ASX Announcement

23 March 2020

FIRST GRAPHENE - MAKING PROGRESS IN GAME CHANGING SUPERCAPACITOR MATERIALS

HIGHLIGHTS

- Technology transfer of University of Manchester process to First Graphene's industrial laboratories is complete.
- Manufacture of novel hybrid-graphene materials successfully demonstrated at kg scale in an industrial pilot plant.
- Manufacture of highly pristine graphene (with zero oxygen) demonstrated at kg scale in an industrial pilot plant.
- Supercapacitor coin cell testing of high capacitance materials is in progress

Advanced materials company, First Graphene Limited ("FGR" or "the Company") (ASX: FGR) is pleased to provide an update on its programme to develop novel graphene hybrid materials.

In September 2019, the Company announced the signing of a worldwide, exclusive licence agreement with the University of Manchester for the manufacture of hybrid-graphene materials by electrochemical processing. Two high value product groups can be synthesised using this approach. Firstly, metal oxide decorated materials with high capacitance for applications in supercapacitors and catalysis and secondly, pristine graphene products with tightly controlled specifications for applications in electrical and thermal conductivity. The manufacturing process to be employed builds on the Company's existing electrochemical processing expertise which is scaled to 100 tonne/year capacity at FGR's manufacturing site at Henderson, WA.

The licence agreement was quickly followed in October 2019; by the initiation of a UK government funded EPSRC (Engineering and Physical Sciences Council) project to transfer the technology from the University laboratories to First Graphene laboratories.

first graphene
The world's leading graphene company

First Graphene Limited

ACN 007 870 760
ABN 50 007 870 760

Registered Office
1 Sepia Close
Henderson WA 6166

Tel: +61 1300 660 448

Directors
Warwick Grigor
Craig McGuckin
Peter R Youd

Joint Company Secretaries
Peter R Youd
Nerida Schmidt

E: info@firstgraphene.net
W: firstgraphene.net

ASX Symbol
FGR
FGROC
Frankfurt Stock Exchange
FSE:M11

Since October, the Company has successfully transferred the technology to its laboratories in Manchester, UK and has also completed two successful pilot trials at its manufacturing facility in Henderson, WA. Specifically, the Company has demonstrated the following

- Synthesis of metal oxide decorated hybrid graphenes at litre scale in FGR laboratories.
- Synthesis of pristine (zero-oxygen) graphene materials at litre scale in FGR laboratories.
- Manufacture of metal oxide decorated hybrid graphenes at multi-kg scale.
- Manufacture of pristine (zero-oxygen) graphene materials at multi-kg scale.

The structure of the new materials has been confirmed by Raman analysis and Scanning Electron Microscopy (SEM). A typical image of metal oxide decorated graphene is shown in Fig. 1 which shows the nanostructured metal oxides on the surface of an exfoliated graphene platelet.

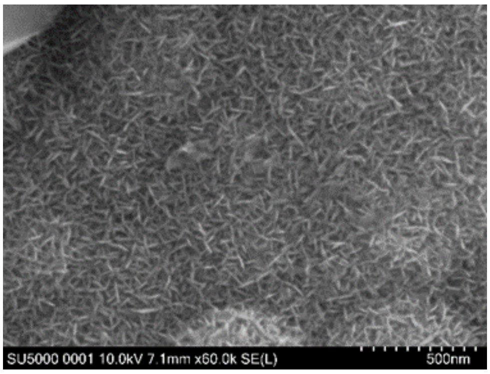

Fig. 1: Metal Oxide decorated graphene surface – crystalline metal oxide nanostructures grown directly onto the graphene platelet. Considered to be an ideal structure for capacitance and catalysis.

Currently the FGR team, is testing the performance of these materials in energy storage and catalysis applications. Initial testing shows that prototype supercapacitor devices (coin cell) can be manufactured with these materials. Currently, additional testing is delayed due to restricted access to test facilities as a consequence of COVID-19 actions. Further updates will be provided.

In parallel to the experimental programme, the Company has been actively seeking end-users for novel supercapacitor products. The need for supercapacitors with higher performance from those currently available have been validated by end-users in the aerospace, marine, electric vehicle and utility storage sectors. The company is also actively seeking government funding to develop a new supply chain for game changing supercapacitor devices and have received letters of support from key players.

"We are really excited by the potential for these hybrid-graphene materials" said Craig McGuckin, Managing Director of First Graphene Ltd. *"we have proven the chemistry does transfer at scale. We are disappointed that testing is being delayed due to current circumstances but will use this time to strengthen our end-user relationships."*

About Supercapacitors:

Supercapacitors offer high power-density energy storage, with the possibility of multiple charge/discharge cycles and short charging times. The market for supercapacitor devices is forecast to grow at 20% per year reaching a revenue value of ca. AUD$3.1 billion by 2022. As with batteries, growth of the supercapacitor market is challenged by the supply of the right, high-performing materials which is dominated today by the use of microporous carbon nanomaterials with typical gravimetric capacitance of 50 to 150 Farads/g.

About the University of Manchester IP:

Earlier research by The University of Manchester1[1] shows that very high capacitance materials of up to 500 Farads/g are now possible which outperform existing materials. The University has filed patent applications to protect the technology and all patents are exclusively licensed to First Graphene Ltd.

For further information on these unique materials, please view the technical article, authored jointly by the University and the Company at https://firstgraphene.net/wp-content/uploads/2020/03/GAME-CHANGING-SUPERCAPS_20200318.pdf

[1] Andinet Ejigu,* Kazunori Fujisawa, Ben F. Spencer, Bin Wang, Mauricio Terrones, Ian A. Kinloch, and Robert A. W. Dryfe*Adv. Funct. Mater. 2018, 28, 1804357

About First Graphene Ltd (ASX: FGR)

First Graphene Ltd. is the leading supplier of high-performing, graphene products. The company has a robust manufacturing platform based upon captive supply of high-purity raw materials and an established 100 tonne/year graphene production capacity. Commercial applications are now being progressed in composites, elastomers, fire retardancy, construction and energy storage.

First Graphene Ltd. is publicly listed in Australia (ASX:FGR) and has a primary manufacturing base in Henderson, near Perth, WA. The company is incorporated in the UK as First Graphene (UK) Ltd. and is a Tier 1 partner at the Graphene Engineering and Innovation Centre (GEIC), Manchester, UK.

PureGRAPH® Range of Products

PureGRAPH® graphene powders are available in tonnage volumes with lateral platelet sizes of 20µm, 10µm and 5µm. The products are high performing additives, characterised by their high quality and ease of use.

With authority of the board, this announcement has been authorised for release, by
Peter R. Youd
Director, Chief Financial Officer and Company Secretary

For further information, please contact

Craig McGuckin
Managing Director
First Graphene Limited
+ 61 1300 660 448

Warwick Grigor
Non-Executive Chairman
First Graphene Limited
+61 417 863187

GAME CHANGING SUPERCAPACITOR CHEMISTRY

Authors:
Prof. Robert Dryfe, University of Manchester
Andy Goodwin and Michael Watson, First Graphene (UK) Ltd.

Introduction:

According to Patrice Simon[1], 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[2]. 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.

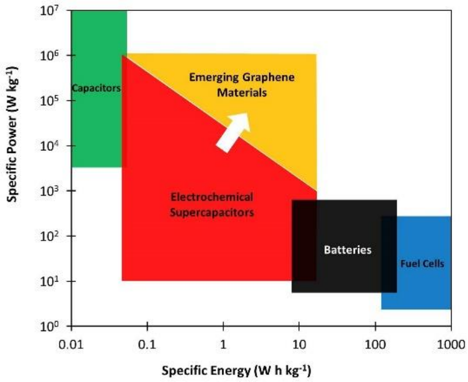

Fig. 1: Ragone diagram comparing the performance of supercapacitors with chemical batteries and showing the opportunity for graphene.

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^{-1} in organic electrolytes which can be increased to 150-300 Fg^{-1} 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^{-1} in organic and 150-200 Fg^{-1} in aqueous electrolytes has been achieved[1].

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_2, Fe_3O_4 or MnO_2 are typically used as pseudo-capacitors and specific capacitances of more than 600 Fg^{-1} have been reported utilising RuO_2 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^{-1} have been reported[3] on nanometre scale deposits of MnO_2 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[4] 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[4].

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 of 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^{-1}, considering only the active materials within the cell) without sacrificing power density (ca. 100 kW kg^{-1}). 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).

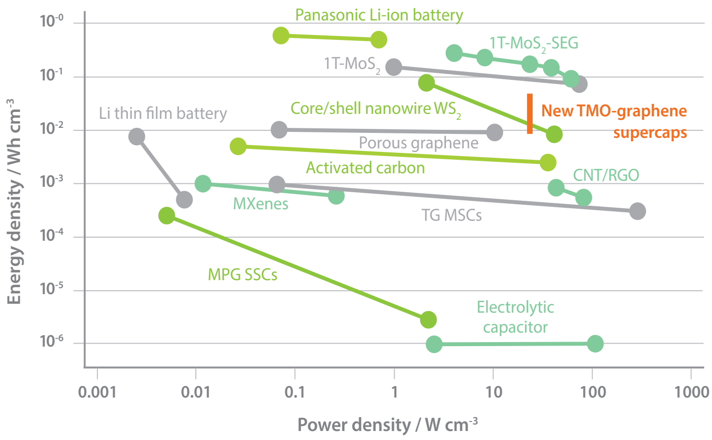

Fig 2: Ragone plot showing the expected performance of the new TMO-Graphene hybrids[4]. Adapted from Ref. 5 with permission from The Royal Society of Chemistry.

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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4. A. Burke and H. Zhao, Research Report – UCD-ITS-RR-15-09
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