

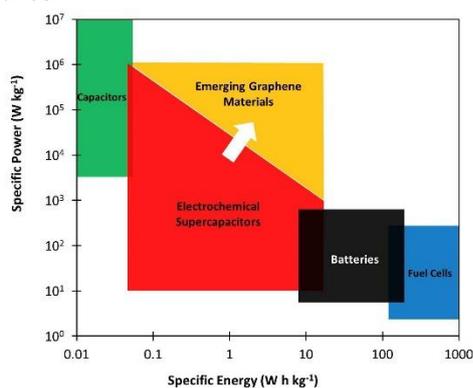
## GAME CHANGING SUPERCAPACITOR CHEMISTRY

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### Introduction:

According to Patrice Simon<sup>1</sup>, supercapacitors or electrochemical capacitors store energy using either ion adsorption (electrochemical double layer capacitors) or fast surface redox reactions (pseudo-capacitors). When represented on a Ragone plot, Fig. 1, they are differentiated from electrical capacitors by their significantly higher energy density or specific energy. Supercapacitors are an emerging technology for energy storage, as they offer higher power density than batteries and higher energy density over traditional capacitors<sup>2</sup>. New materials such as graphene are forecast to increase both the specific power and specific energy of supercapacitor devices. Other advantages over chemical batteries are their improved safety and robustness over multiple cycles (typically  $> 10^5$ ) with little degradation in performance.



**Fig. 1: Ragone diagram comparing the performance of supercapacitors with chemical batteries and showing the opportunity for graphene.**

Supercapacitors are generally categorised into three groups: **electrostatic double-layer capacitors** (EDLCs) using carbon electrodes, **electrochemical pseudo-capacitors** which use metal oxide or conducting polymer electrodes and **hybrid capacitors** such as the lithium-ion capacitor. These use differing electrodes – the first exhibiting mostly electrostatic capacitance and the others offer some chemical performance.

**EDLC capacitors** are based upon activated carbons; the double layer capacitance can reach levels of 100-120 Fg<sup>-1</sup> in organic electrolytes which can be increased to 150-300 Fg<sup>-1</sup> in aqueous electrolytes, but at a lower cell voltage. Reduction in pore size distribution to the range 2-5 nm, was then identified as a way to improve the energy density and the power capability, however only a moderate improvement of 100-120 Fg<sup>-1</sup> in organic and 150-200 Fg<sup>-1</sup> in aqueous electrolytes has been achieved<sup>1</sup>.

**Pseudo-capacitors or redox supercapacitors** are based on metal oxides or conductive polymers which give fast, reversible redox reactions at the surface of active materials, thus defining what is called the pseudo-capacitive behaviour. As pseudo-capacitance is achieved by Faradaic (electronic, usually coupled with ionic) charge-transfer via redox reactions, these materials would also be expected to produce increased specific energy when compared with EDLC capacitors. Despite these advantages, no commercial supplier of true pseudo-capacitor devices exists today.

Metal oxides such as RuO<sub>2</sub>, Fe<sub>3</sub>O<sub>4</sub> or MnO<sub>2</sub> are typically used as pseudo-capacitors and specific capacitances of more than 600 Fg<sup>-1</sup> have been reported utilising RuO<sub>2</sub> but these devices are not economically viable due to the high cost of Ru metal and their low operational voltage window (the latter because of the reliance on aqueous electrolytes). Less expensive oxides of iron, vanadium, nickel and cobalt have been tested in aqueous electrolytes, and specific capacitances as high as 1,300 Fg<sup>-1</sup> have been reported<sup>3</sup> on nanometre scale deposits of MnO<sub>2</sub> on conductive substrates such as metal collectors, carbon nanotubes or activated carbons. This study clearly demonstrates the potential for nanoscale deposits of transition metal oxides on conductive carbon substrates, although the scalability of these approaches has not been demonstrated hitherto.

**Hybrid capacitors combine** a capacitive or pseudo-capacitive electrode with a battery electrode, there are some commercial examples with enhanced performance, e.g. those supplied by Yunasko<sup>4</sup> often at much higher cost.

### Supercapacitor Suppliers:

Supply of supercapacitors is a rapidly changing environment with privately owned, small capital and corporate companies involved. EDLC based supercapacitors are supplied by AVX/Kyocera, Eaton, Maxwell, Ioxus and Skeleton Technologies. Skeleton Technologies claim to be the leading manufacturer in Europe with a graphene-based product, while Maxwell (now owned by Tesla) and Ioxus claim market leadership in the USA with carbon-based electric double layer capacitors. Skeleton Technologies claim best-in-industry power density at 45 kW/kg with an energy density of ca. 7Wh/kg, which is confirmed in a UC Davis study<sup>4</sup>.

We have not identified a supplier of pseudo-capacitors. Some start-ups claim pseudo-capacitor materials based upon carbon/metal oxides mixtures; however little performance data is published.

### University of Manchester approach

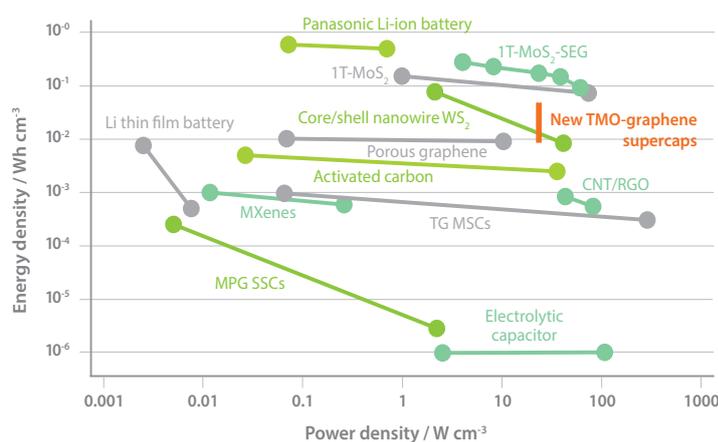
The approach presented herein offers a significant advance over the purely double-layer, pseudo-capacitive or hybrid approaches outlined above, as our method combines two of the above approaches, specifically the double-layer and pseudo-capacitive methods. This is achieved by forming a

composite structure of metal oxides deposited on a high quality (i.e. conducting) graphene support. The metal oxide is formed via a unique (patent applied for) process involving simultaneous exfoliation of the graphene and deposition of the oxide thereon, which ensures that the two materials are in intimate contact. Moreover, this process has already been proven at kg scale by First Graphene UK Ltd. and would use similar process equipment to their graphene exfoliation plant currently scaled at 100 tonne/yr.

The approach also allows some “tuning” (via electrolyte composition and applied cell voltage) of the metal loading and, therefore, morphology. The term “synergistic” is often over-used in the context of nanomaterials, but it genuinely applies to this case because the presence of the metal oxide serves to prevent re-aggregation of the graphene platelets, whereas the interleaving of the graphene between the metal oxide particles enhances the electrical conductivity of the (normally relatively low conductivity) oxide materials. These factors mean that a composite material with very high surface area and high conductivity (both ionic and electronic) is readily formed, which therefore is an ideal capacitor material, functioning both as a double-layer capacitor via the graphene, and as a pseudo-capacitor because of the metal oxide.

It is important to realise that electrolyte identity also plays a part here. Pseudo-capacitors typically give their best performance (in terms of energy density) in aqueous solutions because rapid protonation/de-protonation of the metal oxides is required. Double-layer capacitors, based on carbon materials, however, typically give highest energy densities in organic solutions because the accessible voltage window of organic electrolytes is higher than that of water. This is why commercial supercapacitors are based on organic solvents such as acetonitrile. Normally the reliance on aqueous solutions for our “mixed” approach would be problematic because it would depress the capacitance of the graphene component, however we have shown that a high pseudo-capacitance can be obtained in organic media by using a protic ionic liquid. This has further advantages of low volatility and toxicity, compared to “conventional” organic solvents such as acetonitrile, hence represents a further strength of the approach we will pursue here.

These structural factors are reflected in the electrochemical performance of the resultant materials, which have been shown to possess high energy density (ca. 40 Wh kg<sup>-1</sup>, considering only the active materials within the cell) without sacrificing power density (ca. 100 kW kg<sup>-1</sup>). This is game-changing improvement in energy density is derived from the presence of the metal oxide component (imparting high energy density) intimately combined with the graphene component (imparting the retention of the power density).



**Fig 2: Ragone plot showing the expected performance of the new TMO-Graphene hybrids.** Adapted from Ref. 5 with permission from The Royal Society of Chemistry.

Two challenges therefore lie in the path to reaching this goal. The first challenge is one of composition: the most promising results (in terms of capacitance, hence energy density) were obtained with a bimetallic oxide (Ru, Mn), where the gains in performance seen are unlikely to be cost-effective given the high cost of ruthenium. The University of Manchester and First Graphene (UK) Ltd. are currently collaborating on an EPSRC-IAA project that is addressing the goal of optimising composition with respect to performance at the small (coin-cell) scale. Once this is achieved, the next phase of the development will be to translate the optimised coin-cell performance to large scale pouch cells, to allow evaluation by “end user” companies.

#### Cost Effective Solutions:

Cost is a critical barrier for further penetration of supercapacitor storage systems. On a material basis, leading carbon material providers have pricing of \$100/kg at performance metric of 80 kW/kg. We anticipate pricing of >\$150/kg to be viable for a material producing 40 Wh/kg and 100 kW/kg.

#### References: Additional Information

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