



# A kish graphitic lithium-insertion anode material obtained from non-biodegradable plastic waste



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## ABSTRACT

Graphitic carbon continues to dominate as the choice anode material in lithium-ion batteries despite its theoretical specific capacity of  $372 \text{ mAhg}^{-1}$ . Tailored forms of graphite with higher practical capacities should, therefore, be of interest to the industry. This paper reports the production of a kish graphitic anode material from polyvinyl chloride by simultaneous carbonization of the polymer and dissolution of the resulting carbon in an iron melt to produce a supersaturated solution of carbon in iron, and subsequent precipitation of the carbon as graphite upon cooling. Our study presents a process for converting non-biodegradable plastic wastes that litter our surroundings into a technologically useful product. The new material exhibits a first-cycle reversible capacity of  $444 \text{ mAhg}^{-1}$  and sustains at least 200 cycles at C/10 rate before its capacity drops below  $372 \text{ mAhg}^{-1}$ .

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## 1. Introduction

Ubiquitous and manifesting in a multitude of forms in everyday products, plastics are among the most wonderful materials invented in the twentieth century. Products made of plastics rank among the fastest growing markets in the world due to their low cost and versatility. However, because the utility period of plastic products is relatively short, humongous quantities of plastic waste accumulate rapidly, which is increasingly becoming a serious environmental problem. In fact, environmentalists have begun to consider plastic waste as hazardous [1] not only because plastics threaten wildlife [2] and marine life [3] but also because some plastics are potentially toxic [4] or absorb pollutants [5]. According to a 2014 report titled *Valuing Plastic* from the United Nations Environment Program [6], financial damages per year to marine ecosystems due to plastic waste accounts for  $1.3 \times 10^{10}$  US dollars. Sustainable development thus calls for proper strategies to deal with such solid waste [7].

Most plastic materials are non-biodegradable, which has resulted in a colossal accumulation of such litter, accentuated by the ‘throw away’ culture. For example, around one trillion plastic bags are discarded each year worldwide, with most of them ending up in landfills, dumpsites and water bodies. The booming electronics industry is another major culprit. Disposal in landfills is increasingly being constrained by legislations. The use of recycled plastic in concrete has also been studied extensively [8]. However, these options mean that the energy content in the waste is not recovered. The inherent energy in the plastic can be recovered by incineration. However, because incineration leads to the conversion of most of the carbon in the plastic into carbon dioxide, pyrolysis is often considered a preferred waste management option [9]. Thermal degradation of plastics yield a variety of products including high-value products such as hydrogen (by pyrolysis of municipal solid waste [10] and catalytic steam pyrolysis–gasification of polypropylene [11]), producer gas [12], a wide range of hydrocarbons (from municipal solid waste [10], contaminated plastic solid waste [13] and mixed real-world plastic waste [14]), and liquid fuels (from plastic waste [15]). In another study of industrial significance, plastic waste was remediated into carbon nanotubes [16]. In this paper, we report a method to convert such industrial and e-waste into technologically useful products.

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With this in mind, we describe here a process by which non-biodegradable plastics such as polyvinyl chloride is converted into kish graphite, a product that holds much promise as an anode-active material in lithium-ion batteries [17–19]. It is obtained by precipitating the excess carbon from a supersaturated solution of carbon in steel. These graphitic products have been shown to be flaky carbon forms with nanocarbon structures embedded in them [20]. The remarkable lithium insertion properties of these materials are attributed to the presence of nanostructured carbons in the kish graphite products [17–19]. Conventionally, kish graphite is generated from coke and coconut charcoal, which are used as carbon precursors in foundries. Kish graphite-like materials have also been produced in the laboratory. Krivoruchko et al. [21] observed the sub-normal melting of iron nanoparticles and the movement of Fe–C particles in a liquid layer during the catalytic conversion of amorphous carbon into graphite. In a subsequent study on the interaction of amorphous carbon films with iron, cobalt and nickel particles by electron microscopy at temperatures between 600 and 750 °C, Krivoruchko et al. [22] found that at these temperatures the metals interact with the carbon, transit to the liquid state and move from the carbon film, leaving behind graphite tracks. In their studies on the catalytic graphitization of amorphous carbon, obtained by catalytic carbonization of polyvinyl alcohol on iron particles between 600 and 800 °C, these authors found that the products contained nanocarbon structures: multi-walled graphite shells wrapping the catalyst particles, cockle-shelled graphite filaments and MWCNTs [23]. Chernozatonskii et al. [24] reported the synthesis of inclusions of fullerenes and nanotubes in alloys of Fe–Ni–C and Fe–Ni–Co–C at temperatures between 1250 and 1300 °C. Reports on the electrochemical lithium insertion properties of such precipitated graphitic products first appeared in 2003 [17,18] and again in 2011 [19]. These investigators employed the customary coke or coconut charcoal as carbon precursors. This study presents results of studies on the electrochemical lithium insertion behavior of kish graphite obtained with PVC, a non-biodegradable solid plastic waste, as a carbon precursor.

## 2. Experimental

The preparative procedure for the generation of kish graphite is given in Fig. 1. PVC and cast iron used in this study were obtained from local sources. Cast iron was melted in a cupola crucible and maintained at 1700 °C. A calculated amount of PVC in the form of small beads was dropped on to the melt. Carbon dioxide released in the initial carbonization step resulted in a non-oxidizing column of gas over the melt, preventing further burning of the polymer. The carbonaceous pyrolytic products then readily dissolved in the molten steel, resulting in a saturated solution of carbon. The cupola crucible was kept shaking to allow uniform dissolution of the carbon in the melt. The melt was poured on to a sand bed and allowed to cool, whereupon the excess dissolved carbon precipitated out as kish graphite between the grain boundaries in the grey steel product. The moulds were then machined into ingots of convenient sizes. The graphite in the ingots was recovered by leaching the metal with 4 M HCl and silica with 20% HF, washing with Millipore water, and drying.

The grain structure of the grey steel was examined by a metallographic microscope (MTI MM500T) fitted with a digital camera. The samples for metallographic examination were prepared by unidirectional polishing of the ingots with sandpapers of successively increasing fineness. The polished, mirror-finish surfaces were finally rinsed with water and acetone to remove soil traces. The surface morphology of the graphite obtained by acid leaching was examined by scanning electron microscopes (Hitachi S-3000H and Jeol JSM 35-CF), a Carl Zeiss field-emission scanning electron

microscope (Supra 55 VP) and an FEI transmission electron microscope (Tecnaï 20 G<sup>2</sup>). A Perkin–Elmer CHN-2000 elemental analyzer was used for determining the elemental composition of the products. However, the iron content was determined by an inductively coupled plasma mass spectrometer (Thermo Electron X Series 2). The X-ray diffractograms of the products were recorded on a Bruker D8 Advance X-ray diffractometer fitted with a nickel-filtered monochromated Cu-K<sub>α</sub> radiation source ( $\lambda = 1.5418 \text{ \AA}$ ) between scattering angles of 10° and 80° in steps of 0.05°. Laser Raman spectroscopic measurements were performed in the 1000–2000 cm<sup>-1</sup> region with a laser radiation wavelength of 632.8 nm (Renishaw InVia; He–Ne laser). The Raman results were fitted with Renishaw software.

The lithium insertion–deinsertion properties of the graphite materials were studied in standard 2032-type coin cells (Hohsen). The graphite powder was made into a slurry with 8% PVdF binder (Aldrich) and 2% conducting carbon black additive (Timcal) in NMP (Merck). Test electrodes were made by slurry-coating on an oxide-free copper sheet (Hohsen), dried overnight, pressed and cut into discs. Lithium metal (Cyprus Foote Mineral) was used as the reference/counter electrode and a 1 M solution of LiPF<sub>6</sub> in a 1:1 (v/v) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (Ferro) was used as the electrolyte. A Celgard 2320 membrane was used as the separator. Galvanostatic charging and discharging of the cells were done at C/10 rate between 2.000 and 0.005 V, unless otherwise stated, by using a multi-channel battery tester (Arbin BT2000).

Thermal stability studies were carried out using a Mettler Toledo temperature-modulated differential scanning calorimeter (DSC1) between 25 and 400 °C at a temperature ramp of 5 °C min<sup>-1</sup> under argon. The samples for the safety studies were obtained by opening the coin cells at different states-of-charge with a Hohsen coin cell disassembling unit. The active material for the thermal stability studies as well as for the *ex situ* XRD and Raman studies was maintained at pre-determined potentials in the Arbin battery cycling unit for 48 h before disassembly. The active material scraped from the copper discs was freed of excess electrolyte by pressing with Kimwipes tissue paper, and transferred into aluminum cups and sealed inside a glove box (MBraun G-120B). However, for *ex situ* XRD and Raman measurements, the scraped material was rinsed in an excess of diethyl carbonate (Merck) and dried inside the glove box. Washing of the material was especially important for Raman spectral studies as any remnant LiPF<sub>6</sub> in the test sample can lead to fluorescence effects that could obscure the Raman signal [25]. For *ex situ* X-ray diffraction studies, the scraped-out products were spread on a glass plate holder (Bruker Scientific), onto which a double-sided PE tape border was fixed. The product was then covered with a Mylar sheet, which spread snugly on the PE tape, allowing no contact between the active material and the surroundings. A similar procedure was followed for *ex situ* Raman studies except that a thin microscopic glass plate was used in the place of the Mylar film.

## 3. Results and discussion

### 3.1. Morphology of kish graphite

The catalytic graphitization of carbons in carbon-rich iron melts was first noted by Austerman et al. [26]. The subject has since been well documented [27–31]. The graphitization process is believed to be due to either the G effect [31], a process by which carbon dissolves in the iron and precipitates out as graphite between the grains of the resulting grey cast steel, or to the formation and decomposition of carbide intermediates [29,31]. According to Oberlin and Rouchy [29] melting a non-graphitic carbon with iron results in the formation of a composite of graphite and a

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