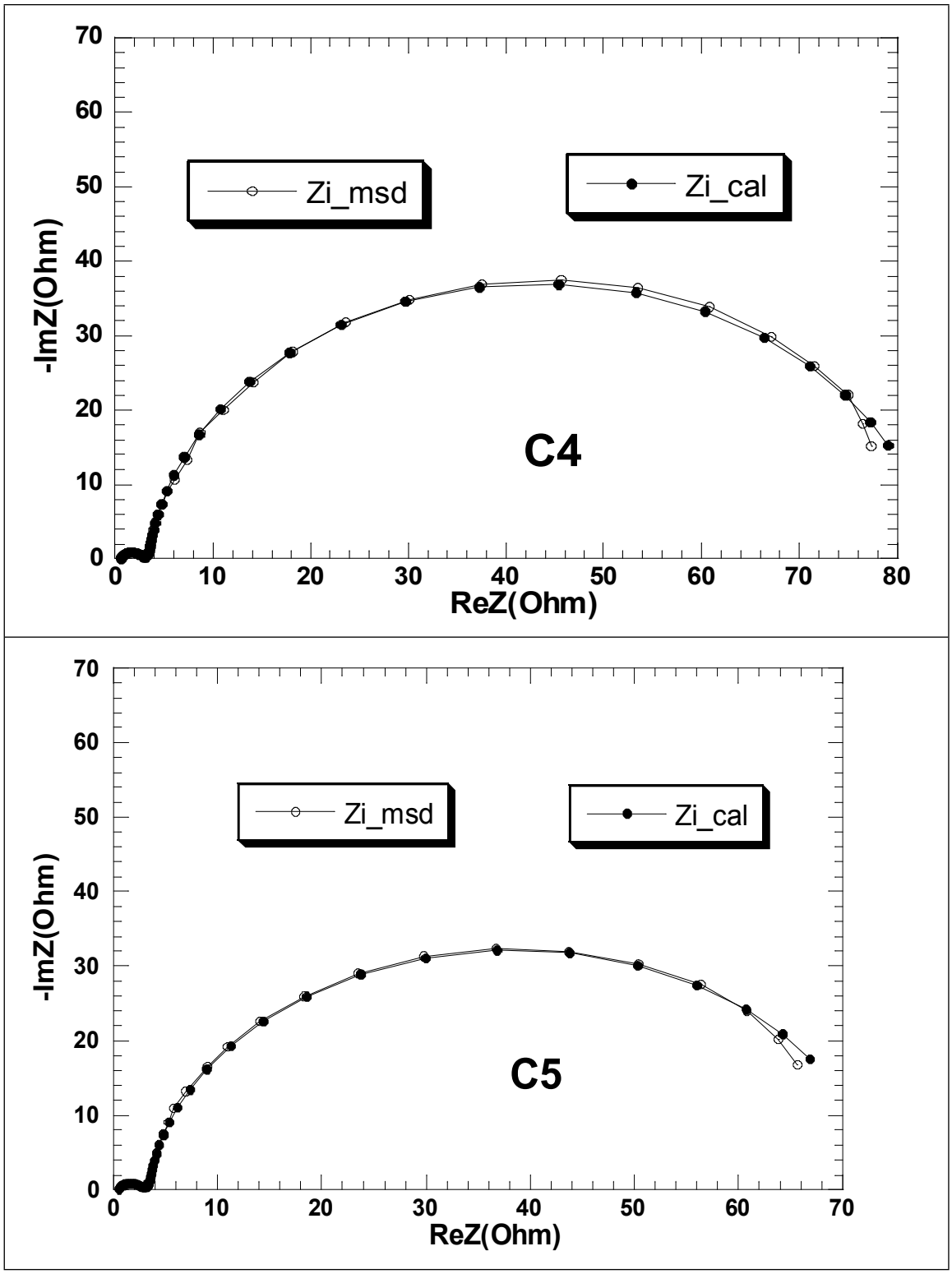
70
80


Zi_msd
Zi_cal
C4
-ImZ(Ohm)
ReZ(Ohm)
0
10
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40
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60
70
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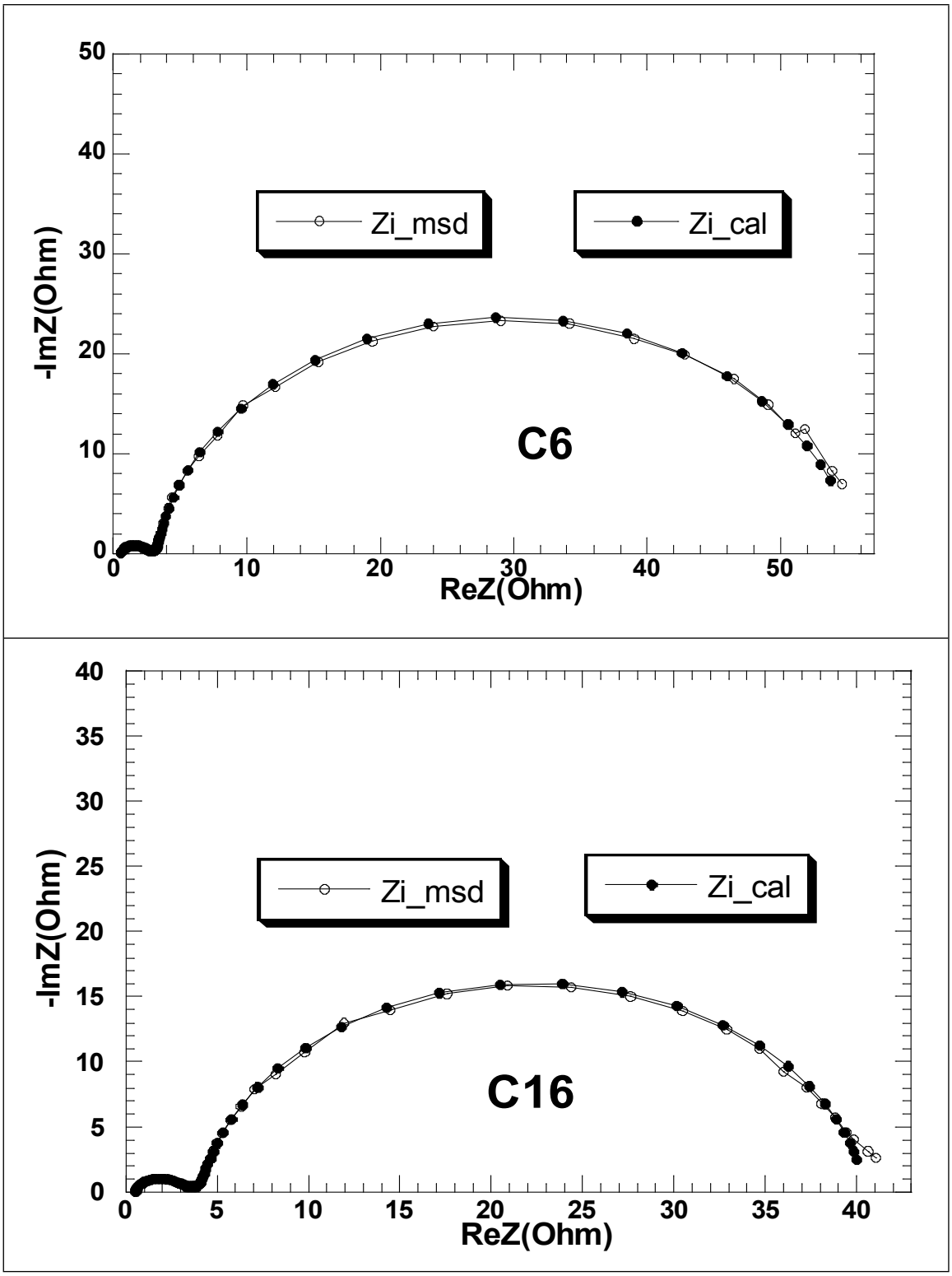
Zi_cal
C5
-ImZ(Ohm)
ReZ(Ohm)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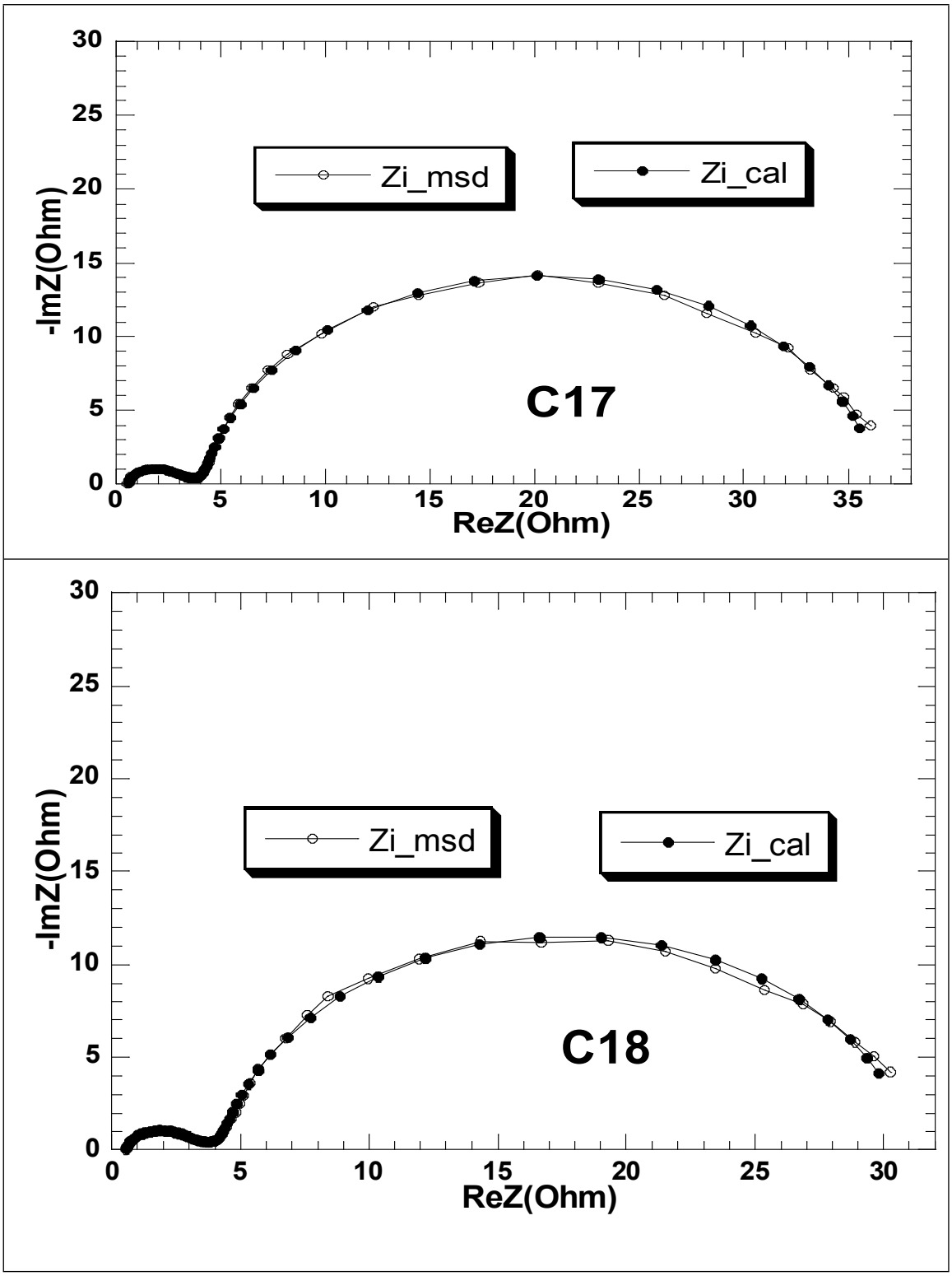
ReZ(Ohm)
Zi_msd
Zi_cal
C6
C16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C17
C18

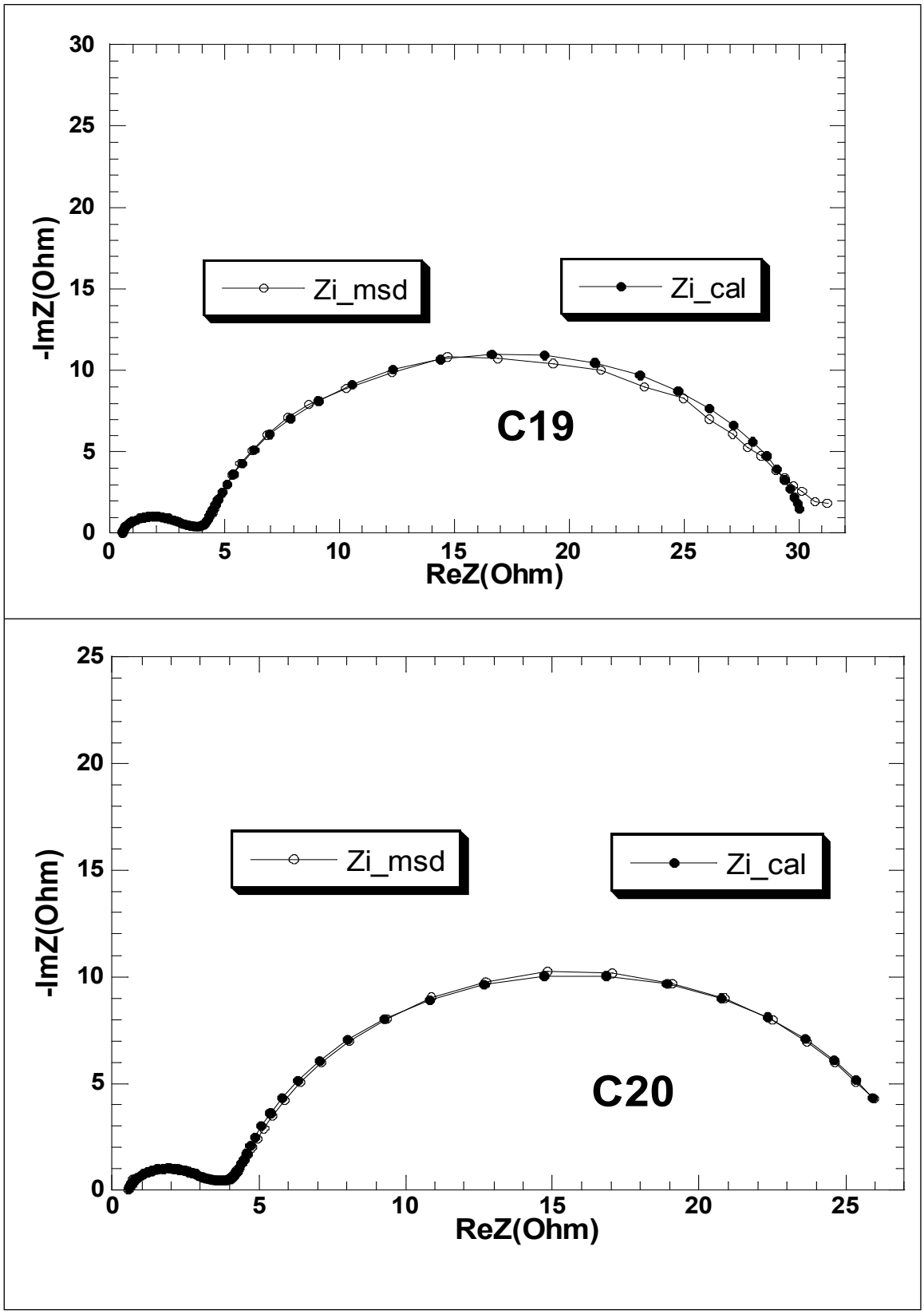

Figure 3. Calculated and Measured Impedance Diagrams of the Compound $MmNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.4}Fe_{0.35}$ as a Function of Cycling for a State of Charge of 10%

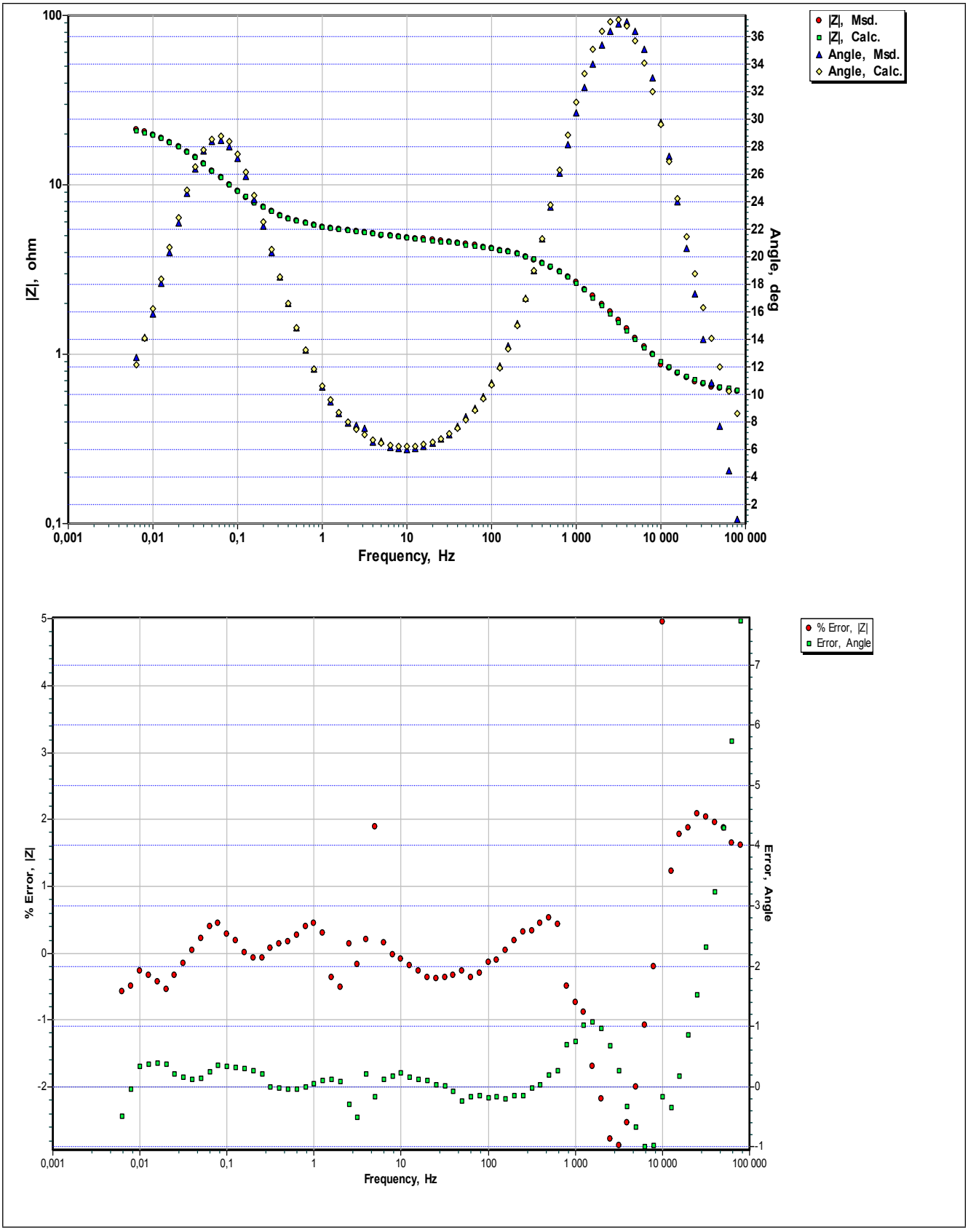

Figure 4. Errors between Measured and Calculated Values of the Phase φ and Moduls

Table 2. Calculated Values of the Different Components of the Equivalent Electrical Circuit and the Corresponding Kinetic Parameters for the Electrode $MmNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.4}Fe_{0.35}$

	$R_e(\Omega)$	$R_{tc}(\Omega)$	$C_{dl}(\mu F)$	$R_{BF}(\Omega)$	$C_{BF}(mF)$	$R_{tm}(\Omega)$	$I_0(mA\ cm^{-2})$	$D_H(cm^2s^{-1})$
$Cycle_0$	0.55	2	282	859	189	0.4	12.8	$3.92\ 10^{-11}$
$Cycle_1$	0.7	1.3	78	132	192	0.47	20	$6.75\ 10^{-11}$
$Cycle_2$	0.65	1.3	63	89	186	0.6	20	$7.08\ 10^{-11}$
$Cycle_4$	0.6	2	48	83	177	1	12.8	$7.08\ 10^{-11}$
$Cycle_5$	0.55	2	42	73	199	1	12.8	$8.1\ 10^{-11}$
$Cycle_6$	0.52	2	44	55	184	1	12.8	$22.7\ 10^{-11}$
$Cycle_{16}$	0.55	2.5	41	40	166	1.6	10.5	$24.9\ 10^{-11}$
$Cycle_{17}$	0.55	2.5	41	36	163	1.6	10.5	$32.7\ 10^{-11}$
$Cycle_{18}$	0.55	2.5	43	31	160	1.8	10.5	$71.8\ 10^{-11}$
$Cycle_{19}$	0.55	2.5	40	30	158	1.8	10.5	$157\ 10^{-11}$
$Cycle_{20}$	0.55	2.5	40	27	148	1.9	10.5	$380\ 10^{-11}$

These results show that the value of the resistance of the electrolyte Re is independent of the cycling, it is about 0.6 Ω. However, the charge transfer resistance R_{tc} varies from 1.3 to 2.5 Ω. We notice that the hydrogen diffusion coefficient increases during cycling. In fact, during cycling the insertion and de-insertion of hydrogen into the metal causes cracking and decrepitation of the grains of the alloy and therefore increases the reaction surface. As a result, the diffusion of hydrogen becomes easier. This decrepitation is not without harmful consequences. Indeed, the phenomenon of corrosion will be more and more accentuated when the particles will be more and more exposed to electrolyte.

4. Conclusion

The experimental impedance spectra, determined at different numbers of cycles, are modeling by an equivalent electrical circuit allowing the ZSimplex software to; determine the different kinetic parameters, namely the charge transfer current density and the load coefficient. diffusion of hydrogen in the material at different charge rates and the parameters which describe the different electrochemical processes taking place at the electrode/electrolyte interface, namely the capacity of the high frequency loop or the capacity of the double layer, the charge transfer resistance and mass transfer resistance (impedance spectroscopy). The results obtained show that the proposed circuit describes well the electrochemical processes that take place at the electrodes-electrolyte interface.

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