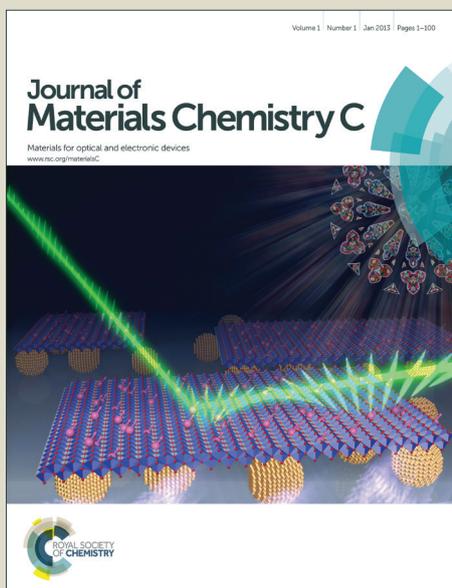


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TransCap: a monolithically integrated supercapacitor and electrolyte-gated transistor

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We report the proof-of-concept of the TransCap, a monolithically integrated device that exhibits the storage properties of a supercapacitor and the low-voltage operation of an electrolyte-gated transistor. The proof-of-concept is based on coupling a polymer channel with a high surface area carbon gate, employing an ionic liquid as the electrolyte. The possibility to recover the stored energy from the TransCap permits to use it to power different microelectronic components.

The increasing demand of energy autonomy for portable electronics is triggering intensive research efforts towards the development of self-powered, sustainable electronic devices.¹⁻³ Within this context, the coupling of electronic devices (sensors, transistors, etc.) with energy harvesters and small size energy storage systems (e.g. micro-batteries or micro-supercapacitors) is actively pursued.²

For their low-voltage operation characteristics, electrolyte-gated (EG) transistors are attractive candidates to be coupled to energy harvester/storage microsystems.⁴⁻¹¹ EG transistors make use of electrolytes, such as polymer electrolytes, ionic liquids and ion gels, to replace conventional gate dielectrics. Ionic liquids are particularly attractive since they are available in a wide range of different molecular structures and chemico-physical properties, thus offering the possibility to specifically control the interactions between the ions and the transistor channel, in view of an optimized doping.¹²⁻¹⁵ The working principle of EG transistors is based on the high capacitance of the electrical double layer at the electrolyte/transistor channel interface. Different doping mechanisms, including electrostatic and Faradaic, have been proposed to explain the gating process. Polymer channel materials are typically characterized by Faradic doping.

A large number of channel materials have been applied to EG transistors, including organic single crystals, organic thin films of small molecules and polymers,^{9,16-22} thin films of metal oxides,^{6,11,23-26} InN,²⁷ CdSe,²⁸ and PbSe.²⁹ EG transistors are intensively investigated because they permit current modulations of several orders of magnitude, upon application of relatively low gate voltages. Low-voltage operation is achieved by exploiting the exceptionally high capacitance of the electrical double layer forming at the electrolyte/transistor channel interface. High electrode capacitances are also exploited for charge and energy storage in electrochemical supercapacitors. Supercapacitors are high specific power systems that, for their capability to

store/deliver charge in relatively short times (a few seconds), may outperform batteries in applications having high peak-to-average power demand. Different classes of supercapacitors making use of electrodes with different nature have been demonstrated. The most common supercapacitors are electrochemical double layer capacitors that use high surface area carbon electrodes, which store/deliver charge by an electrostatic process. Pseudo-supercapacitors feature battery-like electrodes (electronically conducting polymers, metal oxides) that are charged/discharged by fast and reversible redox processes. Hybrid supercapacitors feature positive and negative electrode materials of different nature that are charged/discharged via different electrostatic and faradaic modes.³⁰⁻³³

Here we report for the first time a monolithically integrated Transistor and superCapacitor (TransCap), where the typical function of a transistor is coupled with the energy storage function of a supercapacitor, within the same EG transistor structure. The proof-of-concept of the TransCap is based on coupling a polymer channel with a high surface area carbon gate, employing an ionic liquid as the electrolyte. The p-doping that brings the polymer channel from the insulating to the conducting state is a pseudocapacitive charging process.^{30,31} The high surface area gate electrode supplies the charge required to dope the transistor polymer channel by a fast, highly reversible, electrostatic process, referred to as double layer charging process, that is at the basis of the energy storage process in conventional electrochemical double layer supercapacitors. The use of a high surface area carbon gate electrode featuring a high double layer specific capacitance and employing an excess mass of carbon with respect to the amount required to balance the doping charge of the polymer is a valuable approach for an effective doping of the polymer channel.⁸

The polymer/electrolyte/carbon stacking of the EG transistor features the cell configuration of a hybrid supercapacitor, where the negative carbon electrode and the positive polymer electrode are charged by an electrostatic and a faradic process, respectively. When the TransCap is ON, the polymer transistor channel is open. The p-doped polymer and negatively polarized carbon gate electrode are storing the charge (Q) at a given gate-source voltage (V_{gs}), hence the system is storing energy (equal to $Q \cdot V_{gs}$). When the TransCap is switched OFF, the channel and the gate are discharged and the delivered energy can be used for subsequent operation of the EG transistor itself or to power other components in the electronic system. The characteristics of the TransCap have similarities with those of floating gate transistor devices.

Specifically, we report a TransCap making use, as the channel material, of a thin film of the organic electronic polymer MEH-PPV, poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene], deposited on top of a SiO₂ substrate pre-patterned with gold drain and source electrodes (Fig. 1 and Electronic Supplementary Information, ESI). A high surface area carbon electrode (Brunauer-Emmett-Teller, BET, specific surface area of 1850 m²/g) was used as the gate electrode. The room temperature ionic liquid N-trimethyl-N-propylammonium bis(trifluoromethanesulfonyl) imide ([N₁₁₁₃][TFSI]), exhibiting remarkable electrochemical stability, was used as the gating medium.

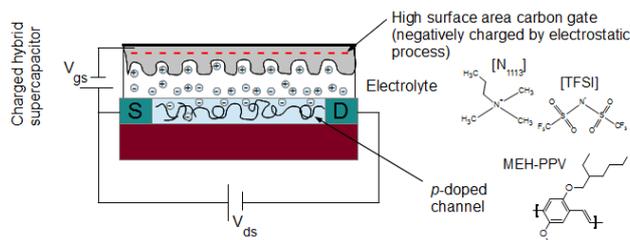


Fig. 1. Device structure and working principle of the TransCap, whose proof-of-principle is proposed in this work. The drain (D) and source (S) electrodes and the p-doped MEH-PPV polymer channel are stacked with the electrolyte and the high surface area carbon gate. The polymer/electrolyte/carbon stacking features the cell configuration of a hybrid supercapacitor.

We initially performed the transistor characterization of the [N₁₁₁₃][TFSI]-gated MEH-PPV TransCap. The output (drain-source current, I_{ds} , vs drain-source voltage, V_{ds}) and the transfer (I_{ds} vs V_{gs}) characteristics of the TransCap (Figs. 2a and 2b) demonstrate the p-type transistor operation. In the output curves, we observe that the saturation regime is achieved at ca 0.25 V. The transistor ON/OFF ratio, calculated between $V_{gs} = -0.8$ V (ON state) and $V_{gs} = 0$ V (OFF state) at $V_{ds} = -0.3$ V, is about 2×10^3 (Fig. S1, ESI). The hole mobility, determined from the transfer linear characteristics is 2×10^{-2} cm²·V⁻¹·s⁻¹. The hysteresis of the transistor current observed in the transfer curve (Fig. 2b) originates from ion diffusion during the doping and dedoping processes, in turn affecting the device response time.³⁴

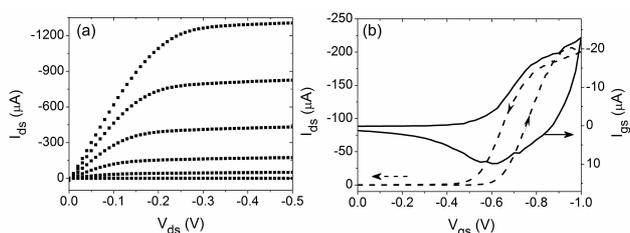


Fig. 2. Transistor characteristics of the [N₁₁₁₃][TFSI]-gated MEH-PPV TransCap: (a) output characteristics ($V_{gs} = 0, -0.6, -0.65, -0.7, -0.75$ and -0.8 V) and (b) transfer characteristics in the linear regime ($V_{ds} = -25$ mV) for a V_{gs} sweeping rate of 10 mV s⁻¹: I_{ds} on the left axis, dashed line, and I_{gs} on the right axis, solid line (please note that 0 V $\leq V_{gs} \leq -0.6$ V do not significantly affect the transistor current).

Upon application of V_{gs} , we observed that I_{gs} decreases within 1 s whereas I_{ds} approaches its plateau value after ca 4 s (Fig. 3). This

suggests that the transistor response time depends on two processes: the penetration of ions from the electrolyte in the polymer, which affects I_{gs} vs time, and the p-doping process in the polymer, which affects I_{ds} vs time.³³ While both the processes are affected by the [N₁₁₁₃][TFSI] ionic conductivity,³³⁻³⁵ they have different rates, with the former being the fastest. This result is not surprising if we consider that the MEH-PPV/[N₁₁₁₃][TFSI]/carbon gate stacking has a similar configuration of a hybrid supercapacitor, which typically exhibits a relatively fast response time.²

The energy used to bring the transistor to the ON state (E_{ON}) and stored in the TransCap is given by the integration of I_{gs} over time multiplied by the value of V_{gs} (0.8 V); this value is of 53 μ J (Fig. 3). Such energy is then delivered upon switch OFF (E_{OFF} , calculated from the integration of I_{gs} over time during the switch off multiplied by 0.8 V) with an efficiency ($E_{ON}/E_{OFF} \cdot 100$) of 99.5% , due to the energy storage capability of the TransCap and the reversibility of the charging/discharging processes at the electrodes.

In our TransCap, where the carbon gate mass is in large excess with respect to that of the polymer (see ESI), the electrochemical response is mainly affected by the polymer doping/dedoping processes.

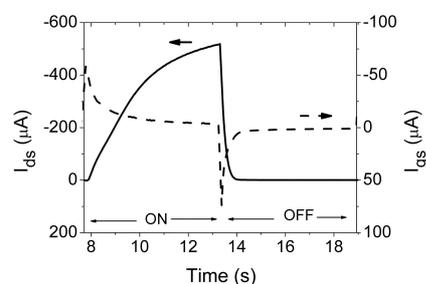


Fig. 3. Switch ON and OFF of the [N₁₁₁₃][TFSI]-gated MEH-PPV TransCap. I_{ds} (left axis) and I_{gs} (right axis) vs time for a switch ON at $V_{gs} = -800$ mV and switch OFF at $V_{gs} = 0$ V. $V_{ds} = -300$ mV. Data taken during a sequential type of acquisition (5.5 s TransCap ON followed by 5.5 s TransCap OFF): during the first 8 s, $V_{ds} = -300$ mV and $V_{gs} = 0$ V.

To characterize the supercapacitor characteristics of the TransCap, we used the polymer transistor channel together with the drain and source electrodes as the positive electrode and the high surface area carbon gate as the negative electrode. Therefore, the supercapacitor cell voltage, V_{cell} , corresponds to $-V_{gs}$. We performed galvanostatically charge/discharge cycles (Fig. 4a) at a current $I = \pm 10$ μ A (where $I = -I_{gs}$) up to 0.8 V, a cut-off cell voltage selected in agreement with the results reported in Fig. 2b. The capacitance (C) obtained by the slope of the discharge voltage profiles ($C = I \int dt/dV_{cell}$) is 0.16 mF. The delivered energy, E , and power, P , were calculated from the galvanostatic discharge curve using Eqs. (1) and (2):

$$E = I \int V_{cell}(t) \cdot dt \quad \text{Eq. (1)}$$

$$P = \frac{E}{\Delta t} \quad \text{Eq. (2)}$$

where Δt is the discharge time. E and P are 27.4 μ J and 4.6 μ W, respectively. The capacitance, energy and power normalized to the TransCap electrode geometric area (0.36 cm²) are 0.44

$\text{mF}\cdot\text{cm}^{-2}$, $0.02\ \mu\text{Wh}\cdot\text{cm}^{-2}$, $13\ \mu\text{W}\cdot\text{cm}^{-2}$. These values are of interest for energy autonomous electronic devices.²

Figure 4a shows that the storage capability of the TransCap permits to keep the transistor channel open even when the transistor is not connected to a power supply. This storage capability can be affected by the presence of leakage currents, resulting in discharging of the device. The leakage currents and discharge were therefore investigated using the following protocol: galvanostatic charge at $10\ \mu\text{A}$, up to a cut-off cell voltage value of $0.8\ \text{V}$; voltage of $0.8\ \text{V}$ held over $10\ \text{s}$; rest step ($I = 0\ \text{A}$) over $30\ \text{s}$; discharge at a constant current of $-10\ \mu\text{A}$ (Fig. 4b). The leakage current during the step at $0.8\ \text{V}$ reaches $3.5\ \mu\text{A}$ after $10\ \text{s}$, thus indicating that the energy consumption to keep the TransCap in the ON state at $0.8\ \text{V}$ is not negligible (ca $0.43\ \mu\text{J}$). These values have to be taken into account if the TransCap is coupled to energy harvester systems that operate at low energy levels. On the other hand, the voltage behaviour over time during the rest step shows that the supercapacitor can keep its state of charge within a voltage drop of $1.4\ \%$ after $0.2\ \text{s}$ (high resolution plot not shown here). After $30\ \text{s}$, the voltage decreases by 30% of its initial value. This result suggests that the TransCap can operate without being connected to an electric grid for relatively short times and that the transistor channel is still open (doped) at relatively long times. Any TransCap switch OFF following the rest step will provide an energy recovery with an efficiency depending on the duration of the previous rest step. The capability of the TransCap to store charge at the polymer/electrolyte/carbon interface holds promise for applications in the electronic industry, such as in displays where the transient switching of the display pixel is desired.

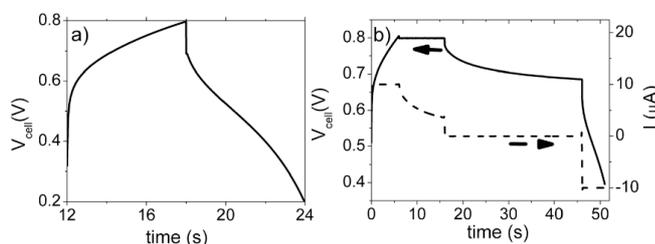


Fig. 4. Supercapacitor characteristics of the $[\text{N}_{1113}][\text{TFSI}]$ -gated MEH-PPV TransCap: (a) voltage profile vs time when the device is galvanostatically charged/discharged at $\pm 10\ \mu\text{A}$ up to $0.8\ \text{V}$ (data taken during the second cycle of a sequential type of acquisition: $6\ \text{s}$ TransCap ON followed by $6\ \text{s}$ TransCap OFF); (b) voltage (left axis) and current (right axis) vs time upon galvanostatic charging at $10\ \mu\text{A}$ up to $0.8\ \text{V}$, followed by $10\ \text{s}$ at $0.8\ \text{V}$, $30\ \text{s}$ rest in open circuit conditions, and galvanostatic discharge at $-10\ \mu\text{A}$.

Conclusions

We report the proof-of-concept of the TransCap, a multifunctional monolithically-integrated device that combines the characteristics of an electrolyte-gated transistor and a micro-supercapacitor. The charge storage capability of the TransCap,

similar to that of a floating gate transistor design, opens the possibility to use the TransCap in memory (latch) applications. The possibility to recover energy from the TransCap permits to use the stored energy to subsequently power different microelectronic components. Remarkably, for the proof-of-concept of the TransCap we used materials such as carbon and organic electronic polymers that exhibit suitable processability characteristics for portable, low-cost, flexible electronics on plastic substrates.

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- †Electronic Supplementary Information (ESI) available: [Fig. S1: Transistor transfer characteristics of the $[\text{N}_{1113}][\text{TFSI}]$ -gated MEH-PPV TransCap in saturation. Experimental details on: polymer thin film deposition; ionic liquid purification; device fabrication; TransCap electrochemical and electrical characterization]. See DOI: 10.1039/c000000x/
1. B. K. Bose, *IEEE Ind. Electron. Mag.*, 2010, **4**, 6–17.
2. M. Beidaghi and Y. Gogotsi, *Energy Environ. Sci.*, 2014, **7**, 867–884.
3. Z. L. Wang, *Adv. Funct. Mater.*, 2008, **18**, 3553–3567.
4. S. H. Kim, K. Hong, W. Xie, K. H. Lee, S. Zhang, T. P. Lodge and C. D. Frisbie, *Adv. Mater. Weinheim*, 2013, **25**, 1822–1846.
5. G. Tarabella, F. M. Mohammadi, N. Coppedè, F. Barbero, S. Iannotta, C. Santato and F. Cicoira, *Chem. Sci.*, 2013, **4**, 1395–1409.
6. B. Nasr, Z. Zhao-Karger, D. Wang, R. Kruk, H. Hahn and S. Dasgupta, *J. Mater. Chem. C*, 2013, **1**, 2534–2539.
7. P. Andersson Ersman, D. Nilsson, J. Kawahara, G. Gustafsson and M. Berggren, *Org. Electron.*, 2013, **14**, 1276–1280.
8. J. Sayago, F. Soavi, Y. Sivalingam, F. Cicoira and C. Santato, *J. Mater. Chem. C*, 2014, **2**, 5690–5694.
9. F. Cicoira, M. Sessolo, O. Yaghmazadeh, J. A. DeFranco, S. Y. Yang and G. G. Malliaras, *Adv. Mater.*, 2010, **22**, 1012–1016.
10. A. Campana, T. Cramer, D. T. Simon, M. Berggren and F. Biscarini, *Adv. Mater.*, 2014, **26**, 3874–3878.
11. H. Yuan, H. Shimotani, J. Ye, S. Yoon, H. Aliah, A. Tsukazaki, M. Kawasaki and Y. Iwasa, *J. Am. Chem. Soc.*, 2010, **132**, 18402–18407.
12. D. De Tullio, M. Magliulo, G. Colafemmina, K. Manoli, L. Torsi and G. Palazzo, *Sci. Adv. Mater.*, 2013, **5**, 1922–1929.
13. T. Fujimoto, M. M. Matsushita and K. Awaga, *J. Phys. Chem. C*, 2012, **116**, 5240–5245.

14. S. Ono, K. Miwa, S. Seki and J. Takeya, *Appl. Phys. Lett.*, 2009, **94**, 063301–3.
15. T. Uemura, R. Hirahara, Y. Tominari, S. Ono, S. Seki and J. Takeya, *Appl. Phys. Lett.*, 2008, **1**, 455–455.
16. H. Shimotani, H. Asanuma, J. Takeya and Y. Iwasa, *Appl. Phys. Lett.*, 2006, **89**, 203501–3.
17. M. J. Panzer and C. D. Frisbie, *Appl. Phys. Lett.*, 2006, **88**, 203504.
18. S. Ono, N. Minder, Z. Chen, A. Facchetti and A. F. Morpurgo, *Appl. Phys. Lett.*, 2010, **97**, 143307–3.
19. M. J. Panzer and C. D. Frisbie, *J. Am. Chem. Soc.*, 2005, **127**, 6960–6961.
20. B. D. Paulsen and C. D. Frisbie, *J. Phys. Chem. C*, 2012, **116**, 3132–3141.
21. J. Liu, I. Engquist, X. Crispin and M. Berggren, *J. Am. Chem. Soc.*, 2012, **134**, 901–904.
22. S. N. Bhat, R. D. Pietro and H. Sirringhaus, *Chem. Mater.*, 2012, **24**, 4060–4067.
23. S. Thiemann, S. Sachnov, S. Porscha, P. Wasserscheid and J. Zaumseil, *J. Phys. Chem. C*, 2012, **116**, 13536–13544.
24. J. Jeong, N. Aetukuri, T. Graf, T. D. Schladt, M. G. Samant and S. S. P. Parkin, *Science*, 2013, **339**, 1402–1405.
25. D. Ruzmetov, G. Gopalakrishnan, C. Ko, V. Narayanamurti and S. Ramanathan, *J. Appl. Phys.*, 2010, **107**, 114516–8.
26. H. Ji, J. Wei and D. Natelson, *Nano Lett.*, 2012, **12**, 2988–2992.
27. E. Alarcón-Lladó, M. A. Mayer, B. W. Boudouris, R. A. Segalman, N. Miller, T. Yamaguchi, K. Wang, Y. Nanishi, E. Haller and J. W. Ager, *Appl. Phys. Lett.*, 2011, **99**, 102106–3.
28. M. S. Kang, A. Sahu, D. J. Norris and C. D. Frisbie, *Nano Lett.*, 2010, **10**, 3727–3732.
29. M. S. Kang, J. Lee, D. J. Norris and C. D. Frisbie, *Nano Lett.*, 2009, **9**, 3848–3852.
30. P. Simon and Y. Gogotsi, *Nat. Mater.*, 2008, **7**, 845–854.
31. B. E. Conway, *Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications*, Springer, 1999.
32. C. Arbizzani, M. Mastragostino and F. Soavi, *J. Power Sources*, 2001, **100**, 164–170.
33. M. Mastragostino and F. Soavi, in *Encyclopedia of Electrochemical Power Sources (J. Garche, C. Dyer, P. Moseley, Z. Ogumi, D. R and, B. Scrosati, Eds)*, Elsevier, 2009), vol. 1, pp. 649–657.
34. R. Kumar, R. G. Pillai, N. Pekas, Y. Wu and R. L. McCreery, *J. Am. Chem. Soc.*, 2012, **134**, 14869–14876.
35. M. Lazzari, C. Arbizzani, F. Soavi and M. Mastragostino, Ch. 9 in *Supercapacitors: Materials, Systems and Applications* (F. Béguin and E. Frackowiak Eds, Wiley-VCH, 2013), pp. 289–306.