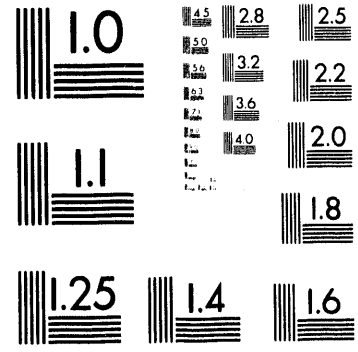

1.0
1.1
1.25
1.4
1.6
1.8
2.0
2.2
2.5
2.8
3.2
3.6
4.0
4.5
5.0
5.6
6.3
7.1

1 of 1

2

SAND93-2621C
Conf-931204--1

Double Layer Capacitance of Carbon Foam Electrodes

F.M. Delnick, D. Ingersoll
Sandia National Laboratories
Albuquerque, NM 87185-5800
and
D. Firsich
EG&G Mound Laboratories
Miamisburg, OH 45343-3000

INTRODUCTION

We have evaluated a wide variety of microcellular carbon foams prepared by the controlled pyrolysis and carbonization of several polymers including: polyacrylonitrile (PAN), polymethacrylonitrile (PMAN), resorcinol/formaldehyde (RF), divinylbenzene/methacrylonitrile (DVB), phenolics (furfuryl/alcohol), and cellulose polymers such as Rayon. The porosity may be established by several processes including: Gelation (1-5), phase separation (1-3,5-8), emulsion (1,9,10), aerogel/xerogel formation (1,11,12,13), replication (14) and activation. In this report we present the complex impedance analysis and double layer charging characteristics of electrodes prepared from one of these materials for double layer capacitor applications, namely activated cellulose derived microcellular carbon foam.

EXPERIMENTAL

The test electrodes consisted of monolithic cellulose derived microcellular carbon foam disks, 1.7 cm in diameter and 0.025 cm thick. Each disk exhibited a density of 880 mg/cc, an electrical conductivity of $\kappa_e = 71\ \Omega^{-1}cm^{-1}$, and a Langmuir surface area of 830 m^2/g.

A compression cell was used for all measurements. In every case, a matched set of porous electrodes was used. One carbon disk served as the working electrode and the other disk served as the counter electrodes. These electrodes were separated from one another by several glass fiber disks, each having a nominal thickness of approximately 0.03 cm. For some complex impedance measurements, a saturated calomel reference electrode was connected to the cell compartment via a salt bridge that terminated in a porous frit at the edge of the glass fiber disk separators. All measurements

were made at ambient temperature in 1.0M H_2SO_4 electrolyte having a specific conductivity of $\kappa = 0.40\ \Omega^{-1}cm^{-1}$.

Capacitance was measured using complex impedance spectroscopy and galvanostatic charge/discharge experiments. In order to interpret the complex impedance spectra, we assumed a semi-infinite cylindrical porous electrode model (15), and computed the capacitance from the frequency dispersion of the complex impedance vector under the simplifying assumption that $\kappa_e >> \kappa$, according to equation [1](16-19).

$$Zp = \frac{(1-j)}{2\pi n\sqrt{r^3\kappa\omega C_{dl}}} \coth\left[l(1+j)\sqrt{\frac{\omega C_{dl}}{\kappa r}}\right] \qquad [1]$$

κ = electrolyte conductivity
r = effective pore radius
n = pore number
l = pore length
ω = angular frequency
$j = \sqrt{-1}$
C_{dl} = double layer capacitance

In order to use equation [1], one must know the double layer capacitance of the carbon surface and the electrolyte conductivity. Kinoshita (20) has reviewed the double layer capacitance on various carbons. The double layer capacitance of the carbon surface depends upon the orientation of the graphitic microcrystals, the electrolyte composition, and the surface functionality. In H_2SO_4 electrolytes, C_{dl} varies from ~3 $\mu F/cm^2$ to 70 $\mu F/cm^2$. For our computations we use the nominal value of 20$\mu F/cm^2$. The accuracy of this assumption is directly reflected in our computation of surface area and pore radius below.

At high frequency, equation [1] reduces to equation [2]:

$$Z_p = \frac{(1-j)}{2\pi n\sqrt{r^3\kappa\omega C_{dl}}} \qquad [2]$$

At low frequencies, equation [1] reduces to equation [3]:

$$Z_p = \frac{l}{2\pi r^2 n\kappa} - \frac{j}{2\pi r n l \omega C_{dl}} = \Omega - \frac{j}{\omega C} \quad [3]$$

where $$\Omega = \frac{l}{2\pi r^2 n\kappa} \quad [4]$$

$$C = SC_{dl} = \text{low frequency capacitance} \quad [5]$$

$$S = 2\pi r l n = \text{electrochemically active surface area} \quad [6]$$

$$r = \frac{2V_e}{S} = \text{effective pore radius} \quad [7]$$

$$l = \sqrt{2\kappa\Omega V_e} = \text{effective pore length} \quad [8]$$

$$n = \frac{S}{2\pi r l} = \text{effective pore number} \quad [9]$$

$$V_e = \pi r^2 l n = \text{total pore volume} \quad [10]$$

For the galvanostatic charge/discharge experiments, capacitance was computed using equation [11]

$$C = \frac{i}{dV/dt} \quad [11]$$

i = applied current

$\frac{dV}{dt}$ = the slope of the voltage response with respect to time

RESULTS AND DISCUSSION

Figure 1 shows two photomicrographs of the cellulose derived microcellular carbon foam electrode for two different magnifications. The large pores are nonuniform, and range in size from ~1-30 μm. The complex impedance of two of these electrodes is shown in Figure 2. Analysis of this impedance spectrum using the semi-infinite cylindrical porous electrode model

described above yields an electrochemical active surface area of 330 m^2/g, an effective pore radius of 36 Å, and an effective pore length of 0.048 cm. The electrochemically active surface area is about 40% of the Langmuir surface area indicating that about 60% of the surface area is in micropores that are inaccessible to the electrolyte. Comparison of the effective pore radius of 36 Å with the photomicrograph in Figure 1 indicates that the visible macropore structure does not define the impedance of the electrode. Instead, smaller pores in the carbon structure which are not evident in the photomicrograph control the electrochemical behavior of the this supercapacitor electrode. The effective pore length of 0.048 cm is consistent with the thickness of the electrode (0.025 cm) if one assumes a tortuosity of 1.9. From the impedance spectrum in Figure 2, the effective series resistance of each electrode is $R_{ESR} = 0.24\ \Omega cm^2$, and the volume specific capacitance of each electrode is 58 F/cm^3.

In Figure 3 we show the volume specific capacitance as a function of potential in the range E = 0.75 to -0.6 volts vs SCE. The curve labeled L corresponds to the electrode described above. The capacitance of this electrode is essentially independent of potential. This indicates that only simple electrostatic processes take place in the double layer on this electrode surface. The curves labeled O and U in Figure 3 represent identical cellulose derived microcellular carbon foam electrodes which have been surface modified to different extents. The surface modifications of these electrodes permit partial charge transfer with the electrolyte. This leads to the strong potential dependence of the capacitance shown in Figure 3 for samples O and U. This behavior is sometimes called psuedocapacitance.

We measured the capacitance of cells comprised of electrodes L/L, O/O, and U/U galvanostatically as a function of the current density. In these experiments we charged the cells from 0.0 to 1.0 V and computed the charging capacitances using equation [11]. The results of these experiments are shown in Figure 4. For all three cells, the capacitance does not change appreciably with current up to 400 mA/cm^2. The charge transfer reaction responsible for the pseudocapacitance in cells O/O and U/U does not limit the electrodes kinetically over this current range. When cells O/O and U/U are fully charge to 1.0 volt, the capacitance of the anode is greater than that of the cathode. Therefore, the voltage drop at the cathode will be greater than that at the anode. To accommodate this asymmetry, the volume specific capacitance reported in Figure 4 is the effective volume specific capacitance of each electrode in the cell computed by multiplying the cell capacitance by two, and then dividing by the volume of one electrode (In

these cells, both electrodes have the same volume.). A more volume efficient cell would accommodate this voltage dependence by using a smaller volume (*i.e.* thinner) anode in comparison to the cathode. However, this design modification can only be accommodated in polarized capacitors.

SUMMARY

Microporous cellulose derived carbon foam is suitable for supercapacitor applications. This material exhibits an effective volume specific capacitance of 58 F/cm^3 to 150 F/cm^3 depending on the extent of surface modification, and an effective series resistance of 0.24 Ωcm^2 for 0.025 cm thick electrodes in 1.0M H_2SO_4.

ACKNOWLEDGMENT

This work was supported by the United States Department of Energy under contract DE-AC04-94AL85000

FIGURE LEGENDS

Figure 1 Photomicrographs of activated cellulose derived microcellular carbon foam.

Figure 2 Complex impedance of two identical activated cellulose derived microcellular carbon foam electrodes in 1.0M H_2SO_4. Frequency range is 60 kHz to 0.15 Hz.

Figure 3 Potential dependence of the volume specific capacitance of cellulose derived microcellular carbon foam. L = no surface modification. O = modest surface modification. U = extensive surface modification.

Figure 4 Effective capacitance of the carbon electrodes in Figure 3 measured as a function of galvanostatic charge current density.

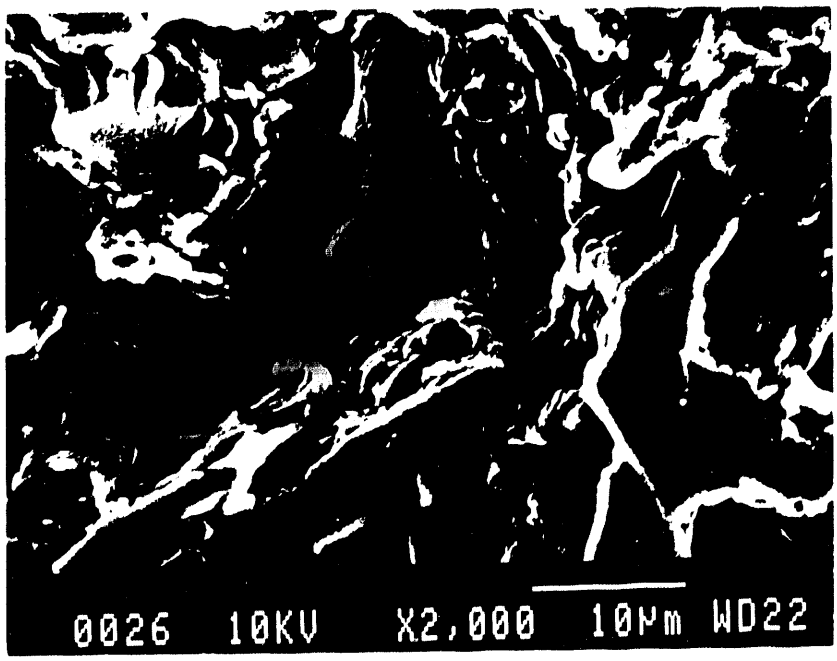
REFERENCES

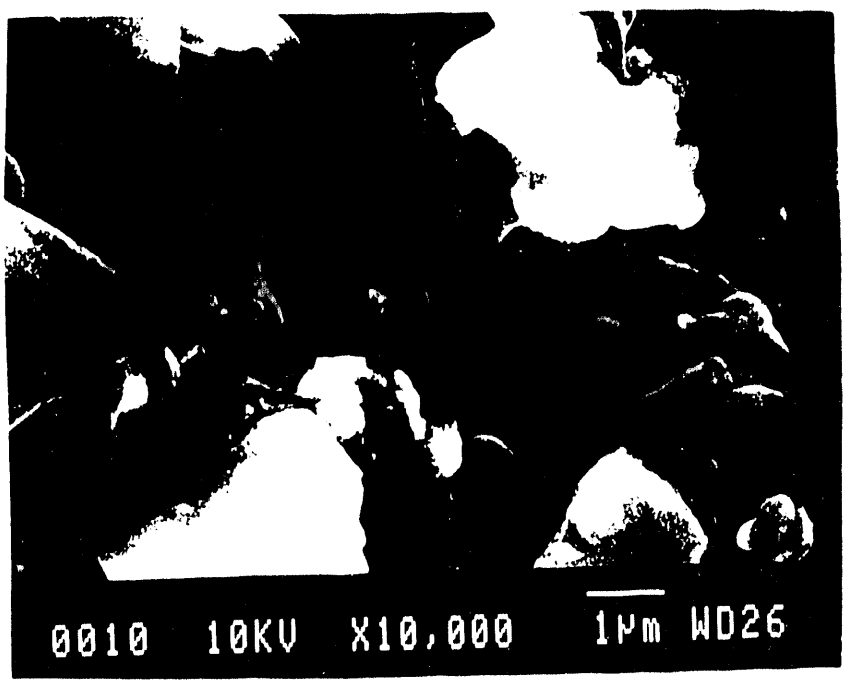
1 J.D. LeMay, R.W. Hopper, L.W. Hrubesh and R.W. Pekala, **MRS Bulletin, December** (1990) 19

2 J.H. Aubert and A.P. Sylwester, **Chemtech, 21** (1990) 234-238 and

290-295
3 C.L. Renschler and A.P. Sylwester, **Materials Sci. Forum, 52-53** (1989) 301
4 R.R. Lagasse, **Extended Abstracts, 21st Bienniel Conf. on Carbon,** June 1993, Buffalo, NY, Americal Chemical Soc. (1993) p 158
5 H. Hatori, Y. Yamada and M. Shiraishi, **Carbon, 30** (1991) 303
6 C. Arnold, J.H. Aubert, R.L. Clough, P.B. Rand and A.P.Sylwester US Patent 4,832,881 (May 23, 1989)
7 R.L. Clough and A.P. Sylwester, US Patent 4,832,870 (May 23, 1989)
8 R.R. Lagasse, P.K. Leslie, K.R. Thompson and R.J. Weagley, **SAND 93-0172** 1993
9 D. Barby and Z. Haq, European Patent No. 0-060-138 (Sept. 3, 1982)
10 C.J.C. Edwards, D.A. Hitchen, M. Sharples, US Patent 4,775,655 (Oct. 4, 1988)
11 R.W. Pekala, US Patent 4,873,218 (Oct 10, 1989)
12 R.W. Pekala, US Patent 4,997,804 (March 5, 1991)
13 R.W. Pekala, C.T. Alviso and J.D. LeMay, **J. Noncrystl. Solids 125** (1990) 67
14 R.W. Pekala and R.W. Hopper, **J. Mater. Sci., 22** (1989) 1840
15 R. De Levie in Advances in Electrochemistry and Electrochemical Engineering, Vol 6, P. Delahay ed., Interscience Publishers, New York, 1967
16 F.M. Delnick, C.D. Jeager and S. Levy, **Chem. Eng. Commun., 35** (1985) 231
17 F.M. Delnick, to be published in : **Proc. of the Symp on the Science of advanced Batteries,** Nov. 8-9, 1993, Cleveland, The Electrochemical Soc., Inc.
18 J.-P. Candy, P. Fouilloux, M. Keddam and H. Takenouti, **Electrochim. Acta, 26** (1981) 1029
19 H. Keiser, K.D. Beccu and M.A. Gutjahr, **Electrochim. Acta, 21** (1976) 5391
20 K. Kinoshita, Carbon: Electrochemical and Physicochemical Properties, Jonn Wiley & Sons, NY, (1988) p294

DISCLAIMER





CL11FCMM-040 dens = 880 mg/cm^3
area = 830 m^2/g

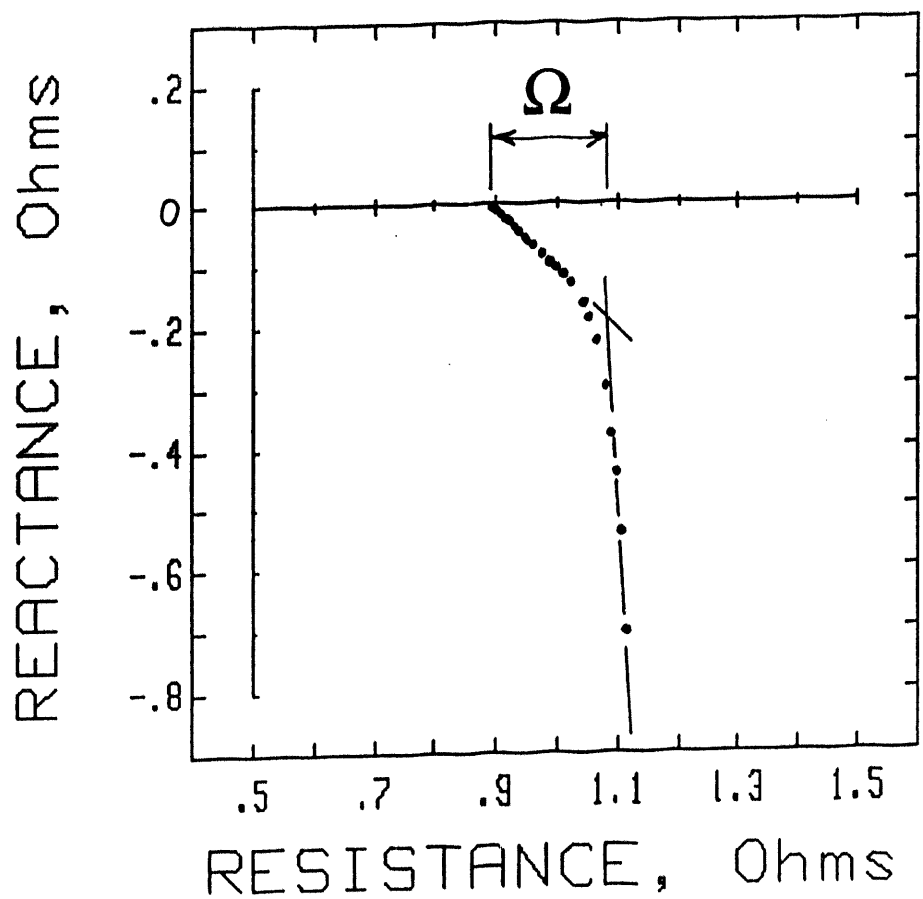


FIG 2

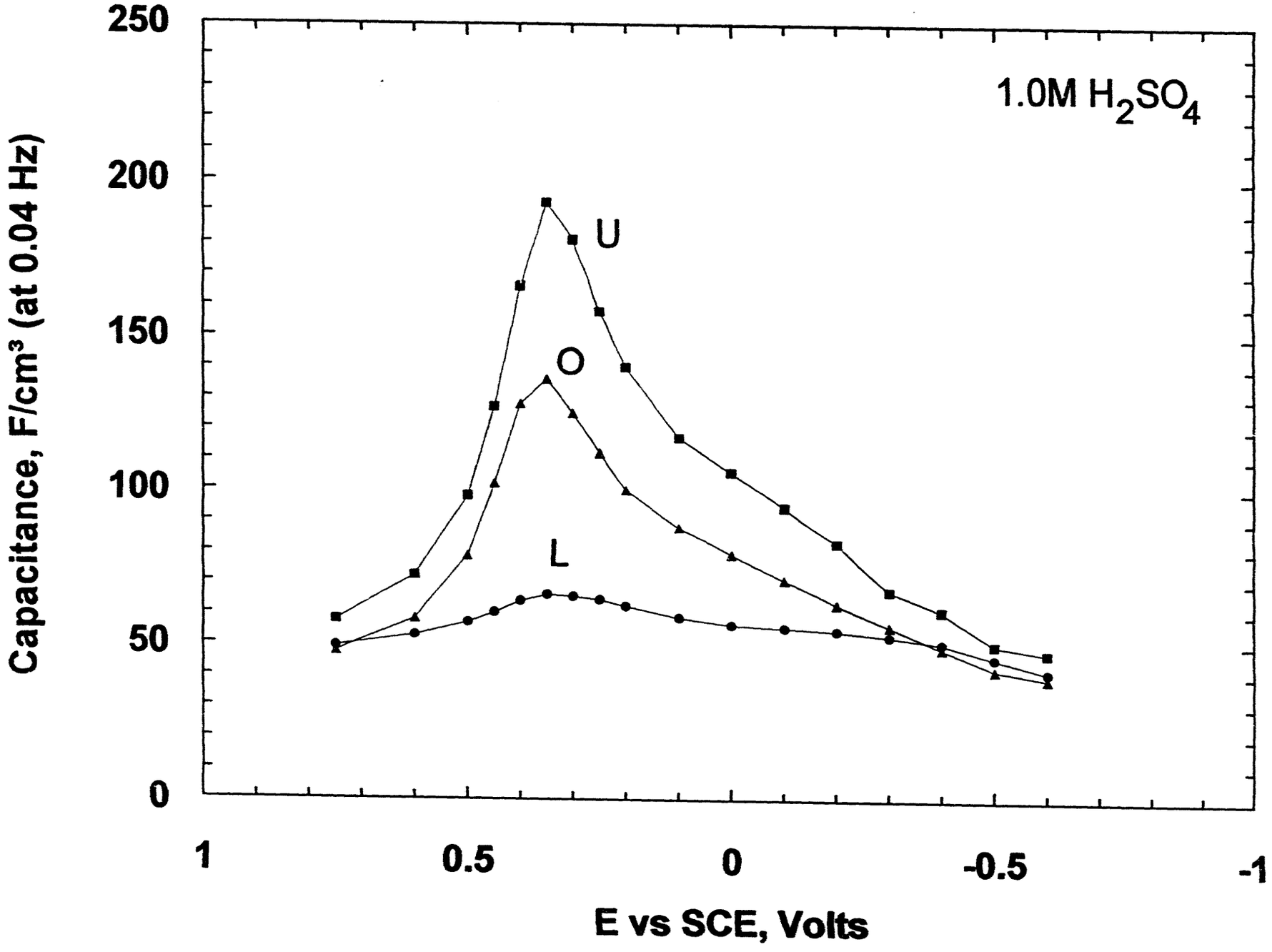

250
200
150
100
50
0
1
0.5
0
-0.5
-1
Capacitance, F/cm³ (at 0.04 Hz)
E vs SCE, Volts
1.0M H2SO4
U
O
L

FIG. 3

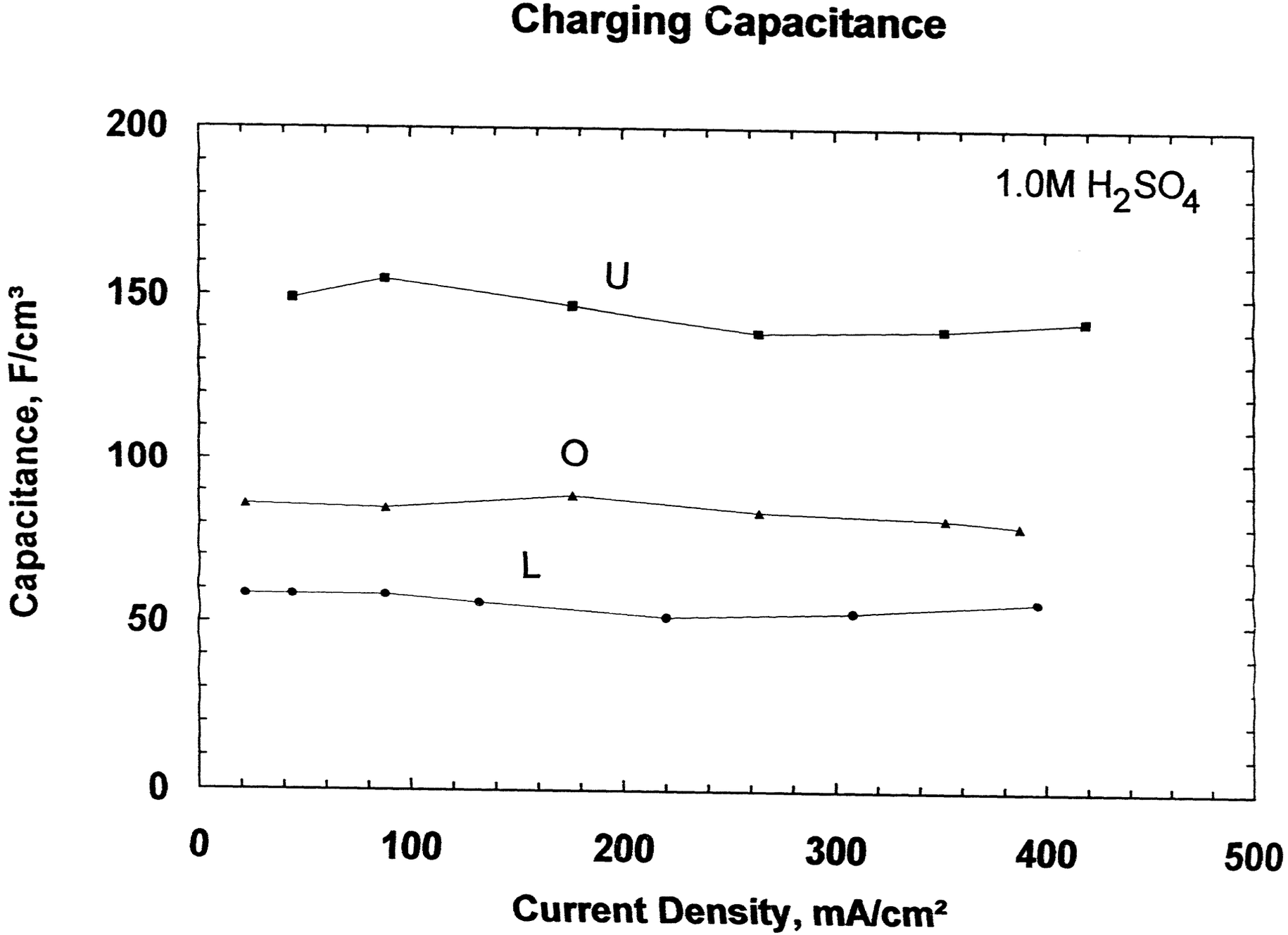

Charging Capacitance
1.0M H_2SO_4
U
O
L
Capacitance, F/cm³
Current Density, mA/cm²
0
50
100
150
200
0
100
200
300
400
500

FIG 4

DATE FILMED

1 / 5 / 94

END