

The Effect of Binder in Electrode Materials for Capacitance Improvement and EDLC Binder-free Cell Design

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Abstract: In the present work we show results related with the influence of the binder type used to elaborate active electrodes made of activated carbon (DLC) for the assembly of supercapacitor cells. A Nafion 5%w solution and/or Kinar Flex (Polyvinylidene fluoride, PVDF) were used as binders at different concentrations, using DLC carbon as the active material to make the electrodes by aerography, and carbon paper as support and current collector. Thickness of the electrodes was controlled by the weight of active material (DLC carbon). Cyclic voltammetry technique was used to investigate the intrinsic capacitive nature of these electrodes, increasing this value from 120 F/g to 245 F/g at 20 mV/s just by improving the type and amount of binder, and the thickness of the electrode. Symmetric 2-electrode cells assembled with binder-free electrodes were electrochemically characterized by galvanostatic cycling, showing capacitance values of 38F/g and a stable behavior during 7000 charge-discharge cycles.

Keywords: Supercapacitor, symmetric assembly, EDLC, Binder Free, activated carbon.

1. INTRODUCTION

An electrochemical double layer capacitor, known as EDLC can be defined as a device that stores electric energy in the electrical double layer that is formed at the interface between an electrolytic solution and an electronic conductor [1]. In general, the double layer capacitance in electrochemical systems can be in the range from 5 to 50 $\mu\text{F cm}^{-2}$. Nevertheless, this limit has been exceeded by the use of carbon based materials, showing high active surface area up to 1500 m^2g^{-1} [2]. Supercapacitors are designed to bridge in the gap between batteries and capacitors to form fast charging energy-storage devices of intermediate specific energy [3]. The use of supercapacitors is growing along with demand for specific requirements for different applications, ranging from small sizes with limited energy content, to levels of hundreds of kW in various vehicles (passenger hybrids cars, hybrid buses and trains) and for electric applications. The variety of applications also determines the need to clarify the measurement procedures to determine the properties of supercapacitors (SC), which may vary when they are

used in different operating conditions.

There have been many studies of carbon materials for EDLC, and testing for small laboratory devices and prototypes, as well for a wide range of commercial products. Many of these tests have involved the use of cyclic voltammetry, galvanostatic cycling, and AC impedance spectroscopy [4-6]. In these tests, small currents, limited potentials intervals, and/or AC frequencies are used. To test larger prototypes and commercial devices, regularly DC tests similar to those used with batteries are used [7]. In our work, we are using cyclic voltammetry and electrochemical impedance spectroscopy for the characterization of our electrode materials with different binders and concentrations, in order to determine the operational voltage window, intrinsic capacitance values, and electric resistance. On the other hand, galvanostatic cycling has been carried out in 2-electrode cell characterization to determine capacitance values and charge-discharge cycling stability.

One of the challenges of today is the portability of energy that can be used on different items from cloth to space applications, in which the cost per weight and volume needs to be decreased [8]. In order to obtain this portability, the devices need to be lighter, more compact, and more flexible with high energy and power

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density. Recent studies show the development of flexible energy storage devices based on different chemistries, including supercapacitors [9-13].

Different binders have been used to elaborate carbon electrodes to assemble EDLC, such as Teflon [14-17], Nafion [18-20], PVDF or Kinar Flex [21-24]. These binders give mechanical properties to carbon particles, but they introduce electric and ionic resistance to the electrode material affecting the power capability of the device. On the other hand, binder-free electrodes have been fabricated to avoid or decrease the detrimental effects in EDLC. Carbon nanotubes (CNT) suspensions have been prepared using a polymer in solution as dispersant, in order to obtain by filtration CNT paper electrodes. The cell assembled with these binder-free CNT electrodes using silver painted current collectors, showed a capacitance value of 44 F/g for the device, with a high electric resistance of 137 Ω due to not optimized silver paste contacts [25]. Also, activated carbon (AC) binder-free electrodes have been elaborated using carbon nanotubes as connecting matrix to obtain AC/CNT papers pressed to a Ni current collectors, resulting in voltamperometric intrinsic capacitance values of 268 F/g at 20mV/s, and low resistance values ($0.33\Omega/\text{cm}^2$).[26].

Our work shows a systematic study on electrode fabrication with activated carbon as the electro-active material, where the type and amount of binders, and electrode thickness were evaluated in order to reduce resistance (ESR), and increase voltamperometric intrinsic capacitance values (C). In addition, 2-electrode EDLC cells were assembled with binder-free electrodes, where current collectors and the electrolyte amount were evaluated by using a lab-scale assembly and a thin prototype cell.

2. EXPERIMENTAL

2.1. Electrode Fabrication

Two series of electrodes were prepared using DLC (activated carbon from NORIT) as active material with Kinar Flex (PVDF polyvinylidene fluoride, Arkema) or Nafion solution (5wt%, Aldrich reagent) as binders in different concentrations. In order to obtain the series of electrodes based on Nafion (N-Elect), an ink was prepared by ultrasonication in an open vessel for 1 hr of a suspension made of 0.01g of activated carbon material (DLC), 2 ml of 2-propanol, and varying the concentration of Nafion (1, 2, 3, 4 and 5wt%). On the other hand, in the Kinar Flex based electrodes (KF-Electr) the active material was stirred for 24 hours with different amounts of Kinar Flex (3, 4, 5, 10 wt%) in acetone. The obtained suspension from N-Electr and KF-Electr were deposited onto the surface of a current collector by an aerography process, and finally a drying procedure was followed at room temperature for 24 hours. This electrode fabrication technique assured a good distribution of the active material on the surface of the current collector (4 cm^2 carbon paper or cloth), making their performance just a function of the type and concentration of binder used in each electrode.

The electrodes were electrochemically characterized first by cyclic voltammetry in a three-electrode cell, using as reference electrode a saturated sulfate electrode (SSE), a platinum mesh as the counter electrode, our fabricated electrodes as the working electrode, and a sulfuric acid 0.5 M solution as electrolyte. The total intrinsic capacitance [27] was calculated from the total voltamperometric charge obtained from the current integer with time and using the next equation (1).



Figure 1. Lab-assembly supercapacitor cell

$$C = Q / \Delta E m \quad (1)$$

where Q is the voltamperometric charge, ΔE is the potential or voltage window, and m is the activated carbon mass. Moreover, impedance spectroscopy was carried out at open circuit potential (OCP) in a frequency range between 0.01 and 10000 Hz. [28-30].

2.2. Lab-Supercapacitor Cell Assembly

A lab-scale 2-electrode assembly was used to evaluate different current collectors with an electrolyte excess. For this assembly two acrylic plates and four Teflon screws were used as mechanical support of the 2-electrode cell. Figure 1 shows the components for this supercapacitor assembly, where two identical electrodes separated by a filter paper to avoid electrical contact are pressed with the acrylic plates, immersed in 0.5 M H_2SO_4 electrolyte, and sealed with a plastic bag to avoid electrolyte evaporation. In this cell assembly, a stainless steel mesh as current collector coupled to a carbon paper support was evaluated and compared to a cell assembled with carbon cloth as current collector and support. A binder-free suspension made from 0.1 g DLC and 2 ml of 2-propanol was ultrasonicated for 1 hr and deposited by aerography on the surface of 4 cm^2 electrodes before the assembly. The electrochemical devices were characterized by galvanostatic cycling at a constant current that was setup to obtain a complete discharge of the supercapacitor cell in 100 s. Cycling tests were carried out by 7000 charge-discharge cycles and the specific capacitance was calculated according to eq. (2).

$$C = I \left(\frac{t}{\Delta V m} \right) \quad (2)$$

where C is the specific capacitance, I is the applied constant current, t is the discharge time ($\approx 100\text{s}$), ΔV is the operational voltage window, and m the mass of activated carbon from both electrodes.

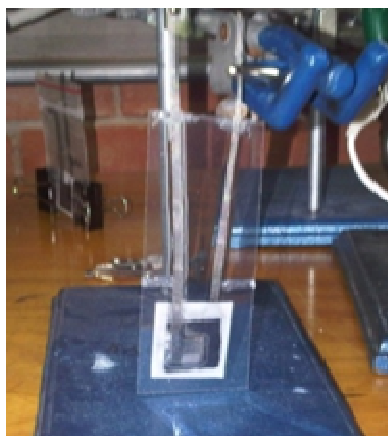


Figure 2. Prototype thin-supercapacitor cell.

2.3. Prototype Cell

A portable prototype using a thin and flat configuration cell package is shown in Figure 2. In this case it is possible to evaluate the minimum amount of electrolyte contributing to the cell performance, since it is restricted by the cell design. The cycling stability through the retained capacitance was investigated in 7000 charge-discharge galvanostatic cycles, using a current that permits a 100 s discharge time.

3. RESULTS AND DISCUSSION

3.1. Electrode Evaluation

The influence of binders on the electrode performance for supercapacitor applications was investigated electrochemically by cycling voltammetry analysis for the two series of electrodes earlier described: N-Elect and KF-Elect, prepared with Nafion and Kinar Flex respectively. All experiments were carried out in 0.5 M H₂SO₄ at 25 °C.

Figure 3 shows the cyclic voltammetry carried out at 20mV/s for all electrodes of N-Elect series with different amounts of Nafion, where a potential range from -0.8 to 0.3 V was used to avoid electrolyte decomposition. For 1 and 2 wt% Nafion concentrations, the voltamperometric profile resulted in the most rectangular form, which corresponds with a typical response of charge accumulation on the double layer (capacitive behavior). For binder concentrations higher than 2 wt% (3, 4 and 5 wt%) an inclination or deviation from the rectangular voltammogram profile is observed on the

Table 1. I intrinsic specific capacitance values for electrodes elaborated with DLC activated carbon and different concentration of binders.

BINDER	w. %	Intrinsic voltammetric Capacitance (F/g)
Nafion	1	245
Nafion	2	202
KF	4	120
KF	5	121
KF	10	149

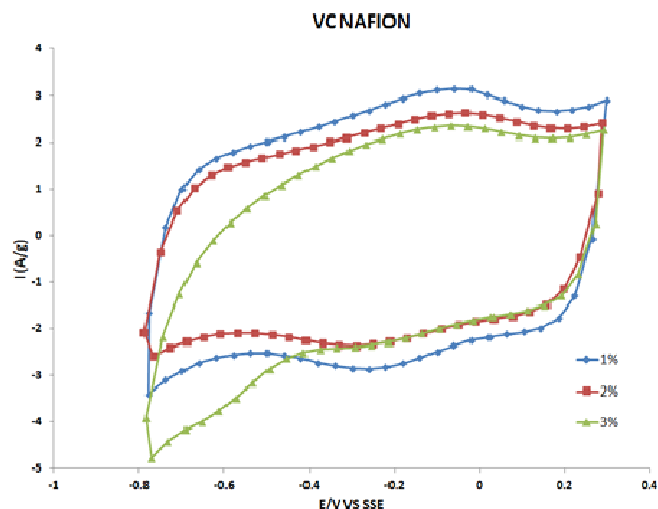


Figure 3. Cyclic voltammetry response of N-Elect at different binder concentration, 0.5 M H₂SO₄ electrolyte, and 20 mVs⁻¹.

cathodic limit, which is related with the increase of electrode ionic resistance. The total intrinsic specific capacitance values calculated from the voltammogram integer using eq. 1 is presented in Table 1 for electrodes with a capacitive behavior (Nafion 1 and Nafion 2). Therefore, Nafion 1% electrode (1%) resulted in the best performance with a higher capacitance value of 245F/g.

Thickness of electrodes in supercapacitor cells is a parameter that needs to be improved due to variation in resistance, which is an important parameter to take into consideration for these high power devices. Therefore, the electrode thicknesses of 1% Nafion formulation was varied, and the resulting electrodes are labeled based on their thickness as 1%N-Thick, 1%N-Thin, and 1%N-Ultrathin. Figure 4 shows the voltammograms of these electrodes, where the capacitive profile is observed with higher current range for the 1%N-Ultrathin electrode. The inclination or deviation from the rectangular profile is related with resistance in the electrode, and these phenomena increases with the thickness increase of the electrode. In the inset of figure 4 the electric response from Electrochemical Impedance Spectroscopy (EIS) of two prepared electrodes are shown as an example: 1N-thin and 1N-thick electrodes. Series resistance (ESR) obtained from the axis intercept is slightly lower for 1%N-thin electrode (1.25 Ωcm⁻²) than for 1%N-thick electrode (1.45 Ωcm⁻²), demonstrating the low resistance of the electrodes using this fabrication method. The impedance spectra show a slightly difference in the total internal resistance of both electrodes, showing a lower resistance value for 1%N-thin electrode than for 1%N-thick electrode. In addition, at very low frequency range it is observed that the species diffusion in 1%N-thin electrode is greater than in 1%N-thick electrode. The behavior observed in these two electrodes can be related with a better surface exposure to the electrolyte for 1%N-thin electrode, since for the thicker electrode, some carbon from the bulk of the electrode does not seem to be contributing. In addition, a combined charge mechanism in 1%N-thick electrode is observed due to the appearance of a non-defined Warburg semi-infinity diffusion at low frequencies, which has been observed in electrochemical systems when an incomplete charge

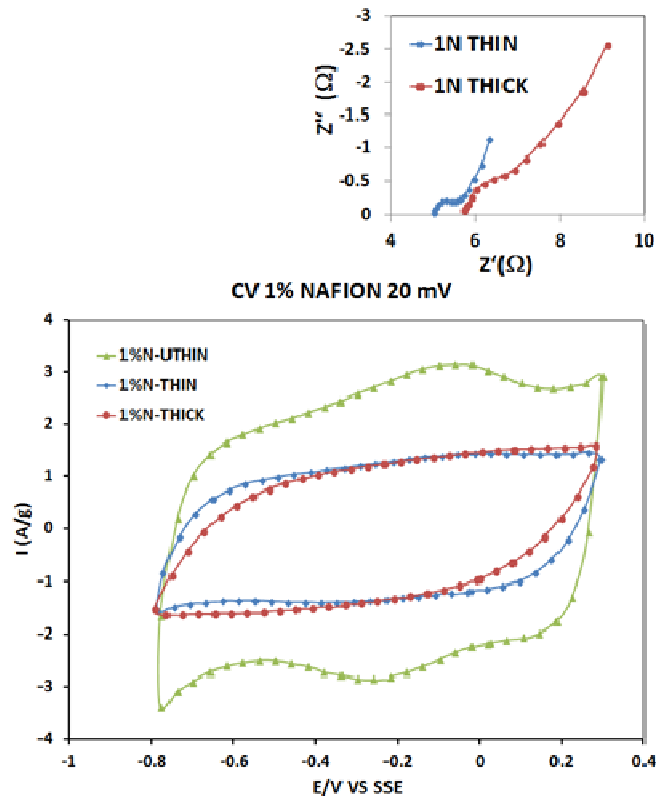


Figure 4. Cyclic Voltammetry of Nafion 1% electrodes with different thicknesses carried out at 20 mV/s, and electrochemical impedance of these electrodes are shown in the inset.

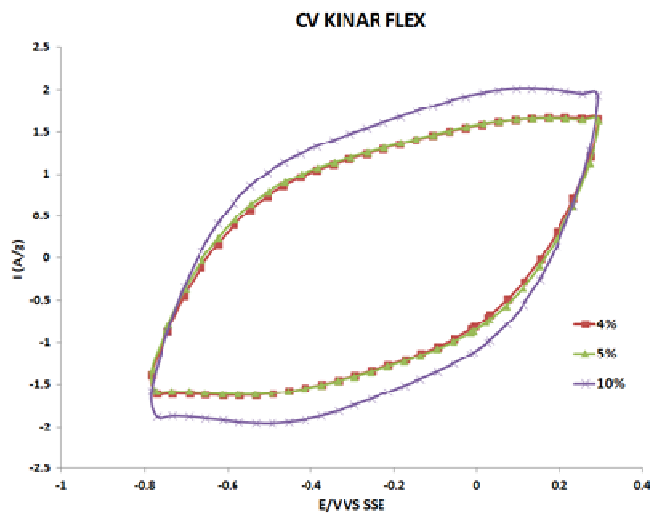


Figure 5. Cyclic Voltammetry of KF-Electr series in 0.5M H_2SO_4 electrolyte using a scan rate of 20mVs⁻¹

transfer process in a non porous medium is taken place.

Figure 5 shows the voltamperometry response for KF-Electr series as a function of binder concentration. The voltammograms show the typical charge storage mechanism (rectangular profile) of carbonaceous materials controlled by double layer capacitance.

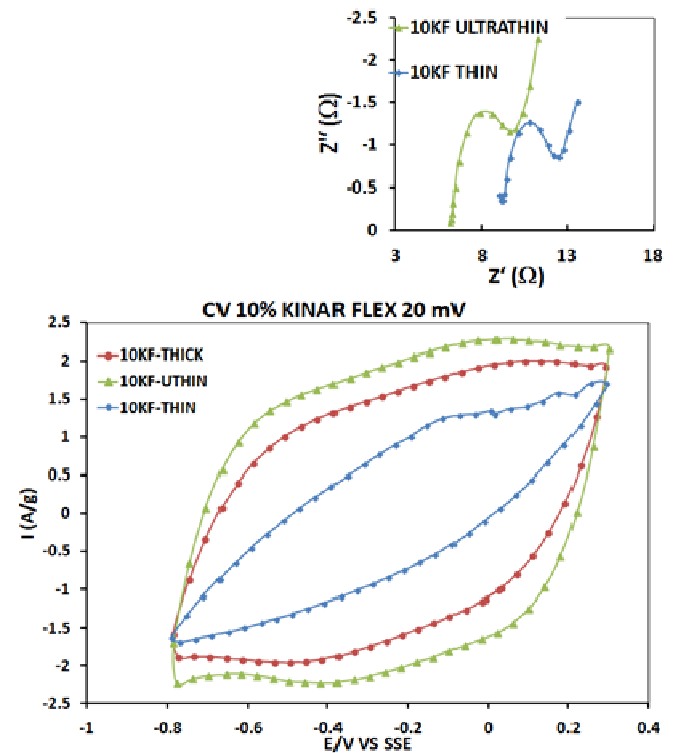


Figure 6. Cyclic Voltammetry of 10%-KF electrodes with different thicknesses, and electrochemical impedance spectroscopy in the inset.

Nevertheless, the observed inclination in all electrode voltamperograms indicates the higher ionic resistance contribution compared to N-Electr series. The use of 10 wt% Kinar Flex showed a moderate current range increase, and the ionic resistance is slightly lower than in the other concentrations. In Table 1 are presented the capacitance values obtained from these profiles, where a value of 120 F/g for KF4%, 121F/g for KF5%, and a greater value of 149F/g for KF10 are obtained.

As for the N-Electr series, variation of the thickness was carried out for 10%-KF electrode, and the cyclic voltammetry and electrochemical impedance spectroscopy (EIS) results are shown in figure 6. In general, the voltamperograms show an inclination previously observed indicative of ionic resistance, which decreases as the electrode went from thick to ultrathin. The EIS experiments of 10%-KF electrodes with the highest amount of used binder are shown on the inset of figure 6. This higher binder concentration does not affect significantly the ESR of the electrodes, but it clearly affects the electron transfer mechanistic processes in both electrodes. Ultrathin electrode (10KF-Uthin) shows a simple electronic transfer formed by a total internal resistance and diffusion process due to the presence of pores on the surface of the electrode. [31] In the case of thin electrode (10KF-thin), it is observed a more complex electron transfer mechanism at intermediate frequencies. It is probably due to resistance coupled to an adsorption process as a function of a thicker semiconductor material (carbon). This combined process produces a change in the response of the electrical properties of ion-electron interaction in this kind of material.

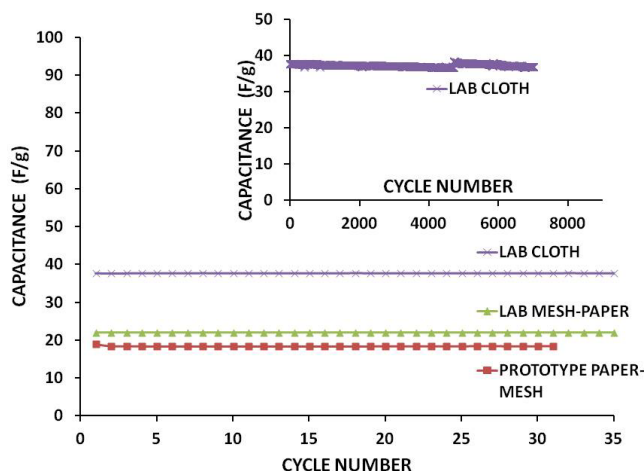


Figure 7. Galvanostatic cycling of Lab and Prototype assemblies, using different current collectors in a voltage window of 1.1 V with 0.5M H₂SO₄ as electrolyte. The current was adjusted based on a 100s discharge time: 6.5 mA Lab-Cloth cell, 3.9 mA for Lab Mesh-paper cell, and 2.8mA for Prototype paper-mesh cell.

3.2. Lab and Prototype Supercapacitor Assembly

Binders are normally used in supercapacitors to promote stability performance over 5,000 charge/discharge cycles, but the use of binders also affects the capacitance value and the electric and ionic resistance in EDLC as mention in the introduction section. A Lab-assembly has been carried out with bind-less electrodes in order to evaluate different current collectors, and a prototype has been developed to evaluate the electrolyte limitations due to design, and the results are shown in Figure 7. Lab assemblies using stainless steel mesh as current collector and carbon paper as support (Lab mesh-paper) resulted in 50% less specific capacitance ($\approx 21\text{F/g}$) than when using carbon cloth as current collector and support (Lab Cloth, 38F/g). This result could be associated to the stainless steel mesh current collector, causing a higher contact resistance with the carbon paper in Lab-Mesh-Paper cell. In addition, the hydrophilic nature of carbon paper makes the electrolyte migrate to the metal connections through capillarity, destroying them when long cycling is carried out. Therefore, since the extra resistance introduced by the stainless steel mesh current collector to prevent contact oxidation cannot be eliminated, the carbon cloth has shown its excellent properties as a current collector and support for electrode materials assembled in a EDLC cell. In addition, the inset on Figure 7 shows the excellent cycling stability of this Lab cell through 7000 charge-

discharge cycles. On the other hand, a thin-prototype using a mesh-paper as current collector and support has been developed to evaluate the electrolyte diminution. In this thin-prototype, no relevant differences in capacitance values can be observed during the first 30 charge-discharge cycles compared to the LAB MESH-PAPER cell assembly. All cells were analyzed using a current that allowed setting up the discharge time to 100 seconds, which is in the range of supercapacitor cell applications. The devices with higher capacitances, higher currents were applied suggesting the enhanced ability for charge storage with lower resistance resulting in an assemble design that directly affects the efficiency in this devices. These results suggest that the electrolyte quantity in the prototype does not affect importantly the capacitance value compared to the lab assembly (2 F/g difference).

Table 2 shows the comparison of our resulting capacitance values obtained for our best electrode material (1%Nafion) and cell assemblies, with other three references found with binder-free electrodes used to assemble a EDLC cells. Our results show similar Intrinsic specific capacitance values for the bare electrodes in spite of using a minimum amount of binder in our case (1%Nafion), and similar capacitance values for our cell assemblies. In addition, the use of carbon nanotubes or the formation of carbon aerogels in the other references makes the fabrication procedure more complicated or the cost of the electrodes higher, making our contribution more valuable.

4. CONCLUSIONS

For conventional electrodes in supercapacitor applications, it is possible to consider the use of 1 wt% Nafion solution as binder for optimum electrode performance, obtaining the maximum specific capacitance and minimum electric resistance contribution, considering the importance of the film thickness in the electrode. The use of carbon cloth as support and current collector for electrode materials resulted in a minimum contact resistance, maximizing the capacitance value up to 38F/g for EDLC 2-electrode cells assembled with binder-free activated carbon electrodes. A prototype design has been proposed and it is also possible to consider the use of carbon cloth in portable devices as current collector, avoiding the ionic source depletion due to reduced amount of electrolyte.

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Table 2. Comparative capacitance values previously reported in literature for EDLC cells assembled with bind-less carbon electrodes..

MATERIAL	SPECIFIC CAPACITANCE	REFERENCE
Carbon nanotubes (binder free)	44 F/g	25
Activated carbon/carbon nanotubes paper	260-290 F/g	26
Carbon cloth-reinforced resorcinol formaldehyde (RF)-aerogels	28 F/g	32
N-1%Ultrathin (DLC with 1% Nafion and carbon paper as current collector)	245 F/g	THIS WORK
LAB-CLOTH CELL (Binder-free DLC electrodes and carbon cloth as current collector)	38 F/g	THIS WORK

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