

Li₄Ti₅O₁₂/poly(methyl)thiophene asymmetric hybrid electrochemical device

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Abstract

Electrochemically prepared poly(methyl)thiophene is characterized by cyclic voltammetry and galvanometry with an activated carbon counter-electrode. It is then used as a cathode in a laminated plastic asymmetric hybrid electrochemical device with a nano-structured Li₄Ti₅O₁₂ anode. This device displays the specific power of a supercapacitor, with a higher specific energy of 10 Wh/kg, and better cycle-life than a Li-ion battery. The matching ratio of the active materials was found to strongly influence cycle-life.

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1. Introduction

Electronically conducting polymers are theoretically considered a very promising material for building electrochemical supercapacitors [1–3]. Among those polymers, poly(methyl)thiophene (PMeT hereafter) has attracted special interest since the 1980s as a cathode for rechargeable batteries [4]. More recently, other substituted polythiophenes have been proposed as suitable active materials for supercapacitor electrodes [5]. This is mainly due to their high specific capacitance, fast doping–dedoping kinetics, and their ability to undergo both n- and p-doping, making them usable in a symmetric configuration. However, differences in specific capacitance, cycle-life and doping kinetics of the n- and p-doping processes have made these devices difficult to balance and unstable upon cycling. To improve the n-doping, electron withdrawing substitution on the monomer has been proposed, and interesting poly-3-arylthiophenes such as poly(fluoro)phenylthiophene have been identified [6]. Although the n-doping was still not stable enough, it has been found that these substitutions also improved the p-doping process, and resulted in a better stability and higher doping levels than polythiophene. In order to reduce cost, improve cycle-life, and still benefit from the higher energy and power yielded by a conducting polymer cathode, alternative

anodes have been proposed too. In particular, activated carbon [7] and nano-structured lithium titanate oxide [8] have been used with a poly(fluoro)phenylthiophene cathode. However, two drawbacks still remain to be overcome with poly(fluoro)phenylthiophene: lower cycle-life and higher cost than activated carbon. For instance, the synthesis of poly(fluoro)phenylthiophene is a two step reaction: preparation of the monomer by coupling of bromo-thiophene with phenyl magnesium, followed by chemical or electrochemical polymerization of the monomer [9]. This is a concern for the cost of the polymer, and the risk of having bromide impurities. By contrast, PMeT of high quality can be directly prepared by electrochemical synthesis of the inexpensive monomer, yielding a lower cost and higher purity polymer. Such a polymer has been used with success with an activated carbon anode [10]. On the other hand, a nano-structured Li₄Ti₅O₁₂ anode has also been successfully coupled with an activated carbon cathode, leading to the so-called nonaqueous asymmetric hybrid supercapacitors. Those devices have demonstrated a packaged specific energy of 11 Wh/kg, a specific power of 800 W/kg at 95% efficiency, and a cycle-life comparable to carbon–carbon supercapacitors [11].

The objective of the present paper is to study the coupling of a PMeT cathode with a nano-structured Li₄Ti₅O₁₂ anode. First, the electrochemical evaluation of the polymer was performed according to the literature against an excess of activated carbon anode, in a three-electrode cell using PC-NEt₄BF₄ electrolyte. Then, laminated devices

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were fabricated and tested with a limited amount of acetonitrile, LiBF₄ 2 M electrolyte. In particular, the specific energy, specific power and cycle-life of a packaged prototype using a Li₄Ti₅O₁₂ anode and PMeT cathode are evaluated.

2. Experimental

2.1. Polymer synthesis

Electrochemical synthesis of PMeT was carried out with an expanded Ti-platinized cylindrical working-electrode (114 cm²) in a cell with two separated compartments in a 0.5 M NEt₄BF₄ in acetonitrile solution plus 1 M 3-methylthiophene in the working-electrode compartment (cf. Fig. 1). The separator was not porous to avoid contamination of the working-electrode compartment by species resulting of acetonitrile reduction that occurs on the counter-electrode during the experiment. All experiments were carried out under an argon atmosphere.

Monomer oxidation was performed under galvanostatic conditions, with $I = 7.5 \text{ mA/cm}^2$. The reaction yield was close to 81%. The dendritic polymer obtained was ground into a very thin powder and washed with methanol using soxhlet extraction for 3 days.

The synthesis provided around 70 g of pure polymer.

2.2. Polymer testing

Four centimeter square polymer electrodes were prepared by mixing the PMeT powder with an electronic conductor (acetylene black AB) and organic binders (3% CMC/2% PTFE mixture). The active material paste was then laminated onto a pre-treated aluminum current collector. The treatment consists in a conductive paint thin film deposition in order to

avoid aluminum re-passivation and to decrease the contact resistance between the active materials and the collector.

Cyclic voltammetry and galvanostatic cycling tests were performed in a three-electrode cell with an activated carbon-based composite electrode as counter-electrode. The reference electrode was a Ag⁺/Ag 10⁻² M in acetonitrile; all the potentials were reported against Li⁺/Li. The separator was made of PTFE (two sheets, each 25 μm thick, 80% porosity).

All cells were assembled in a MBraun glove box (oxygen and water content <1 ppm) and placed in a sealed plexiglass box ensuring air tightness; cells were then tested by cyclic voltammetry using a PARC EG&G Model 273 A potentiostat controlled by a computer with M270 software. Constant current experiments were carried out using a Biologic VMP multipotentiostat.

3. Results

3.1. Powder physico-chemical characteristics

The PMeT as obtained was a brown powder. This is the color of the oxidized form of PMeT, which is red in thin films, and blue in its reduced form. The PMeT powder was tested for density and conductivity. For these measurements, a special piston and cylinder cell was designed. It allowed a cylinder of PMeT powder to compress between two copper electrodes, while measuring its volume and electrical resistance. By using a constant weight of 1 g powder, the density was calculated as the inverse of the cylinder volume until the maximum compression was achieved. For several piston heights h , the carbon resistivity was calculated as:

$$\sigma = R \times \frac{S}{h}, \quad \text{with } S = \text{surface of cylinder base}$$

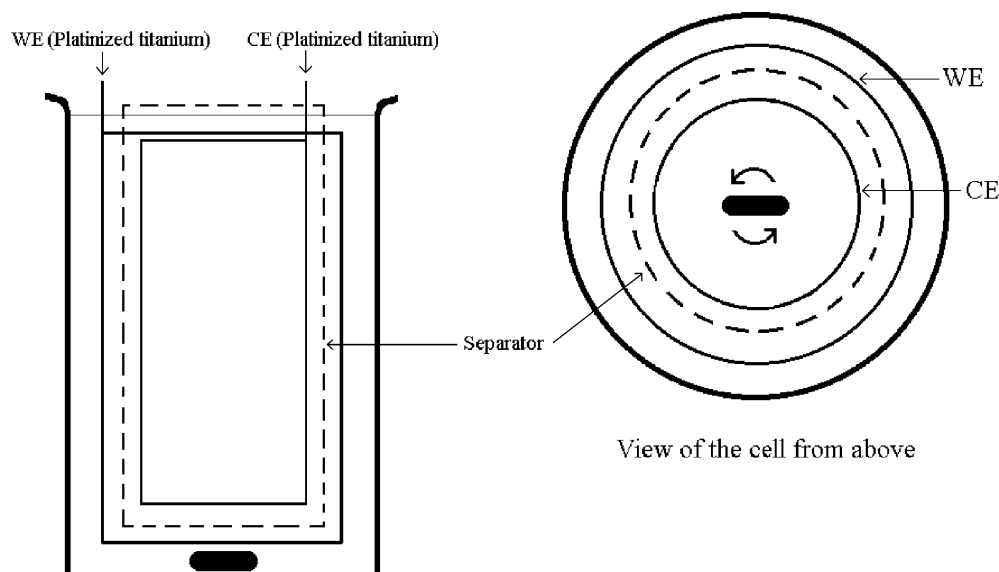


Fig. 1. Scheme of the PMeT electro-synthesis cell.

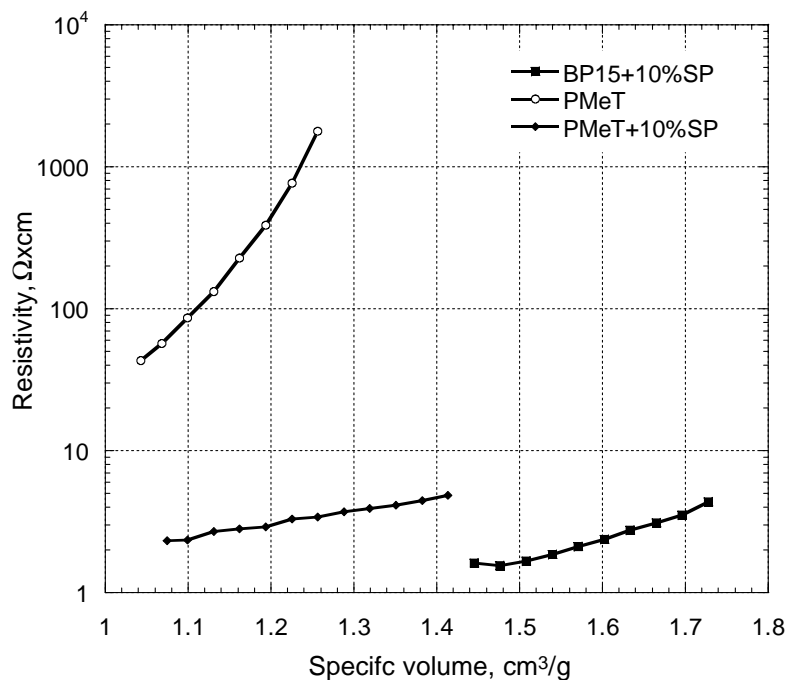


Fig. 2. Specific resistivity vs. specific volume curves for PMeT with and without 10% carbon black and activated carbon with 10% carbon black.

Using this method, the compressed PMeT powder was found to have a resistivity of $43 \Omega \text{ cm}$, for a specific volume of $1.04 \text{ cm}^3/\text{g}$. In order to prevent large swings in electrode resistivity during the doping and dedoping processes and increase overall electrode conductivity, 10% ‘SuperP’ (Erachem, Europe) conductive carbon black was mixed with the PMeT powder. With these conditions, the specific volume slightly increased to $1.07 \text{ cm}^3/\text{g}$, but the powder resistivity dropped to $2.24 \Omega \text{ cm}$. For comparison, a similar mixture of supercapacitor grade activated carbon ‘BP15’ (Kuraray,

Japan) with 10% ‘SuperP’ had a resistivity of $1.53 \Omega \text{ cm}$ and a specific volume of $1.47 \text{ cm}^3/\text{g}$ (Fig. 2).

3.2. Cyclic voltammetry of PMeT with *p*-doping at a low polymer-content

Fig. 3 shows the voltamogram of a 4 cm^2 composite polymer electrode with 30% PMeT, 65% AB and 5% binders (3% CMC, 2% PTFE). The electrolyte used was a 1 M NEt_4BF_4 in propylene carbonate solution. The *p*-doping

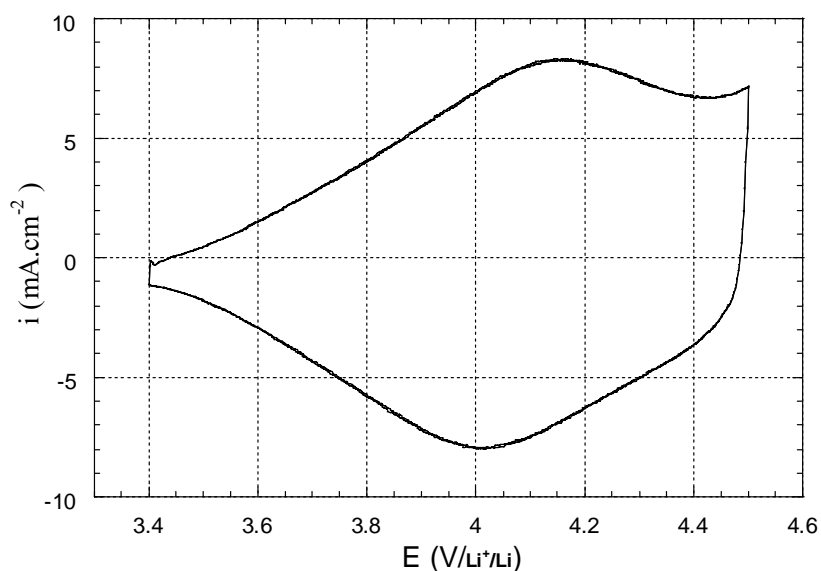


Fig. 3. Cyclic voltamogram of a 4 cm^2 PMeT composite electrode in a 1 M NEt_4BF_4 in propylene carbonate solution; scan rate = 20 mV/s , $m_{\text{PMeT}} = 6.4 \text{ mg}$. Electrode composition: 30% PMeT, 65% AB, 5% PTFE/CMC. Current collectors: treated-aluminum.

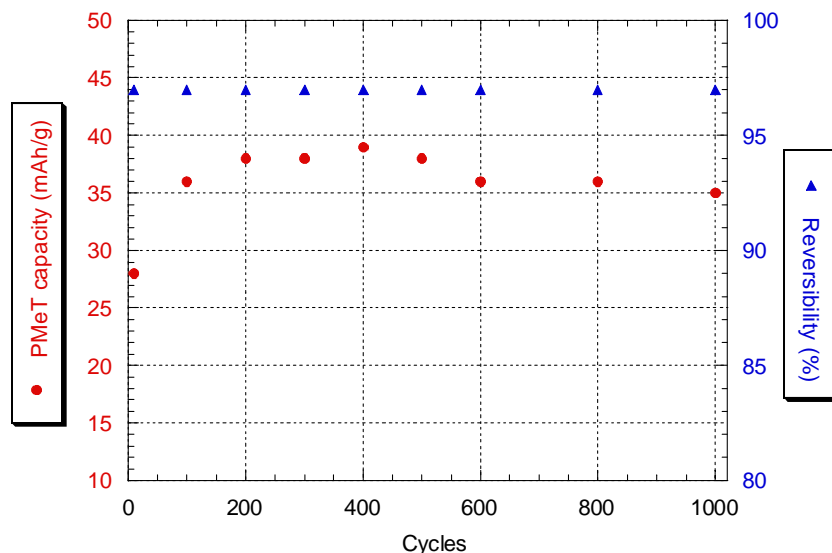


Fig. 4. PMeT p-doping capacity and reversibility in a 1 M NEt_4BF_4 in PC electrolyte. Electrode composition: 80% PMeT, 15% NA, 5% CMC/PTFE. Current collector: treated aluminum.

process starts around 0 V/Ref and increases up to 0.5 V/Ref; it corresponds to an electron extraction from the polymer. Polymer p-doping is achieved at 0.9 V/Ref, and electrolyte oxidation occurs at higher potentials. On the reverse scan, the undoping peak can be seen at 0.4 V/Ref; the polymer is fully undoped at -0.2 V/Ref. The specific capacity of the polymer calculated from the voltamogram by current integration was found to be 48 mA h/g, obtained with a 97% coulombic efficiency ($Q_{\text{dedoping}}/Q_{\text{doping}}$).

3.3. Electrochemical behavior of the PMeT with cycling

Fig. 4 shows the cycleability and coulombic efficiency of a PMeT electrode when cycled between -1.0 and $+1.0$ V/Ref at 20 mV/s. An activation step can be observed: the capacity discharged initially is about 28 mA h/g and increases to 38 mA h/g along the 200th first cycles. This step is explained by the increase of electronic conductivity inside the electrode in the 200th first cycles, leading to an increasing amount of polymer participating in the doping process. However, the electronic percolation inside the electrode is never optimized, as the maximum polymer capacity obtained is 39 mA h/g instead of the 48 mA h/g expected.

The capacity remains approximately constant from the 600th to the 1000th cycle. These results are in good agreement with the results of Mastragostino et al., who described such stability for PMeT electrodes in NEt_4BF_4 1 M in PC. The p-doping reversibility was found to be constant to 97%, showing the absence of an irreversible degradation process.

3.4. Galvanostatic cycling of the PMeT high-content composite electrode

Fig. 5 presents the galvanostatic cycles of a PMeT composite electrode in a three-electrode cell. An activated

carbon-based electrode was used as a counter-electrode. As previously observed in cyclic voltammetry, the doping process takes place from 3.4 to 4.6 V/Li.

PMeT capacity was 40 mA h/g at the beginning of cycling, and reached a pseudocapacitance of 270 F/g.

Fig. 6 presents the polymer capacity changes during cycling. The stability of the polymer during cycling is once again demonstrated. Experiments were not run over more than 1000 cycles as it is difficult to ensure good air tightness (and then to maintain a low water and oxygen content) after more than 4 days of cycling, which is not the case for the laminated devices.

3.5. Power and energy density of laminated devices

Hybrid cells were assembled by hot-lamination of plastic battery technology-based electrodes onto aluminum grids. Such electrodes were prepared by doctor-blade casting of a mixture of the active material powder, carbon black, PVDF-HFP binder, propylene carbonate and acetone. Active material content in the electrodes was 70 wt.%. The electrode-current collector assemblies were further hot laminated on to a microporous polyolefin-based separator. Typical test-cells were 5 cm \times 3.2 cm laminates packaged in a multifoil PE/Al/Surlin material. The electrolyte used to activate the cells was CH_3CN , LiBF_4 2 M, which has a ionic conductivity of 17 mS/cm, while being stable at the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode potential. Three weight matching ratios of the positive to negative active materials were tested: 2.1, 3.5 and 4.8.

Fig. 7 is the discharge voltage profile of LTO/PMeT and LTO/C cells at slow rate, and full utilization of the positive electrodes. By knowing the specific volume and weight of the active materials in the cathodes, we plotted the voltage profiles as function of volumetric energy of the powders.

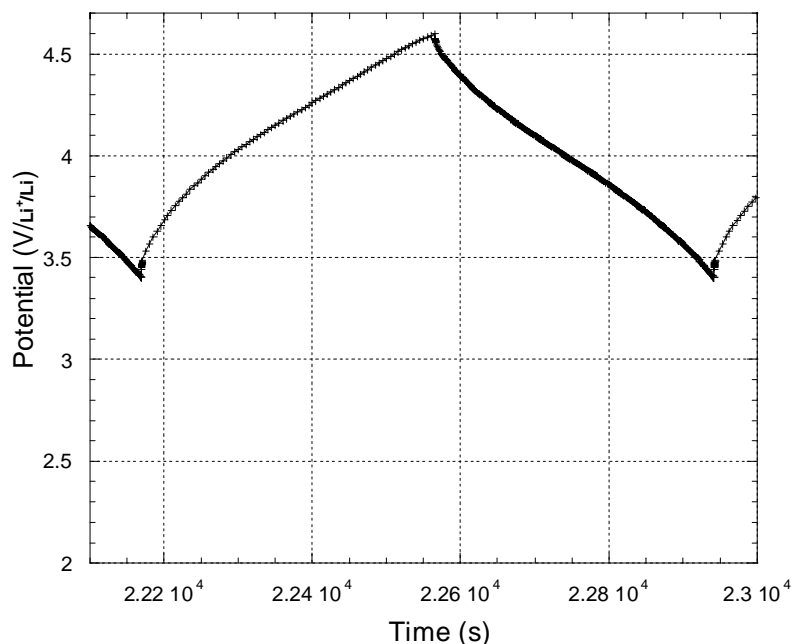


Fig. 5. Galvanostatic cycle of a 4 cm² PMeT composite electrode in a 1 M NEt₄BF₄ in propylene carbonate solution; $I = \pm 5$ mA/cm², $m_{\text{PMeT}} = 34.6$ mg. Electrode composition: 80% PMeT, 15% AB, 5% PTFE/CMC. Current collectors: treated-aluminum.

We found around 40 mWh/cm³ for the activated carbon, and 95 mWh/cm³ for the PMeT. This illustrates the volumetric advantage of PMeT. The energy versus power ‘Ragone plot’ of the devices was measured and is shown in Fig. 8. As expected, we found decreased energy and power at higher matching ratio (excess PMeT). The packaged devices attained 10 Wh/kg at 200 W/kg, and 8 Wh/kg at 1000 W/kg. Those are not optimal numbers due to the large (40%) weight

fraction of packaging material in those prototypes. With 20 wt.% of packaging material, the maximum energy would be 14 Wh/kg (Fig. 9).

3.6. Cycle-life of the laminated devices

The three cells of various matching ratio were cycled galvanostatically between 3.0 and 1.5 V, with a current density

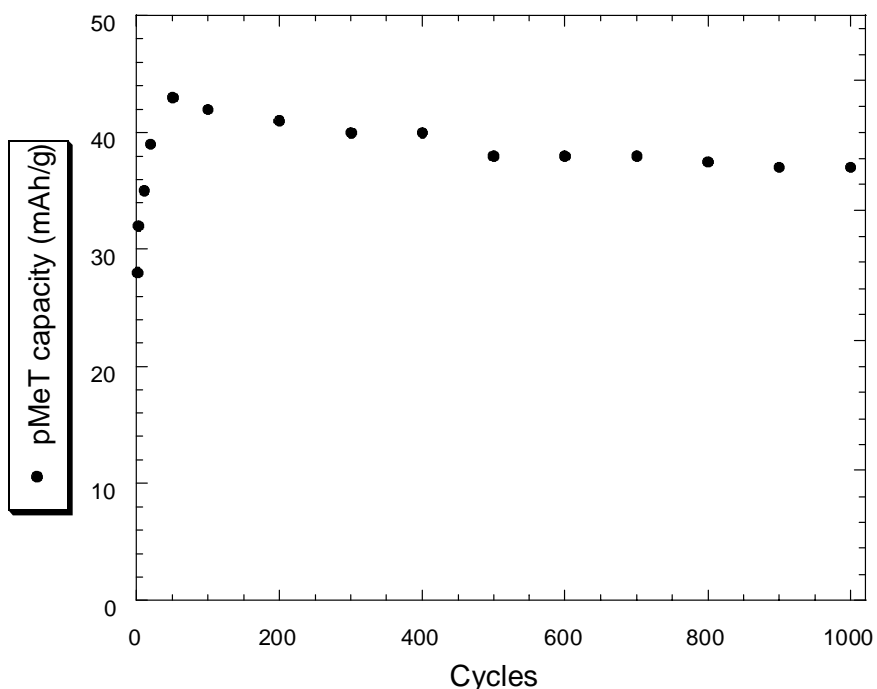


Fig. 6. Polymer capacity evolution during galvanostatic cycling at ± 5 mA/cm² in a 1 M NEt₄BF₄ in PC electrolyte. Current collector: treated aluminum.

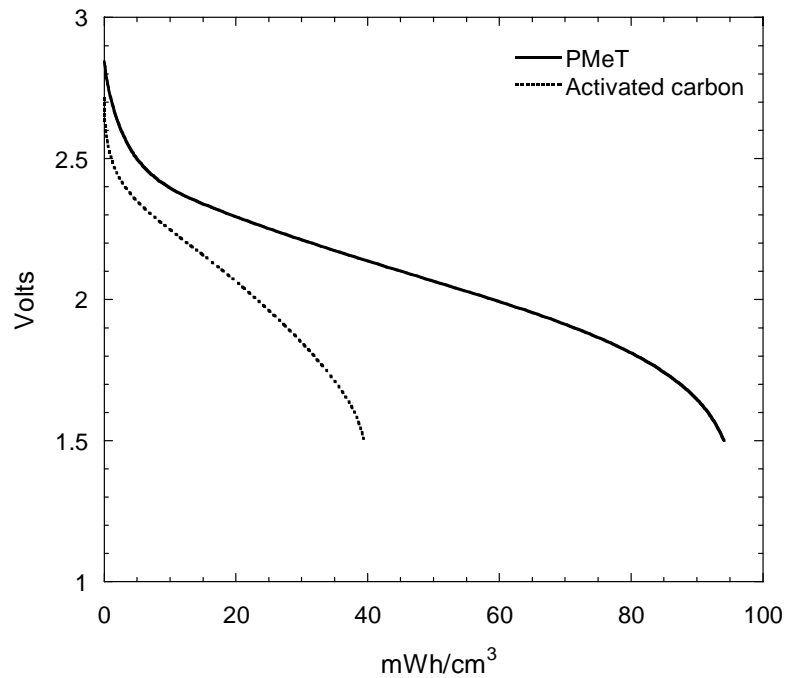


Fig. 7. Discharge voltage vs. volumetric energy of activated carbon Kuararay BP15 and PMeT powders.

of 7 mA/cm^2 for the charges, 20 mA/cm^2 for the discharges ($\sim 60^\circ\text{C}$). We followed the specific capacity changes for the PMeT in the electrodes. The cell with a matching ratio of 2.1 had a full utilization of the PMeT, with an initial capacity of 55 mAh/g . However, the capacity gradually decreased during cycling to reach 28 mAh/g after 10,000 cycles. The

two other cells, of matching ratio 3.5 and 4.8, had respective initial capacities of 38 and 27 mAh/g . In both cases, there was an initial drop of capacity over the first 200 cycles, but they reached stable values of respectively 25 and 17 mAh/g over 7000 and 8000 cycles (Fig. 10). Thus, it appears that when the PMeT is fully utilized, it displays a higher

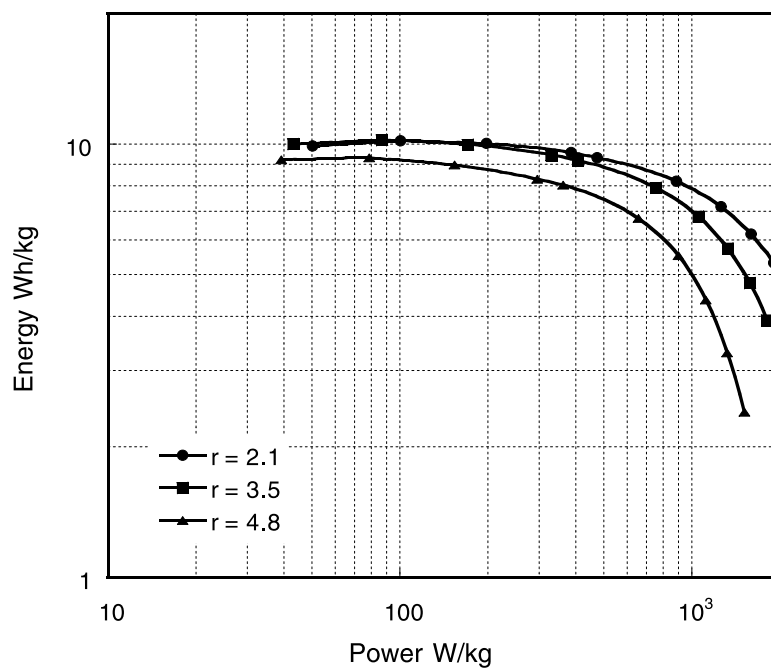


Fig. 8. Ragone plots of laminated $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{PMeT}$ prismatic devices of $63 \text{ mm} \times 48 \text{ mm}$ footprint, for three weight matching ratios of the active materials.

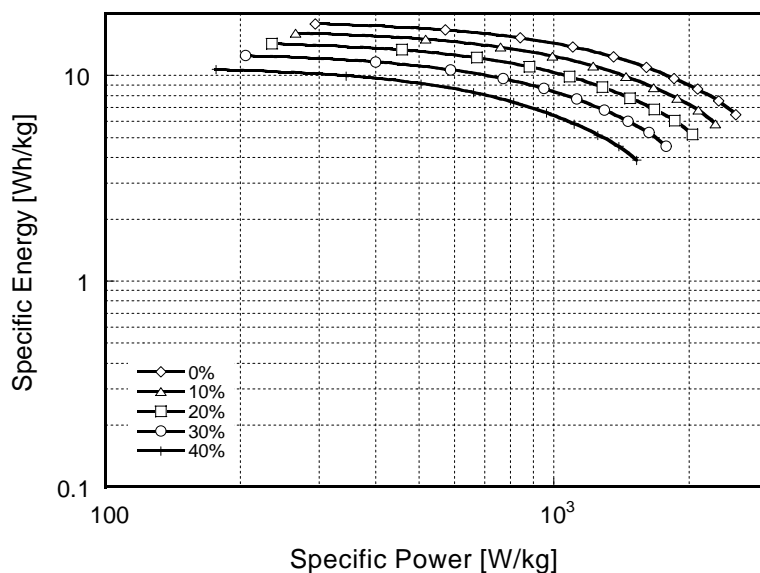


Fig. 9. Effect of the packaging weight fraction on the Ragone plot of a laminated $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{PMeT}$ prismatic device of $63 \text{ mm} \times 48 \text{ mm}$ footprint area.

capacity fade. In the present case, this was due to low matching ratio (e.g. an excess LTO). It could also have been due to a too high charge cutoff voltage. In both cases, it seems that the capacity fade is due to overoxidation of the PMeT, which probably degrades the conjugated backbone. We can also assume that lower molecular weight oligomers are most sensitive to oxidation, and are degraded first, explaining the initial capacity fade. Therefore, it is preferable to have a polythiophene free of oligomers.

3.7. Impedance changes with cycling and state of charge

Impedance diagrams were recorded between 10 kHz and 0.1 Hz, and plotted as Nyquist plots for the initial non-charged LTO/PMeT cell and for the same cell after 7000 cycles at various states of charge: 0–1.0–1.2–2.0–2.7 V (Fig. 11). For the non-charged cells, the vertical double-layer capacitance of blocking electrodes is observed. After cycling, the impedance plots are shifted to the right, indicating

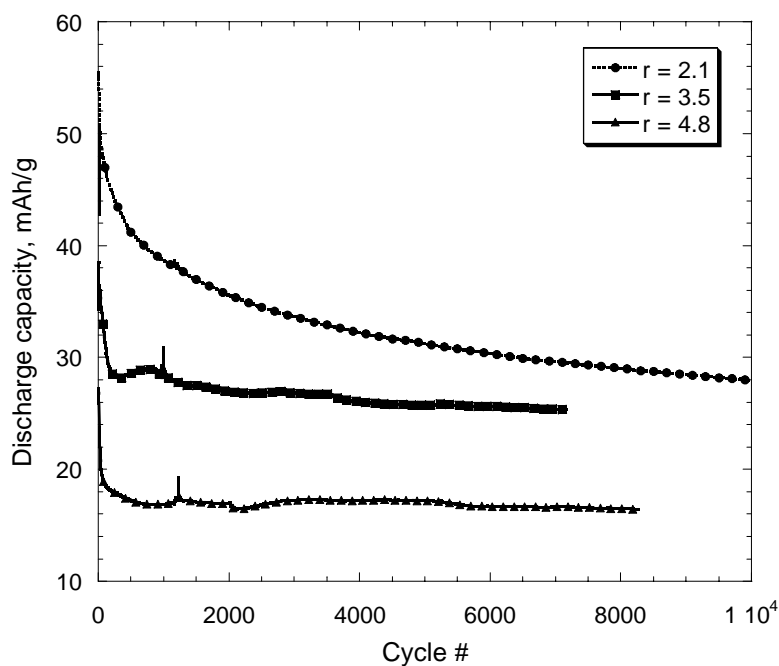


Fig. 10. Specific discharge capacity vs. cycle number of PMeT in laminated $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{PMeT}$ prismatic devices of $63 \text{ mm} \times 48 \text{ mm}$ footprint, for three weight matching ratio of the active materials.

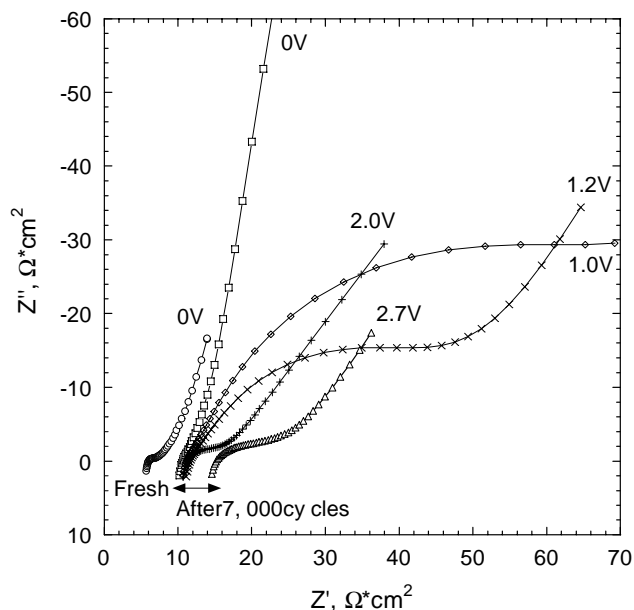


Fig. 11. Nyquist plots recorded from 10 kHz to 0.1 Hz for LTO/PMeT cell with matching ratio 3.5, fresh and after 7000 cycles at various states of charge.

an increase in electrodes resistivity. When charging the cell, a large charge-transfer resistance semi-circle appears, indicating the occurrence of a faradic process. The diameter of the semi-circle decreases during charge (1.2–2.0 V), indicating that the resistance in the electrodes decreases, mostly because of the doping of PMeT. At full charge (2.7 V), the high-frequency impedance is increased. We attribute this to the ionic depletion in the electrolyte due to doping of the BF_4^- anions into PMeT and insertion of Li^+ cations into the LTO, resulting in lower ionic conductivity. During discharge, the high frequency impedance shifts back to its original value, indicating a replenishment of ions in the electrolyte.

4. Conclusion

We confirmed the good cycle-life and superior volumetric and gravimetric energy content of PMeT compared to

activated carbon. The use of a nano-LTO anode did not appear to impact cycle-life, confirming the exceptional cycling characteristics of lithium titanate. However, when fully utilized, PMeT displays a somewhat high capacity fade by supercapacitor standards. Increased cycle-life can be obtained when PMeT utilization is limited to ca 35 mAh/g by either the matching ratio or the maximum cut-off voltage. This partially offsets the gravimetric capacity advantage of PMeT, but the volumetric advantage is still significant. We see a possibility of improvement in cycling characteristics by having a high molecular weight polymer free of oligomers and impurities. However, the main difficulty resides in the fact that poly(methyl)thiophene is insoluble, and therefore, the molecular weight distribution cannot be measured by steric exclusion chromatography. To some extent, the cyclic voltammetry shape can be related to the conjugation length, but more studies are needed to correlate molecular weight to cycling characteristics.

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