COMPREHENSIVE ANALYSIS OF CARBON FELT ELECTRICAL PROPERTIES BEING IN DIFFERENT ENVIRONMENTS

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Abstract

Electro-conductive carbon felt (CF) material composed by bonded together different lengths carbon filaments has porous structure and significant internal surface for ensuring rapid electrochemical redox reactions. Owing good hydrodynamic and electrical properties CF found in numerous electrochemical applications for electrodes design in redox flow batteries, fuel cells, electrochemical desalination apparatus etc.

Felt internal structure is composed by bonded together different lengths carbon filaments, which stochastically oriented interconnections resulting good electrical conductivity. Its electro-conductivity is ensured mostly by long bonded carbon fibers located between electrodes and touching at the same time both of electrodes surfaces. Electro-conductivity property of CF is extremely important for the efficient activities of different appliances where CF is used including electrochemical cells for diverse purposes. Hence, this property should be studied deeply and essentially.

Improved electrical conductivity is achieved by a small pressing of CF to the direction of conducting electrodes substrate. Increasing stress on a felt provides supplementary electrical contacts of carbon filaments inside a felt that causing improved electrical conductivity. Moreover, internal interconnects enhance an active surface of a felt electrode boosting redox chemical reactions. However, additional CF pressing diminishes its hydrodynamic permeability and this circumstance should be considered for the optimal design of electrochemical cells.

CF electrodes are used in different conditions. For heating elements, it is used as a dry substance. However, in electrochemical cells felt electrodes are immersed in different electrolytes, which are capable to change fibers interconnections and influence conductivity. Consequently, the impact of electrolyte characteristics on CF electro-conductivity should be investigated as well.

Designer of specific electrochemical system must know CF electrical characteristics for selecting optimal design of a cell.

Presented article provides the results of numerous measurements and analysis of CF electrical properties like a dry and immersed in several non-conductive liquids having various electrical permittivity.

The article includes: Introduction, Methodology of Experimental Research, Conductivity Measurements, Math Interpretation of Experimental Data and Conclusions.

I. Introduction

Carbon felt material is widely used for electrodes substances in different applications including electrochemical [1-7]. For today its most prominent utilization is in the Vanadium Redox and others flow batteries regards its good electrical conductivity, hydraulic permeability and durability to sustain in strong acid and alkali electrolytes [8-20].

The following research works [21-30] dedicated for investigation and measurements of different including electrical properties of CF. Factual physical parameters of rayon-based CF and which is being manufactured in Mersen C^{o}. as large sheets with a width of several mm up to a few cms could be found in [31].

As a material for heating elements or for electrodes, carbon felt must possess necessary electric conductivity. Its conductivity could be improved by felt squeezing because of diminishing distance between carbon fibers and producing additional quantities of fibers interconnections. However, this automatically causes a decrease of an empty volume and cross-section of microchannels connecting pores inside felt framework. The results of this process it a decrease of a felt permeability or increase of hydraulic resistance preventing free electrolyte flow through electrode.

Since for optimal development of a specific appliance with CF one must consider electrical properties, numerous scientific works studied they experimentally and theoretically. Because of significantly stochastic framework structure of a carbon felt, theoretical analysis as a rule have many assumptions and their conclusions may be far away of a real situation. Therefore, most of well-known investigation of carbon felt electrical conductivity were provided experimentally with the following analysis of obtained results.

One of the first measurements of CF electrical resistivity was carried out for furnace heating elements [3]. The work [26] describes the design of a new bipolar cell with proton-exchange-membrane where flat electrodes were made of flexible and loose carbon fiber bunches representing an analog of CF. Due to the need to ensure good electrochemical reactions on electrodes, tests of CF resistivity were conducted. For the first time, the results of CF area-specific resistance (ASR) were represented as a function of a squeezing pressure. It should be noted that ASR represents a parameter equal to a total resistance in the perpendicular-plane direction of CF electrodes divided by the value of its area. The decrease of the bulk resistance was observed as an exponential function with negative exponent value depending on the pressure applied to the CF electrode.

Important and original results of measured ASR for CF [27] were expressed as a function of a compression pressure. Different electrode-bipolar plate assemblies and adhesive conducting materials were investigated in this work.

The same (as in [26]) exponential diminishing of a resistance versus compression pressure was observed, however with different coefficients of the exponential function, which depend on the type of construction and adhesive materials. However, the above-mentioned references don't include an analytical expression of resistance versus felt porosity and specific resistivity of a carbon filaments. This shortcoming is improved in [28-30]. Specific area electrical resistance (ρ_{felt}) [28] is approximated by electrical resistance of a carbon material (ρ_{carbon}) comprising felt filaments and by a felt porosity as:

$$\rho_{felt} = \frac{4}{(1-\lambda)}\rho_{carbon} \quad , \qquad (1)$$

Expression (1) is in good agreement with the measurements results provided in [29]. ASR of CF electrodes (denoted as (R_{ASR}) in [30]) for vanadium redox batteries was determined experimentally. Approximation of R_{ASR} [$m\Omega\cdot cm^2$] versus V_f (fiber volume fraction, %, the opposite of the porosity λ, i.e.. $V_f/100=1-\lambda$) was evaluated by following exponential function:

$$R_{ASR} = 144.456\cdot\left(3-\frac{10}{V_f}\right)^{-1.117} \qquad (2)$$

Approximation (2) is more accurate for describing electrodes resistance of specific vanadium redox batteries assumes only carbon content. Also, the important roles of a specific carbon conductivity value and interconnections density between carbon filaments inside a felt, were not considered. Furthermore, all experimental measurements were carried out in dry conditions only, i.e.. in air. Thus, neglecting fibers interconnections in expression (2) can't precisely predict electrical conductivity of a CF being immersed in different electrolytes. However, real electrodes work in electrochemical cells filled with different electrolytes and our experiments showed the dependence of resistivity on the type of electrolyte. Resistivity or conductance of CF seems to be influenced by some liquids 'specific properties conducive to the penetration of fluid between fibers and in this way decreasing the interconnection density and diminishing the felt conductivity or conversely causing the convergence of fibers and the decrease of resistance.

Because of a significantly stochastic framework of felt structure, theoretical analysis as a rule requires many assumptions, making the real-world validity of its results questionable.

Therefore, it was decided to conduct a parallel study of both electrical and hydraulic properties of the same CF. The results of the experimental research together with the analytical approximations are presented below.

II. Methodology of Experimental Research

The experimental research main objective was the investigation and determination of electrical properties of CF in a wide range of external conditions.

Characteristics of CF

The CF for experiments was a rayon-based material made from high-quality carbon fibers. It has a porous structure with a large superficial surface. Rayon based CF from the well-known producer "Mersen" USA Greenville-MI Corp [26] was the matter for the tests. Its structure shown in (Fig.1). Additional characteristics of this kind of CF could be found in Table 1.([31])

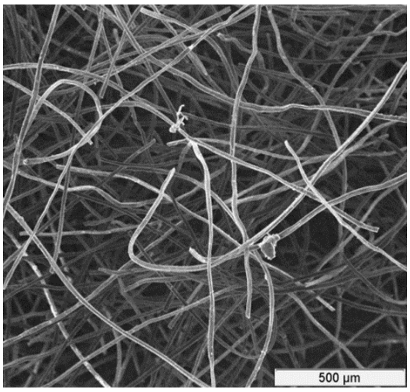


Fig.1. A magnified picture of CF structure

Table 1. Mechanical properties of a CF

	Average	ndard deviatic
Fiber diameter, µm	19.2	1.66
Felt density, [kg/m^3], ρ_f	88	-
Carbon density, [kg/m^3], ρ_c	1954	-
Porosity, [%], θ	95.5	-

lative carbon volume, p.u. [%], V	0.045 (4.5%)	-
Specific felt surface, [m^{-1}], S	$9.8 \cdot 10^3$	-

The special testing cell was made (Fig.2), which construction permits electric conductivity measurements for differently squeezed CF. Cells dimensions (Fig.3) allowed testing felt samples 47×28.7 mm whereas felts height has been changed by pressing from 6.6 to 1.2 mm by four screw bolts. A symmetry of a felt squeezing and its height measurements have been provided by electronic caliber having 0.01 mm accuracy.

Electrical conductivity was measured for the felt is in the cell between two thin copper sheets simulating electrode's substrate.

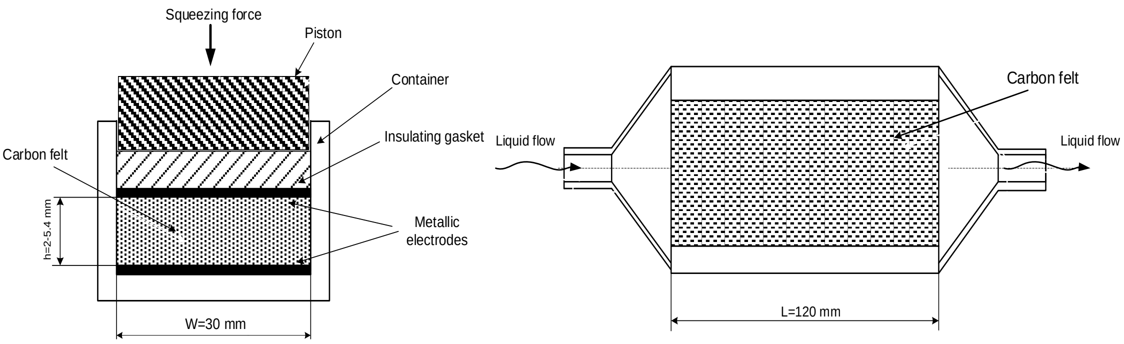


Fig.3. Special experimental cell for conductance measurements

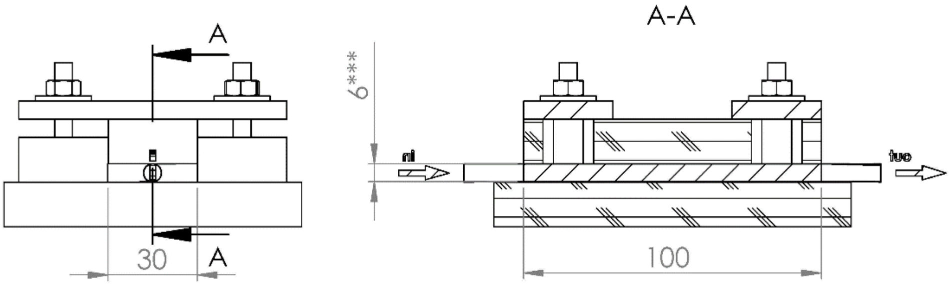


Fig.3. Dimensions of the experimental cell (from [21])

Electrical conductivity was determined in the cell for differently squeezed CFs, firstly, in dry conditions and later when CF was immersed into three different dielectric liquids having dissimilar electrical permittivity. These liquids were glycerol, alcohol, and cyclohexane. Conductivity estimation was provided by bench type R/L/C METER IX 3131B able to measure resistance by applying 100Hz, 120 Hz, 1kHz, and 10 kHz AC frequencies with the error of ~0.6%. In addition, resistance by applying DC was measured by Fluke multimeter. Results of conductivity measurements are presented in the following sections.

III. Conductivity Measurements

Electrical measurements outcomes will be presented here both for dry felt electrodes and for those immersed in different however dielectric (nonconductive) liquids. The reason for applying dielectric liquids was preventing the influences of own (ion) liquid conductivity on the resistance of the felt which was the main object of the investigation. Major supposition for the conductivity description was an assumption that the resistance of the felt determined mainly by the density of filament's interconnections inside a felt as well as by the density of filament's contacts with electrode's surfaces.

Three dissimilar liquids were chosen: glycerol, alcohol, and cyclohexane all with significantly different electric permittivity ε. Below is the Table 2 representing the most important physical parameters of them. Resistance values of dry CF are shown in Table 3.

Table 2. Physical parameters of glycerol, alcohol, and cyclohexane.

Parameter	Liquid		
	Glycerol	Alcohol	Cyclohexane
Density, [g/cm^3] (25°C)	1.26	0.789	0.8
Dielectric constant, ε_r, [p.u. (0.57MHz, 25°C)	~42.5	~21.6	~2.02
lectrical conductivity, [(Ω·c ^{1}], 25°C	$5\cdot10^{-8}$	$\sim1\cdot10^{-6}$	$<5\cdot10^{-9}$
Viscosity, [Pa·s], 20°C (30°	141 (61.2)	~0.11	0.61

Table 3. Resistance of dry CF.

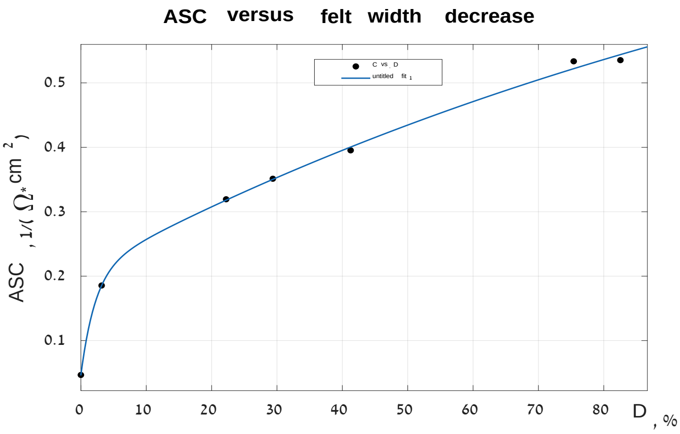
Parameter		h, [mm]						
		6.2	6.1	4.9	4.45	3.7	1.55	1.1
		Volume decrease, [%]						
		0	2	21	28	40	74	81
Rdc [mΩ/cm^2]		48.184	41.2	18.2	10.100	6.672	5.189	5.930
Rac, [mΩ/cm^2]	100, [Hz]	54.855	39.8	16.3	6.820	5.930	4.374	4.374
	120, [Hz]	54.633	38.9	16.6	7.042	6.079	4.522	4.299
	1, [kHz]	54.633	40.1	15.9	6.894	6.375	4.522	4.225
	10, [kHz]	49.296	38.7	14.9	6.746	5.930	4.670	4.299
Rac average, [mΩ/cm^2]		53.354	39.740	16.38	7.520	6.197	4.655	4.626

Measurements approve the decrease of CF resistivity during it pressing in the direction perpendicular to its surface. In the beginning, CF resistance falls fast and in the continuation, resistance decrease becomes slower. The more inclusive analysis is given in the following section.

IV. Math Interpretation of Experimental Data

We suggested representing electrical CF properties resistance by an opposite parameter - average surface conductance (ASC) instead of the use of ASR. The advantages of such representation will be seen later.

A typical graph of ASC versus felt squeezing D, [%], is shown in Fig.4.



<u>**Fig.4**. ASC of a dry CF versus relative felt decrease</u>.

Similar graphs were obtained for CF in glycerol, alcohol, and cycloxane. The behavior of ASC $[\frac{1}{\Omega \cdot cm^2}]$ can be sufficiently described by the exponential function (3) precisely approximating virtual data:

$$ASC = a \cdot \left(1 - e^{-b \cdot D}\right) + c\,, \qquad (3)$$

Below is given a Table 4 representing magnitudes of the coefficients a, b and c for describing ASC in different environments. The proximity of the theoretical function to real data is estimated by coefficient R^2 having significantly high value (see Table 4).

<u>Table 4. Coefficients quantities of approximating function for ASC</u>

ε_r	ASC	ASC=a*(1-exp(-b·D))+c			coeff. R^2
		a	b	c	
1	**dry**	**0.5071**	**0.02488**	**0.0933**	**0.969**
42.5	**glycerol**	**0.9134**	**0.01278**	**0.0996**	**0.967**
21.6	**alcohol**	**0.4269**	**0.02377**	**0.322**	**0.982**
2.02	**cyclohexane**	**0.5024**	**0.02008**	**0.2116**	**0.988**

One can put the mind on the dependence of ASC from liquid dielectric parameters. Obviously, enlarged electric permittivity ε positively influences CF conductivity. It could be explained by the increasing the density on internal filaments interconnections between themselves and electrodes surfaces. Owing to the interconnections between carbon filament as the main factor, its relative increase (R_{incr}) was calculated as:

$$R_{incr} = \frac{(ASC)_{Di}}{(ASC)_{D_0}} \cdot \frac{(V_0)}{(V_i)}\,, \qquad (4)$$

Where: $(ASC)_{Di}$ and $(ASC)_{D0}$ conductance for current CF width squeezing versus its initial value; V_0 and V_i initial volume and its current values.

R_{incr} has a common approximating expression (4) and a similar graphic interpretation (Fig.5).

$$R_{incr} = A \cdot (e^{B \cdot D} - 1) + 1\,, \qquad (5)$$

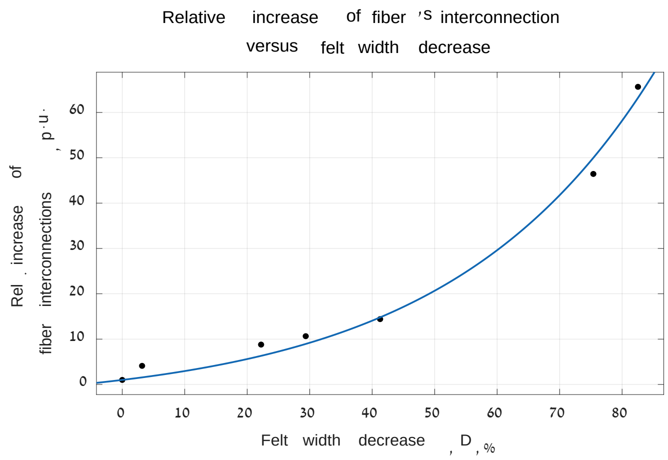


Fig.5. The relative increase of filaments interconnections versus relative volume decrease

Considering the measurements results and coefficients of approximation function (5) for each liquid, Table 5 that presenting quantities of R_{incr} versus CF width decrease, was established.

Table 5. Coefficients quantities of approximating function for the relative increase of filaments interconnections

ε_r	R_{incr}	$R_{incr}=A(e^{B\cdot D}-1)+1$		coeff. R^2
		a	b	
1	dry	5.499	0.03042	0.991
42.5	glycerol	2.832	0.0322	0.98
21.6	alcohol	0.5523	0.05052	0.996
2.02	cyclohexane	0.8402	0.03486	0.986

Conclusions

1. CF material has widespread requests in different appliances including heating elements and diverse electrochemical cells.
2. Electrical (electronic) conductivity of CF plays a crucial role for electrons to reach the surface of the electrodes and to participate in reactions. Likewise, electrical resistivity (the inverse of electrical conductivity) plays a significant role in generating heat or causing electrical losses diminishing the efficiency of electrochemical equipment.
3. Owing to a significant assignment of CF resistivity and conductivity, a special comprehensive investigation was carried out aiming to find magnitudes of these parameters.
4. Electronic resistivity was measured by a special device applying for this purpose DC and AC currents with different (100 Hz, 120 Hz, 1 kHz and 10 kHz) frequencies. Considering the requirement to verify the influence of dielectric liquid parameters on CF conductivity, four sets of tests were performed. Resistance was measured in dry conditions and with the CF immersed in different (glycerol, alcohol, and cyclohexane) non-conducting (dielectric) liquids. Usage of dielectric liquids instead of real electrolytes was justified to prevent an influence of electrolyte ionic conductivity on the measurement results.
5. It was observed that electrical resistivity was diminished during felt compression having a non-linear relation versus volume decrease like the

negative exponential function. In the initial stage of volume decrease, the resistance drops quickly. However, after 80-60% of its initial value, additional compression has a negligible effect on conductivity.

6. Electrical conductivity moderately depends on liquid permittivity properties. Dielectric constant (ε), among other liquid parameters, obviously has a main role influencing the quantity of interconnection between carbon filaments and electrodes. The increase of ε causes a slight improvement in CF conductivity.
7. It seems to be important to continue the present work for finding solid theoretical explanations for observed data of CF conductivity by the methods of statistical approach.

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