Cite this: Faraday Discuss., 2017, 199, 405

# PAPER



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# Strain-capacitance relationship in polymer actuators based on single-walled carbon nanotubes and ionic liquid gels<sup>†</sup>

Hyacinthe Randriamahazaka\*a and Kinji Asaka<sup>b</sup>

Received 18th November 2016, Accepted 5th December 2016 DOI: 10.1039/c6fd00232c

We investigate the electromechanical properties of bucky-gel electrochemical actuators incorporating various amounts of single-walled carbon nanotubes and an ionic liquid electrolyte, 1-butyl-3-methylimidazolium tetrafluoroborate, that are able to convert electrochemical energy into mechanical energy. The interplay between mechanical and electrochemical effects is studied. The electromechanical responses are investigated by means of electrochemical impedance spectroscopy and bending displacement measurements. We develop a theoretical model that allows us to rationalize the electrochemical stress due to the intercalation (de-intercalation) process, which generates the strain and bending of the actuators. We then analyze the relationship between the strain and the real part of the complex capacitance by introducing a strain-capacitance coefficient. This coefficient is related to the electrochemical stress and the amount of the ionic adsorption (desorption) at the double-layer. From a practical point of view, the determination of the strain-capacitance coefficient is helpful for characterizing and optimizing the performance of electrochemical actuators.

# Introduction

Recently, much attention has been focused on soft materials that can transform electrical energy directly into mechanical work, because they are useful for a wide range of applications including actuators and artificial muscles, robotics, tactile and optical displays, medical devices, and micro- and nano-electromechanical systems.<sup>1–3</sup> For the development of artificial muscles, polymers and gels present an interesting technology because they possess inherent compliance as well as being light and generally cheap. However, in order to optimize these devices, it is

<sup>&</sup>lt;sup>a</sup>Université Paris Diderot, Sorbonne Paris Cité, ITODYS, UMR 7086 CNRS, 15 rue J-A de Baïf, 75205 Paris Cedex 13, France. E-mail: hyacinthe.randria@univ-paris-diderot.fr

<sup>&</sup>lt;sup>b</sup>National Institute of Advanced Industrial Science and Technology (AIST), 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan

<sup>†</sup> Electronic supplementary information (ESI) available: Calculation of the chemical capacitance from the impedance data, and a schematic of the electrochemical actuator. See DOI: 10.1039/c6fd00232c

necessary to evaluate their electromechanical behaviour in terms of response time, power and energy. The interplay of mechanical and electrochemical effects is important for further understanding of the fundamental properties of the electroactive material–electrolyte interface in electrochemical actuators. In the relevant experiments, the electrode potential is most often controlled and the mechanical strain of the surface is the observed quantity.

Providing a comprehensive understanding of actuation mechanism characteristics in electrolytes is becoming one of the major focus areas of nanocarbon based actuators.4-6 The actuation properties of carbon nanotubes were first described by Baughman et al., who demonstrated that thin sheets of SWCNTs possess quantum-chemical and double-layer electrostatic effects that trigger electrochemical-based actuation.<sup>7,8</sup> The application of a potential induced an electron/hole charge injection into the nanotubes, which is compensated for at the nanotube-electrolyte interface by electrolyte ions, forming the so-called electric double layer. No dopant intercalation is required, but the resulting change in band structure is believed to cause a change in the C-C bond length during the charge injection.9-13 The change in C-C bond length can be detected by Raman spectroscopy.14,15 Under these assumptions, the electronic/hole current is, in principle, able to instantaneously compensate for the ionic current. Since the electronic/hole resistance is much lower than the ionic resistance then the ion transport, by means of diffusion and/or migration, controls the charging process dynamics. Thus, the rate of charging determines the bending behaviour of the system.<sup>16</sup> In this case, the kinetics of ion exchange between the carbon nanotubes and electrolyte solution can control the actuator performance.

In previous papers,<sup>17,18</sup> we have investigated bucky-gel actuators composed of SWCNTs and an ionic liquid.<sup>19,20</sup> The actuator strip, which is structurally supported by a fluorinated polymer, adopts a bimorphous configuration, in which gelatinous SWCNT/ionic liquid electrode layers (bucky-gel electrodes) laminate an ionic liquid electrolyte gel layer. It was demonstrated that the actuator (buckygel actuator) could work in air for a long time with a small battery. SWCNTs have attracted much interest because of their intrinsic mechanical and electrical properties,<sup>21</sup> and the possibility of functionalizing and incorporating them into composite materials.<sup>22</sup> Meanwhile, ionic liquids are also receiving a lot of interest for their possible use as an alternative reaction media to volatile organic solvents.9,10,23,24 An ionic liquid usually consists of organic ions, and it is possible to tailor its properties by changing the combination of these ions.<sup>25,26</sup> Most ionic liquid molecules consist of combinations of a soft heterocyclic cationic species and a soft fluorinated anionic species, such as 1-butyl-3-methylimidazolium tetrafluoroborate (BMIBF<sub>4</sub>). Since ionic liquids possess characteristics such as nonvolatility, non-flammability, and high electric conductivity, many researchers have attempted to use them as constituent materials in electronic devices.<sup>27-29</sup>

We have reported previously the electrochemical impedance spectroscopy (EIS) measurements and electromechanical behaviour of bucky-gel actuators, and shown that they have stable electrochemical responses and behave as supercapacitor devices.<sup>30</sup> Supercapacitors are electrochemical capacitors that store energy through reversible ion adsorption onto active materials that have a high specific surface area.<sup>31</sup> Indeed, EIS appears to be an excellent technique for investigating the bulk and interfacial electrical properties of any kind of solid or liquid material connected to or being part of an electrochemical system.<sup>32,33</sup>

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Recently, we reported that the electromechanical behaviour of bucky-gel actuators can be studied by analysing the displacement caused by an applied sinusoidal voltage and EIS measurements.<sup>34,35</sup> The electrochemical responses could be expressed in terms of a complex capacitance, and the frequency dependence of the real and imaginary components of that capacitance allowed for the determination of the following parameters: the time constant, energy, and power. When the electrochemical responses are expressed in terms of the complex capacitance, we can show a correlation between the strains and the real part of the complex capacitance.

Herein, we develop a theoretical model that takes into account both the electrochemical and mechanical properties of the active materials for electrochemical actuators. The model analyzes the influence of the electrochemical stress due to the intercalation (de-intercalation) process, which generates the strain and bending of the actuators. We analyze the relationship between the different strains and the real part of the complex capacitance by introducing a strain–capacitance coefficient  $\xi_{\rm C}$  (F<sup>-1</sup>). This coefficient is related to the electrochemical stress and the amount of the ionic adsorption (desorption) at the double-layer. A combination of EIS and bending displacement measurements allows us to determine  $\xi_{\rm C}$ . In addition, we investigate the effect that the amount of SWCNTs has on the electrochemical performance of the actuators. The interplay between the electrical and mechanical responses is shown. To our best knowledge, this is the first report in which this kind of approach has been used to analyze the electromechanical behaviour of carbon nanotubes or carbon nanotube-based composites.

# Experimental

## Materials and preparation of the actuator

The ionic liquid, 1-butyl-3-methylimidazolium tetrafluoroborate (BMIBF<sub>4</sub>) was used as received from Fluka. SWCNTs (Purified HiPco®) from Unidym Inc. and polyvinylidene fluoride-*co*-hexafluoropropylene (PVDF(HFP): Kynar Flex®2801) from Arkema Chemicals Inc. were used as received without any further purification. Methylpentanone (MP) and propylene carbonate (PC) were purchased from Aldrich, and dimethylacetamide (DMAc) from Kishida Chemicals Co. The preparation of the actuator was described in our previous work.<sup>34</sup> The electrode layer was fabricated by casting 1.6 ml of the electrode solution composed of 136 mg of BMIBF<sub>4</sub>, 80 mg of PVDF(HFP) and different amounts of SWCNTs in 9 ml DMAc into a Teflon mold (area:  $2.5 \times 2.5 \text{ cm}^2$ ) and evaporating the solvent. The electrode film obtained was 70–80 µm thick. The amounts of SWCNTs used in the bucky-gel electrode layers prepared for the various kinds of actuators are reported in Table 1.

Gel electrolyte layers were fabricated by casting 0.3 ml of BMIBF<sub>4</sub> and PVdF(HFP) (0.5 mmol/100 mg) in a mixture of 1 ml of MP and 250 mg of PC into a Teflon mold (area:  $2.5 \times 2.5 \text{ cm}^2$ ) and evaporating the solvent. The gel electrolyte film obtained was 20–30 µm thick. An actuator film was fabricated by hotpressing the electrode and electrolyte layers, which have the same internal ionic liquid, at 70 °C. The actuator film was 130–145 µm thick, which is less than the sum of two electrodes and one electrolyte layer, since the thickness of each layer is

Table 1	Characteristic electrochemical parameters of the bucky-gel electrodes. C <sub>0</sub> is the
real capa	acitance at low frequency determined from the complex impedance spectra, $ au^0$ is
the relax	ation time constant, $C_{\text{max}}$ and $K_{\text{el}}$ are the parameters defined in eqn (30) and (31).
$\delta$ and $\varLambda$	are relative volume variation and the effective elastic constant, respectively

SWCNTs/%	<i>m</i> /mg	$C_0/\mathrm{mF}$	$t^{\circ}/{ m s}$	$C_{\rm max}/{ m mF}$	$K_{\rm st}$	δ	Λ
10	24.3	3.2	2.51	3.8	0.065	55.3	0.278
20	49.9	9.5	0.63	18.3	0.432	224.5	0.010
26	70.8	11.0	0.40	19.2	0.435	249.2	0.009

decreased by the hot-pressing process. The surface and cross-section of the film were examined with a scanning electron microscope (Hitachi S5000).

## **Displacement measurements**

Actuator displacement measurements were performed by applying sinusoidal wave voltages to a 10 × 1 mm<sup>2</sup> sized actuator strip clipped between two gold electrodes; the displacement at a point 5 mm away (free length) from the fixed point was continuously monitored from one side of the actuator strip by using a laser displacement meter (KEYENCE model LC2100/2220) (see ESI – Fig. S1†). Sinusoidal wave voltages  $\Delta V$  of 4 V peak-to-peak amplitude at various frequencies were used in order to study the frequency dependence of the displacement. A Hokuto Denko model potentiostat/galvanostat with a Yokagawa Electric model FC 200 waveform generator was used to activate the bucky-gel actuator. The electrical parameters were measured simultaneously.

## **Electrochemical measurements**

Electrochemical impedance spectroscopy (EIS) measurements were performed for ionic liquid gel layers sandwiched between two 7 mm diameter bucky-gel



Scheme 1 Schematics showing one kind of mobile ion intercalation and de-intercalation during the electrochemical actuation. One observes a volume increase of one electrode during the intercalation concomitant to a volume decrease of the other electrode leading to the bending of the flexible electrode. The membrane containing the ionic liquid acts as an ion reservoir.



Fig. 1 An SEM image of the bucky-gel electrode consisting of SWCNTs (10% w/w), PVdF(HFP) and  ${\sf BMIBF}_4.$ 

electrode layers by using a two-electrode electrochemical cell (Hosen Co. Ltd., Japan). The impedance spectra were obtained using a Solartron 1260 Frequency Response Analyzer, operating at an applied DC voltage of 0 V associated with a sinusoidal wave with amplitude 10 mV at frequencies from 10 mHz to 100 kHz. Measurements were made at room temperature.

# **Results and discussion**

## Theoretical model

For the bucky-gel electrochemical actuators, the bending results from a volume change at the double-layer due to the intercalation (de-intercalation) process during actuation. As shown in Scheme 1, the intercalation and de-intercalation processes induce a volume change in each electrode leading to the bending of



Fig. 2 A cross sectional SEM image of a bucky-gel actuator consisting of bucky-gel electrodes (SWCNTs (10% w/w), PVdF(HFP) and BMIBF<sub>4</sub>) sandwiching an ionic gel electrolyte layer (PVdF(HFP) and BMIBF<sub>4</sub>).



Fig. 3 Complex impedance plot, -Z'' vs. Z', of the bucky-gel electrode consisting of SWCNTs (10% w/w), PVdF(HFP) and BMIBF<sub>4</sub> at 0 V.

the flexible device. In order to gain further understanding into the energy conversion during the electrochemical actuation, a theoretical model able to analyze the double-layer properties and the associated volume change will be helpful. The coupling of ion motions to the material's degrees of freedom and the interactions with counter-ions are major factors in explaining the peculiarities in their properties. While cross-correlations between different ions are important, the basic mechanism governing the electrical response can be essentially be traced back to the motion of single ions. Accordingly, we consider only one kind of mobile ions in the model described in Scheme 1.

A general thermodynamic theory of the stress-composition interaction was developed by Larché and Cahn.<sup>36–38</sup> This theory implies the existence of a coupling between the elastic properties of the host material and the structure and/or the dynamics associated with the guest species. Recently, Vakarin and Badiali have developed a unified description of the host–guest coupling in the course of insertion into a disordered matrix.<sup>39,40</sup> In this model, it is assumed that the host response to the accommodation of the guest is not negligible because the insertion (or intercalation) induces stress in the host matrix. The host may undergo a structural transformation or local distortion which may lead to segregation effects. In this case, the elastic effects should be taken into account.

We consider that the total free energy  $F_{\rm T}$  can be expressed as

$$F_{\rm T} = F_{\rm ch} + F_{\rm el} \tag{1}$$

where  $F_{ch}$  is the chemical part, and  $F_{el}$  is the elastic (mechanical) part. Herein, we assume for simplicity that only one type of ion (for instance a cation) is involved in the intercalation (de-intercalation) process and we estimate the coupling term



Scheme 2 Equivalent circuit model of the porous electrode consisting of the distributed resistance of the electrolyte in the pore and the distributed capacitance.

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Fig. 4 Variation of the real part C' (top) and imaginary part C'' (bottom) of the capacitance with the frequency (in semi-log plot) of bucky-gel electrode consisting of SWCNTs (10% w/w), PVdF(HFP) and BMIBF<sub>4</sub> at 0 V.

based on the continuum theory of elasticity with concentration dependent stress and strain fields. When an ion intercalates into the carbon nanotube layer, it can only take certain energetically favorable interstitial sites. In the simplest



**Fig. 5** Variation of the real part of the capacitance C'(f) as a function of the strain (%) of bucky-gel electrode consisting of SWCNTs (10% w/w), PVdF(HFP) and BMIBF<sub>4</sub> at 0 V.



Fig. 6 A plot of  $\frac{\varepsilon(f)}{C'(f)}$  vs.  $\varepsilon(f)$  for the bucky-gel electrode consisting of SWCNTs (10% w/w), PVdF(HFP) and BMIBF<sub>4</sub>.

continuum approximation of intercalation into a lattice, we use a statistical thermodynamic model with mean-field approximation, also called the regular solution model, to estimate the chemical part of the free energy  $F_{ch}$  as

$$F_{\rm ch}(x) = F_0 C^0 x + k_{\rm B} T C^0 [x \ln(x) + (1-x)\ln(1-x)] + \frac{1}{2} k_{\rm B} T C^0 g x^2$$
(2)

with  $x = \frac{C}{C^0}$ , where  $F_0$  is the site energy, x is the fraction of occupied site concentration C with respect to the total number of available sites  $C^0$ , g is the mean-field interaction parameter,  $k_{\rm B}$  is Boltzmann's constant, and T is the temperature. The first term in (2) is the internal energy, the second is the entropic term of mixing and the third is the mean-field interaction term.  $gk_{\rm B}T$  represents



Fig. 7 The real capacitance vs. the real part of the corrected impedance of the bucky-gel electrode consisting of SWCNTs (10% w/w), PVdF(HFP) and BMIBF<sub>4</sub>.

 Table 2
 Characteristic energy parameters of the bucky-gel electrodes. Calculations are based on the total weight of SWCNTs

SWCNTs/%	<i>m</i> /mg	$\mathrm{ESR}/\Omega$	$E_{\rm max}/{\rm kJ}~{\rm kg}^{-1}$	$P_{\rm max}/{\rm kW~kg^{-1}}$
10	24.3	21.9	1.2	7.5
20	49.9	19.2	1.5	4.2
26	70.8	35.1	1.3	1.6

the interaction energy of an occupied site with respect to its surroundings. The interaction is repulsive when g is positive and attractive when g is negative.

For the mechanical part of the free energy, we follow the approach developed by Vakarin and Badiali to estimate the coupling term based on the continuum theory of elasticity with concentration dependent stress and strain fields.<sup>39,40</sup> By assuming that the strain is purely dilatational, one has

$$F_{\rm el}(x) = \frac{\Lambda}{2} \varepsilon(x)^2 - \sigma(x)\varepsilon(x)$$
(3)

where  $\Lambda$  is the effective elastic constant,  $\varepsilon(x)$  is the strain, and  $\sigma(x)$  is the loading stress. Accordingly, one can write

$$\frac{\mathrm{d}F_{\mathrm{el}}(x)}{\mathrm{d}\varepsilon(x)} = \frac{\mathrm{d}F_{\mathrm{el}}(x)}{\mathrm{d}x}\frac{\mathrm{d}x}{\mathrm{d}\varepsilon(x)} \tag{4}$$

Then

$$\frac{\mathrm{d}F_{\mathrm{el}}(x)}{\mathrm{d}x} = \frac{\mathrm{d}F_{\mathrm{el}}(x)}{\mathrm{d}\varepsilon(x)}\frac{\mathrm{d}\varepsilon(x)}{\mathrm{d}x} = S(x)\frac{\mathrm{d}\varepsilon(x)}{\mathrm{d}x} \tag{5}$$

where S(x) is the total stress which can be expressed as

$$S(x) = \frac{\mathrm{d}F_{\mathrm{el}}(x)}{\mathrm{d}\varepsilon(x)} = A\varepsilon(x) - \sigma(x) \tag{6}$$

The total stress S(x) contains two terms: the internal (self-stress) due to the host's reaction to the intercalation process (=  $\Lambda \varepsilon(x)$ ), and the stress resulting from the loading procedure (=  $\sigma(x)$ ). We assume that all of the stress applied to the sample by the intercalation process is transformed into elastic energy. In this case, one obtains

$$\frac{\mathrm{d}F_{\mathrm{el}}(x)}{\mathrm{d}x} = \Lambda\varepsilon(x)\frac{\mathrm{d}\varepsilon(x)}{\mathrm{d}x} \tag{7}$$

The strain can be measured as a volume dilatation of the host matrix during the course of insertion

$$\varepsilon(x) = \frac{V(x) - V_0}{V_0} \tag{8}$$

where  $V_0$  is the initial host volume (at x = 0). If the host-guest system forms a solid solution the guest partial molar volume  $V_m$  is related to the total volume as

 $V(x) = xV_{\rm m} + V_0 \tag{9}$ 

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If the volume varies linearly with *x*, one obtains

$$\varepsilon(x) = x \frac{V_{\rm m}}{V_0} \tag{10}$$

and

$$\frac{\mathrm{d}\varepsilon(x)}{\mathrm{d}x} = \frac{V_{\mathrm{m}}}{V_0} \tag{11}$$

Let us introduce the relative volume variation  $\delta$ 

$$\delta = \frac{V(1) - V(0)}{V(0)} \tag{12}$$

and the modulation function p(x)

$$p(x) = \frac{V(x) - V(0)}{V(1) - V(0)}$$
(13)

Then, the strain can be expressed as

$$\varepsilon(x) = \frac{V(x) - V(0)}{V(0)} = \delta p(x) \tag{14}$$

Thus, eqn (7) can be rewritten as

 $\frac{\mathrm{d}F_{\mathrm{el}}(x)}{\mathrm{d}x} = \Lambda \delta^2 p(x) \frac{\mathrm{d}p(x)}{\mathrm{d}x} \tag{15}$ 

In order to study eqn (15), we will adopt the phenomenological model developed by Bisquert *et al.*, in which they used a scaling  $law^{41,42}$ 

$$p(x)\frac{dp(x)}{dx} = \frac{(1+\eta)x^{\eta}}{2}$$
 (16)

and

$$2G = \Lambda \delta^2 \tag{17}$$

where  $\eta$  is a coefficient, and G(G > 0) is a parameter.

The integration of eqn (16) gives

$$p(x) = x^{\left(\frac{n+1}{2}\right)} \tag{18}$$

By introducing eqn (18) into eqn (14), one obtains

$$\varepsilon(x) = \delta x^{\left(\frac{\eta+1}{2}\right)} \tag{19}$$

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One can remark that if  $\eta = 1$ , the Verlag law is recovered<sup>42</sup>

$$\varepsilon(x) = \delta x \tag{20}$$

Now, let us determine the chemical potential of the intercalating ions. By definition, the chemical potential is a derivative of the free energy with respect to the concentration. Since the total free energy of the system has a chemical and mechanical part, we determine each contribution successively for clarity. The chemical contribution for the chemical potential of the cations is calculated from eqn (2)

$$\mu_{+}(x) = \mu_{+}^{0} + k_{\rm B}T \ln\left(\frac{x}{1-x}\right) + k_{\rm B}Tg(x-0.5)$$
(21)

For the mechanical part, by combining eqn (16) with (17) and (15), one has

$$\frac{\mathrm{d}F_{\mathrm{el}}(x)}{\mathrm{d}x} = (1+\eta)Gx^{\eta} \tag{22}$$

The chemical capacitance  $C_+^{\text{chem}}$  is the second order derivative of the free energy with respect *x*. Therefore, one has

$$C_{+}^{\text{chem}}(x) = \frac{e^2 C_{+}^0}{k_{\text{B}} T} \left[ \frac{1}{x} + \frac{1}{1-x} + g + \eta (1+\eta) G x^{(\eta-1)} \right]^{-1}$$
(23)

For low loading ( $x \ll 1$ ), *g* can be neglected, and eqn (23) can be rewritten as<sup>41</sup>

$$C_{+}^{\text{chem}}(x) = C_0 \left[ \frac{1}{x} + \eta (1+\eta) G x^{(\eta-1)} \right]^{-1}$$
(24)

with

$$C_0 = \frac{e^2 C_+^0}{k_{\rm B} T}$$

By combining eqn (19) with eqn (24), the expressions of the chemical capacitance become

$$C_{+}^{\text{chem}}(x) = \frac{C_0(\varepsilon(x))^2}{\delta^2} \text{ for } \eta = 0$$
(26)

$$C_{+}^{\text{chem}}(x) = \frac{C_{\max}\varepsilon(x)}{\varepsilon(x) + K_{\text{st}}} \text{ for } \eta = 1$$
(27)

with

$$C_{\max} = \frac{C_0}{2G} \tag{28}$$

and

$$K_{\rm st} = \frac{\delta}{2G} \tag{29}$$

Including eqn (17) into eqn (28) and (29) gives

$$C_{\max} = \frac{C_0}{\Lambda \delta^2} \tag{30}$$

and

$$K_{\rm st} = \frac{1}{\Lambda\delta} \tag{31}$$

In the following section, eqn (26) or (27) will be used to analyze the influence of the strain on the chemical capacitance.

## Electromechanical properties of the bucky-gel actuators

Scanning electron microscopy (SEM) is a useful tool to study the morphology of materials. Fig. 1 shows an SEM image of the bucky-gel electrode. This magnified SEM image of the film shows that the nanostructure of the bucky-gel electrode contains highly exfoliated SWCNT bundles. In addition, we can also observe the nanoporous nature of the film. A cross section image of the film shows the typical compact layer-by-layer structure of the bucky-gel actuator (Fig. 2).

EIS anaylses were performed to provide an understanding of the complex phenomenon occurring in the nanotube-based electrochemical actuators.<sup>30,34,35</sup> Experimental data from EIS measurements are usually plotted in a Nyquist diagram, which represents the imaginary part of the impedance *versus* the real part. As shown in Fig. 3, a depressed semicircle is observed in the region of high frequency (1000 Hz < f < 10 kHz), which can be explained by the resistance of the charge transfer process at/inside the bucky-gel electrodes. At low frequency (f < 200 Hz), the so-called finite length capacitive effect was observed (Fig. 3).

Previously, we have reported that bucky-gel actuators behave as supercapacitors at low frequency.<sup>30</sup> According to the complex form of the impedance  $Z(\omega)^{32,33}$ 

$$Z(\omega) = Z'(\omega) - jZ''(\omega) \tag{32}$$

where  $j^2 = -1$ , and  $\omega$  is the angular frequency of the applied ac-signal, the supercapacitive behaviour in the low-frequency range can be represented simply as:

$$Z(\omega) = -jZ''(\omega) \tag{33}$$

Therefore, the electrochemical responses at low frequency can be represented by a series:  $R(\omega)-C(\omega)$ , where  $R(\omega)$  and  $C(\omega)$  are the resistance and capacitance, respectively, and both depend on the frequency f (where  $\omega = 2\pi f$ ). We have previously reported that the use of the complex capacitance allowed a straightforward analysis of the electrochemical responses of electrochemical actuators.<sup>30</sup> For CNT bucky-gel electrodes, the bending strain is related to the ionic transfer.<sup>43,44</sup> This ionic transfer depends on the applied potential, the ion size and the host material. In the context of electrochemical impedance spectroscopy, the electric charge/potential transfer function,  $\frac{\Delta q}{\Delta E}(\omega)$ , can be used to investigate the strain frequency dependence and calculated experimentally by using the following expression:

$$\frac{\Delta q}{\Delta E}(\omega) = \frac{1}{j\omega} \frac{\Delta i}{\Delta E}(\omega) \tag{34}$$

with  $\frac{\Delta i}{\Delta E}(\omega)$  is the admittance. Then, the complex capacitance is

$$C^*(\omega) = \frac{1}{j\omega Z(\omega)} \tag{35}$$

Here, we propose to perform the capacitive analysis to stress out the electromechanical process. It is important to demonstrate that physically the capacitive interpretation is more useful for giving physical information about the storage processes in the internal interfaces of the electrochemical junctions. In our previous work, we have demonstrated that the low frequency impedance responses of the bucky-gel electrochemical actuators can be analyzed by means of a transmission line model (Scheme 2).<sup>34,45</sup>

In order to calculate the complex capacitance, the real part of the impedance  $Z'(\omega)$  was corrected for the ohmic drop in the solution, characterized by the electrolyte resistance,  $R_{\rm el}$ . Then, the impedance data could be transformed into the complex capacitance, defined as (see ESI<sup>†</sup>)

$$C^*(\omega) = C'(\omega) - jC''(\omega)$$
(36)

where  $C'(\omega)$  and  $C''(\omega)$  are the real and imaginary parts of the complex capacitance, respectively. These capacitance values are calculated according the following equations<sup>30,46,47</sup>

$$C'(\omega) = \frac{Z''(\omega)}{\omega |Z(\omega)|^2}$$
(37)

and

$$C''(\omega) = \frac{-Z'(\omega)}{\omega |Z(\omega)|^2}$$
(38)

where  $|Z(\omega)|$  is the impedance modulus. The real part of the capacitance  $C'(\omega)$  corresponds to the capacitance of the cell measured under low-frequency alternating current conditions, and  $C''(\omega)$  is the imaginary part of the capacitance corresponding to losses in the form of energy dissipation. The real capacitance C' of the complex capacitance function is related to the parallel capacitance, while the imaginary part is related to a conductive term. The imaginary capacitance includes the dc-conductance and other relaxation-associated losses.<sup>32</sup> In Fig. 4, the real parts  $C''(\omega)$ , and imaginary parts  $C''(\omega)$  of the complex capacitance were plotted as a function of the ac frequency. These plots provide an intuitive way of interpreting the impedance spectroscopy of an electrochemical capacitor, and evaluate the total specific capacitance  $C''(\omega)$  increases monotonically from 0 to a maximum value, while the imaginary capacitance  $C''(\omega)$  plot peaks. This is a general feature for electrochemical capacitors, such as porous electrodes with ion diffusion. One observes that, at high frequency, the bucky-gel actuator

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behaves like a pure resistor. From the peaked imaginary capacitance profiles (*C'' versus* log *f*), two important parameters can be estimated: the real capacitance at low frequency  $C^0$ , and the relaxation time constant  $\tau$ , where  $\tau = \frac{1}{2\pi f_0}$ . From a thermodynamic point of view, the real capacitance represents the ability of the system to store electrical energy.

Herein, our main goal is to investigate the relationship between the electrical and the mechanical properties of the bucky-gel actuator. For an electrochemical actuator, the stored energy is converted into mechanical energy. The macroscopic mechanical responses can be characterized by the frequency dependent strain  $\varepsilon(f)$ . Indeed, the measured displacement  $\beta$  is transformed into the strain  $(\varepsilon)$  between two bucky-gel electrode layers by using the following equation, on the assumption that the cross-sections are planar at any position along the actuator (*i.e.* there is no distortion of the cross-sections):

$$\varepsilon = 2 \frac{d\beta}{\left(L^2 + \beta^2\right)} \tag{39}$$

where L is the free length and d is the thickness of the actuator strip.<sup>34</sup>

Since the bucky-gel actuator behaves as supercapacitor, it is important to have an adequate parameter that allows us the possibility to quantify the influence of the electrochemical constraint on the surface stress. A capacitive charge in the electric double layer is the main parameter that influences the surface stress. This can provide better understanding of the microscopic origin of the surface stresscharge response. The overall picture concerning surface stress is as follows: variations of the surface stress in an electrolyte that allows changing and controlling of the surface charge directly can be explained by ion adsorption (desorption). The work of Haiss made an important contribution by demonstrating a linear dependence of the surface stress to the charge.<sup>48</sup> Recently, *in situ* electrochemical EDX analysis showed that the actuation mechanism of an artificial muscle containing an ionic liquid based actuator can be governed by ionic transfer.<sup>49</sup> Now, we will analyze the relationship between the strain  $\varepsilon(f)$  and the real part of the complex capacitance C'(f). As shown in Fig. 5, a non-linear relationship is observed between  $\varepsilon(f)$  and C'(f).

Using the theoretical model presented previously, we find that C'(f) vs.  $\varepsilon(f)$  can be analyzed by means of eqn (27). Indeed, we can linearized eqn (27) as

$$\frac{\varepsilon(x)}{C_{+}^{\text{chem}}(x)} = \frac{\varepsilon(x)}{C_{\max}} + \frac{K_{\text{st}}}{C_{\max}}$$
(40)

So,  $\frac{\varepsilon(x)}{C_{+}^{\text{chem}}(x)} \nu s. \varepsilon(f)$  should give a straight-line. As shown in Fig. 6,  $\frac{\varepsilon(x)}{C_{+}^{\text{chem}}(x)} \nu s.$  $\varepsilon(f)$  gives a straight line with a slope of  $\frac{1}{C_{\text{max}}}$  and an intercept of  $\frac{K_{\text{st}}}{C_{\text{max}}}$ . This plot allows us to determine  $C_{\text{max}}$  and the parameter  $K_{\text{st}}$ . According eqn (27), the parameter  $K_{\text{st}}$  can be viewed as a specific strain  $\varepsilon_{1/2}$  where the capacitance is equal to  $C_{\text{max}}/2$ .

Furthermore, we introduce a strain–capacitance coefficient,  $\xi_{\rm C}$ , that is related to the intrinsic stress–charge response and to the amount of ionic adsorption (desorption) at the double-layer, which can be defined as

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$$\xi_{\rm C} = \frac{K_{\rm st}}{C_{\rm max}} = \frac{\delta}{C_0} \tag{41}$$

This strain–capacitance coefficient  $\xi_{\rm C}$  is related to the strain response induced by the electrochemical stress due to ionic adsorption (desorption) at the carbon nanotube interface. One can observe that if  $\varepsilon(f) \ll K_{\rm st}$  (for very low strain or high frequency range), one has

$$C_{+}^{\text{chem}}(x) = \frac{C_{\max}}{K_{\text{st}}} \varepsilon(x) = \xi_{\text{C}} \varepsilon(x)$$
(42)

In this case, the strain varies linearly with the real capacitance. This approximation allows the use of linear theory for defining the mechanical impedance.

The characteristic parameters for electrochemical actuators containing different amounts of SWCNTs are reported in Table 1. The results indicate that  $C_{\text{max}}$  varies linearly with the low frequency capacitance  $C_0$ . One should keep in mind that  $C_{\text{max}}$  (eqn (30)) includes both the electrochemical (*via*  $C_0$ ) and mechanical properties (*via*  $\Lambda\delta^2$ ). On the other hand,  $K_{\text{st}}$  (eqn (31)) depends only on the mechanical properties (*via*  $\Lambda\delta$ ). From eqn (41), one can write

$$K_{\rm st} = \frac{\delta}{C_0} C_{\rm max} = \xi_{\rm C} C_{\rm max} \tag{43}$$

From the linear variation of  $K_{\rm st} \nu s. C_{\rm max}$  (Fig. S2 – ESI†), a strain–capacitance  $\xi_{\rm C}$  of 23 F<sup>-1</sup> is obtained.

As shown in Table 1, the relative volume variation  $\delta$  (eqn (12)) increases with the amount of SWCNTs. This trend is due to the increase in the proportion of the active area within the bucky-gel where ionic intercalation (de-intercalation) occurs. On the other hand, the effective elastic constant  $\Lambda$  decreases as the amount of SWCNTs increases. This behaviour indicates that SWCNTs act as filler and increase the stiffness of the bucky-gel actuators. Recently, Weissmüller and Duan calculated the effect of the surface topology on the measured surface stress value.<sup>50</sup> Their theoretical work shows that the measured surface stresses, depending on the roughness of an electrode, should differ from the intrinsic surface stress of the metal surface. Here, we show that changing the amount of SWCNTs in the bucky-gel actuators modifies not only the electrochemical responses, but also their mechanical behaviours. Since the bucky-gel actuator behaves as a supercapacitor, the electrical energy is stored in the double layer.<sup>30</sup> Accordingly, the electroactive surface is determined by the amount of SWCNTs. These results indicate that SWCNTs in bucky-gel actuators have a three fold effect: increasing both the capacitance and the relative volume variation  $\delta$ , and decreasing the effective elastic constant  $\Lambda$ . Indeed, the imidazolium ions can be adsorbed through possible cation  $-\pi$  and/or  $\pi$ - $\pi$  interaction onto the  $\pi$ -electronic surface of the carbon nanotubes.19,20 These interactions may modulate the electromechanical parameters ( $\xi_{\rm C}$ ,  $\delta$ , and  $\Lambda$ ). These results indicate that the correlation of the strain and the real capacitance is an interesting tool for analyzing and optimizing the electromechanical responses of the actuators.

(44)

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In order to evaluate the performance of these actuators, as in the case of a supercapacitor, the values of the maximum power density  $P_{\text{max}}$  and energy density  $E_{\text{max}}$  were determined from the following equations<sup>31</sup>

$$P_{\rm max} = \frac{V_{\rm max}^2}{4mR_{\rm E}} \tag{44}$$

$$E_{\rm max} = \frac{C_{\rm LF} V_{\rm max}^2}{2m} \tag{45}$$

where m is the mass of SWCNTs and  $R_{\rm E}$  is the so-called equivalent series resistance (ESR) of the system that is extracted from Z-C (real capacitance vs. real part of the corrected impedance).  $R_{\rm E}$  corresponds to the intercept of Z' axis when C' is equal to zero (Fig. 7).  $C_{LF}$ , the low-frequency capacitance (equal to  $C^{0}$ ), can be determined from the imaginary part of the impedance at low frequency  $(Z''(\omega))$  $-1/j\omega C$ ).  $V_{\text{max}}$  is the maximum voltage. In the case of BMIBF<sub>4</sub>, a  $V_{\text{max}}$  of 4 V is attained. As shown in Table 2, it is interesting to note that the performance of these bucky-gel actuators is higher than that of natural muscle in terms of power density. Indeed, the energy density of muscle is of the order of 150 J kg $^{-1}$  and can peak at around 300 J kg $^{-1}$ .<sup>1</sup> To the best of our knowledge, this is the first time that capacitance-strain plots have been used to analyse the influence of the amount of an active material on the electromechanical behaviour of electrochemical actuators. These results are promising and will have a major impact on both the modelling and the optimization of electrochemical actuators.

# Conclusions

Analysis of the electrochemical responses in terms of the complex capacitance allows a simple determination of the time constant, and low frequency capacitance. The actuation response (strain) is directly related to the charge storage (related to the real capacitance) in the material. The strain-capacitance coefficient allows for characterization of the electromechanical response. Since the capacitance in buckygel actuators is determined by the electric double layer, an improvement in the stored energy can be obtained by increasing the interfacial surface area. At the same time, the strain-capacitance coefficient allows us to determine the ability of the actuator to transform electrical energy to mechanical energy (strain). We believe that the performance of electrochemical actuators can be further improved by studying the influence of the amount of electroactive material, and its interactions with the electrolyte, on energy conservation and energy dissipation. The major contribution reported in this work is the introduction and determination of the strain-capacitance coefficient. The strain-capacitance coefficient gives a clear picture about the energy storage and mechanical responses within the electrochemical actuators. In a subsequent paper, we will report the influence of the chemical nature of the ionic liquid on the electromechanical behaviour.

# Acknowledgements

K. A. acknowledges the Iketani Science and Technology Foundation for financial support of part of this work. H. R. thanks the CNRS and the Université Paris

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## Paper

Diderot for financial support. The authors are particularly grateful to Dr J. S. Lomas (ITODYS, Université Paris Diderot) who kindly revised our text. The authors also thank Dr T. Furukawa (AIST) who took the SEM images of the bucky-gel actuators.

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