Flexible Perovskites on CNT as integrated batteries for powering optoelectronics


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Introduction

This work is give a small insight about the electrochemical performance of flexible Carbon NanoTube based energy storage devices fabricated with and without perovskite microplates with further integration of optoelectronic devices for powering perovskite LEC. These devices behaved as a super-capacitors.

The results show how to use perovskite materials to increase the capacitance and energy density of flexible energy storage devices and how can we apply it in optoelectronics in a future work.

[a] Example of an inorganic perovskite oxide, CaTiO₃ (orthorhombic).
[b] Example of a HOIP with an organic cation at the A-site, MAPbI₃ (orthorhombic; MA = methylammonium)

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Introduction

Recently halide perovskite materials with general formula ABX\textsubscript{3} (A is a organic or inorganic cation, e.g., methylammonium (CH\textsubscript{3}NH\textsubscript{3}+) or cesium ion (Cs\textsuperscript{+}), B is a larger size divalent metallic cation (Pb\textsubscript{2}+, Sn\textsubscript{2}+), and X is halogen anion (Cl\textsuperscript{-}, Br\textsuperscript{-}, I\textsuperscript{-}) have attracted much attention owing to unique optoelectronics and electronics properties such as low-temperature solution processability, high color purity with narrow spectral width (FWHM of 20 nm), bandgap tunability and large charge carrier mobility [1,2,3].

One of important developments in our lab is a powering such PeLECs with small and powerful capacitors of energy.

[1] 11473, Organic and Hybrid Light Emitting Materials and Devices XXIV; 114731N

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Mechanism of PeLEC device. a) Initial PeLEC state demonstrating ions uniformly distributed all over the active layer. b) Intermediate PeLEC state showing cations drifting toward the cathode and anions toward the anode. c) Steady-state PeLEC operation with ions accumulated at the electrodes and light emission upon current injection. d) Top views of the SEM images of CNT electrode

Fabrication of flexible CNT based SCs

The CNT-based SCs were fabricated using the following procedure:

1. a transparent polyacrylic plastic was cleaned with water, ethanol, and isopropyl alcohol by ultrasonication.
2. CNTs were pulled out from a nanotube forest (synthesized by CVD method) and 1 layer of CNTs were manually transferred on the polyacrylic plastic (steps 1 and 2) to form the CNT electrode.
3. 100 \( \mu \)l of an aqueous solution with Ca\( _{2.9} \)Nd\( _{0.1} \)Co\( _{4.0} \)O\( _{9+\delta} \) (CaNCo perovskites, synthesized by a solid state reaction method [4]) was deposited on the CNTs by spin coating at 1000 rpm and dried for 60 min at 100 C (step 3).
4. A semipermeable acrylic membrane (SAM) was deposited on the CNT/CaNCo layer, the SAM worked as a separator.
5. Another electrode made exclusively with CNTs was put on the SAM and the device was sealed using a hot press.

As a result, we obtained the CaNCo/CNT electrode (the weight ratio between the CaNCo perovskite and CNTs is 2:98). Later, the CNT electrode with CaNCo perovskite was subjected to acid treatment using nitric acid at 80 C [5].

A semitransparent and flexible device is obtained. The CNT/CaNCo perovskite electrode is considered as the anode and the electrode made with only CNT was the cathode. In this work, all of the devices contained a gel electrolyte (80 mg) made of PMMA, acetone, water, and phosphoric acid (H\( _3 \)PO\( _4 \), 70% conc.) and the weight ratio among these components was 0.4:1:1:0.8. This gel was included between the SAM and the cathode. Two CNT based SCs were studied in this work using the following architectures: CNT/SAM/CNT and CNT+CaNCo/SAM/CNT, which were named CN and CaNCo devices respectively. In all the devices, the weight ratio of CaNCo perovskite/CNT electrode was 0.05:1. The CN device is considered as the reference device in order to elucidate the effect of the CaNCo perovskite on the supercapacitor’s performance.

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Morphological, structural and optical characterization

The electrodes of each supercapacitor device (CNT and CaNCo/CNT electrodes) were analyzed using scanning electron microscopy (SEM Quanta 250) and energy of 15 kV. The Energy-dispersive X-ray Spectroscopy (EDS) was carried out using a Thermo- scientific detector coupled to the SEM equipment. The X-ray diffraction (XRD) patterns of all the samples were obtained by using a Bruker D8 equipment with Cu-K radiation (λ=1.54056 Å) in the 2θ range of 10-80°. The absorbance and transmittance spectra of the samples were measured in the range of 250–800 nm utilizing a Perkin-Elmer Lambda 900 UV-VIS-NIR Spectrometer.

XPS and FTIR characterization of the electrodes

X-ray photoelectron spectroscopy (XPS) spectra were recorded for the CNT and CaNCo/CNT electrodes by using Thermo Scientific K-Alpha Spectrometer equipment. The Al-Kα source produced X-rays with energy of 1486.7 eV that are focused on a 200 x 200 μm² spot (power density = 66 W/m²). The Fourier transform infrared (FTIR) were recorded in the range of 400-4000 cm⁻¹ by employing a Thermo Scientific Nicole i50 equipment and the ATR method.

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Electrochemical characterization of the CNT- based SCs

The cyclic voltammetry (CV) and galvanostatic charging/discharging (GCD) curves for the SCs were recorded using an electrochemical station (Galvanostat/Potentiostat Wavenow) with a two-electrode configuration. The scanning rates for the CV measurements were 50, 70 and 100 mV/s in the potential range of 0-1.2 V. The GCD curves were obtained as follows:

1. positive current of 40 mA was applied during 20 seconds until a positive voltage of 2.5V was observed (charging time),
2. the current applied was zero and the voltage decreased as a function of time (discharging process) until a stable output voltage is observed.

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For all the devices, the negative electrode (anode) was the CNT electrode decorated with CaNCo perovskite (CaNCo/CNT electrode). Electrochemical impedance spectroscopy (EIS) was achieved by applying an AC voltage with 0.03 mV amplitude in the frequency range from 10 Hz to 100 kHz under open circuit potential conditions.

For the two electrodes configuration employed in this work, the specific gravimetric capacitance ($C_s$) was calculated from the GCD curves with [6,7]:

$$C_s = \frac{2I \int V(t)dt}{m(\Delta V^2)}$$

where $I$ is the discharge current, $\int V(t)dt$ is the total area under the discharge curve, and $\Delta V$ represents the potential change after a full discharge.

The specific energy density ($E$) in Wh/kg was calculated from the equation:

$$E = \frac{1}{2} \left[ \frac{C_s \cdot \Delta V^2}{3.6} \right]$$

It is worthy to mention that all the experimental curves for the CNT based SCs characterized in this work were obtained by averaging the results of four devices.

Structure and morphology of the CNTs and CaNCo/CNT composite electrodes.

a) the CNT sheets deposited on the polyurethane plastic. As observed, they look like fibers or “conductive cables” oriented in one direction (see yellow arrow). Besides, the inset of shows the “fibrous” interconnected conductive network formed by the CNTs.

b) the CaNCo perovskites employed in the devices are thin microplates with thicknesses in the range of 200-400 nm. Most of them have irregular shapes but some of them have a pentagonal morphology, see green circles. The inset shows the size distribution for the microplates and most of them (65%) have sizes in the range of 1-3 μm.

c) When the CNT sheets are decorated by these microparticles, a CaNCo/CNT composite electrode is formed. The biggest CaNCo microparticles remain on the surface of the CNTs and the smallest ones are embedded into the entangled CNT network, see red circles. This arrangement of CaNCo microparticles on the CNT allows and efficient charge extraction as demonstrated later by the electrochemical experiments. Finally, the composition of the CaNCo/CNT composite electrode was analyzed by EDS measurements.

d) the presence of Ca, Nd, Co, O, and C elements in that composite is shown. The EDS spectrum also indicates that calcium is the main component of the perovskite.
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**XRD, FTIR and Absorption Analysis of the CNT and CaNCo/CNT composite electrodes.**

a) The XRD pattern. The inset shows the XRD patterns of the bare CNT electrodes employed as support for the perovskites. CaNCo/CNT corresponds to composite material. However, not all the diffraction peaks of the perovskite powder were present in the XRD pattern of the CaNCo/CNT electrode because it obtained by many microplates.

b) The surface of the CaNCo powders, CNT electrode, and CaNCo/CNT composite electrode was analyzed by FTIR and absorbance spectra in order to understand the chemical changes on their surface after interacting with the solid electrolyte since these surface modifications played an important role in the electrochemical performance of the solid state SCs.

c) The absorbance spectrum. This indicates that coating the CNT electrode with the electrolyte increased considerably the number of oxygen vacancies on it. The absorbance spectrum of the CaNCo/CNT composite electrode coated with the solid electrolyte also presented a higher absorbance than the CNT electrodes and CaNCo powder, we could infer that the interaction between the CNT electrode or CaNCo/CNT electrode and the solid electrolyte-enhanced the formation of Vo defects on the electrodes, and this will play an important role in the energy storage capabilities.
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Electrochemical performance of CNT-based and perovskite-based solid state energy storage devices

a) the CV curves of the CN device. No oxidation and/or reduction peaks were observed, indicating that the devices are storing charge by EDL mechanism. As the scan rate increases, the oval-like shape and size of the CV curves remain similar, suggesting good reversibility, quick ion diffusion, and fast charge-discharge properties.

b) When the CaNCO perovskite is introduced, the CV curve changes drastically. Firstly, the CaNCo perovskite increased the current by ≈288%. Faradaic peaks appeared, indicating that the energy storage mechanism changed from EDL to redox reactions. The broader CV curve of the CaNCo device and its higher current indicates that its capacitance is higher than that for the CN device. Some Faradaic peaks appeared, see green circles.

c) The CN device (made without perovskite) showed a total discharge after 925 seconds while the discharge profile of the CaNCo device (made with the CaNCo perovskite) presented two components (see black curve).

d) 13 cycles of charge/discharge for the CaNCo device, each cycle lasted 20 min. As observed, the maximum voltage (2.5 V) reached after each cycle of charge is quite reproducible as well as the same level of stabilized voltage (1.37 V).
In order to explain the presence of the redox peaks and to understand the capacitive/battery-like properties of the devices, we performed XPS measurements for the CNT electrode and CaNCo/CNT composite electrode before and after its use in the supercapacitor devices, that is: 1) we measured the XPS spectrum of the electrode. 2) the electrode was used to assemble a supercapacitor and the device was fully characterized (CV, GCD, etc. were obtained). 3) the electrodes were removed from by disassembling the device (the encapsulation was broken) and their XPS spectrum was obtained again.

a) the deconvoluted XPS spectra of the O1s orbital corresponding to the CNT electrode.

b) the XPS spectrum for the Ca 2p orbital, which was taken from the CNT electrode before its use in the SC device.

c) the deconvoluted XPS spectra for the Nd 2p orbital and corresponds to the CaNCo/CNT electrode before its (curve I) and after its use (curve II) in the battery-like device.

d) the deconvoluted XPS spectra for the Co 2p orbital.

Consequently, the CaNCo device is surely storing charge by the simultaneous redox reactions of the Ca, Nd and Co elements; therefore, the capacitance of this device (620.4 F/g) is much higher than that for the CN device (53.6 F/g). After all the stored energy by redox reactions is released, the CaNCo/CNT electrode starts its faradaic decomposition, provoking a continuous release of charge and a constant output voltage as observed in Figure 4c. This leads to a battery-like behavior.
Electrochemical impedance measurements for the CN and CaNCo devices

The electrochemical impedance spectroscopy (EIS) was performed to understand the charge transfer process in the CN and CaNCo devices and to determine the resistance associated with the charge storage at the electrode/electrolyte interface. The Nyquist plots exhibit two parts: a straight line in the low-frequency region and a semi-circle in the high-frequency region. According to the literature [8, 9], the EIS curves can be fitted using an equivalent circuit (see inset) to obtain the serial resistance Rs (total cell resistance which includes electrodes, electrolyte, and contact resistance) and the charge transfer resistance \( R_{ct} \) (at the electrode/electrolyte interface). After fitting with the equivalent circuit, the calculated values for \((R_s, R_{ct})\) were: \((66.2 \, \Omega, 18.9 \, \Omega)\) and \((58.6 \, \Omega, 12.4 \, \Omega)\) for the CN, and CaNCo devices, respectively. As observed, the introduction of CaNCo perovskite in the CNT electrode decreased the internal series resistance from 66.2 \( \Omega \) to 58.3 \( \Omega \) and the charge transfer resistance from 18.9 \( \Omega \) to 12.4 \( \Omega \). The lower \( R_s \) and \( R_{ct} \) values of CaNCo device indicate that the ion transport through the electrolyte and ion diffusion from the electrolyte to the CNT electrode is faster in such a device. Those last effects also facilitated the ion storage in the CaNCo device, therefore, it presented \( \approx 10.57 \) times more capacitance than the CN device.

As a new device created, we can approach our future steps about how a new Super-Capacitive Device can be connected to LEC with Carbon Nano Tubes as a tandem:

(SC-CNT)—(CNT-LEC).

They will have a COMMON CNT electrode, connecting them in a monolithic structure.
1. incorporating the perovskite in the CNT anode electrode increased the capacitance and energy density of the devices ≈10.57 and ≈4.68 times,

2. The device made with perovskite microplates presented a longer discharge time (8900 s) compared to that made without the perovskite (950 s)

3. Device with CNT has capacitance and energy density 53.6 F/g and 16.7 Wh/Kg, while the device with perovskites has a better ones because it stores charge efficiently by the redox reactions of Ca, Nd, and Co elements

4. This last device had a capacitive component and a battery- like component, since it provided a stable output voltage for at least 800 minutes

5. The future work is a step to create a tandem Perov-LEC and Super Capacitor

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