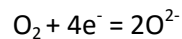


CHEMICAL ECONOMICS - GRAPHITE AND GRAPHENE

In a previous article I discussed pending developments in rechargeable batteries based on lithium, and particular the lithium/air battery which uses of lithium metal as the anode. The cathode of the optimum battery is based on graphite.

The duty of the cathode is to absorb oxygen from air and facilitate electron transfer:



with the anode reaction being:

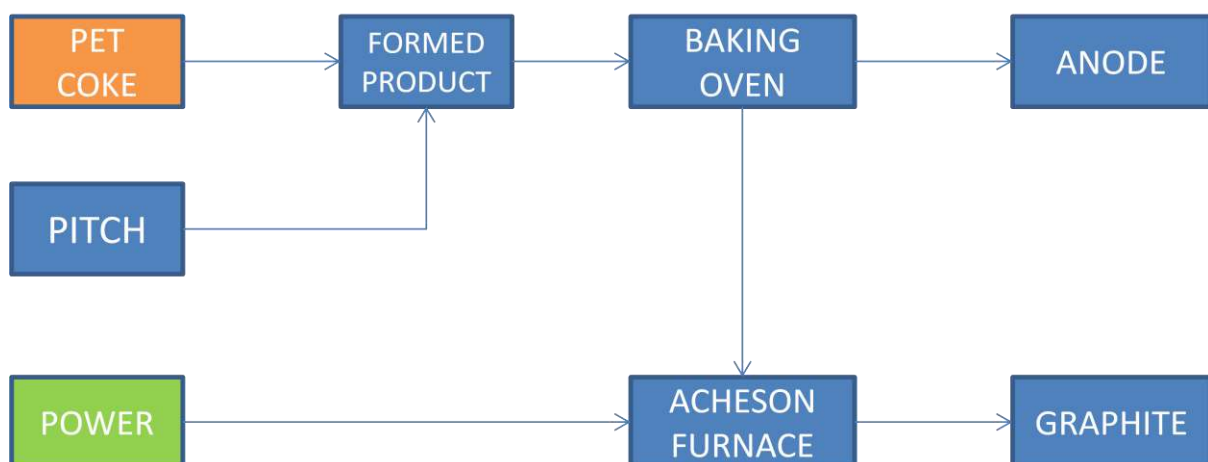


For maximum capacity the absorbed oxygen should be held within interstitial planes in the graphite structure, so theoretically mono-layers of graphene should be the optimum form of graphite. In passing it should be noted that lithium reacts irreversibly (and violently) with water and carbon dioxide so the air in contact with the graphite anode should be free from these materials or be impervious to them.

There are two forms of graphite, mined as a mineral or produced synthetically from carbon sources. Graphite is an allotrope of carbon stable at high temperatures and low pressures and for synthetic graphite any carbon source could be used. In practice the preferred starting materials are carbon sources where the carbon is highly graphitised in the first instance, such as anthracite coal or petroleum coke, and which have a low quantity of impurities. A preferred binding material is coal tar pitch which readily transforms to graphite when heated.

The production of synthetic graphite follows several steps shown in Figure 1.

Figure 1: Graphite production from petroleum coke (pet coke).



The required article is first formed by a combination of the petroleum coke (pet coke) and coal tar pitch. This is then transferred to a baking oven where the article is baked at typically 1000°C. This process produces electricity conducting products such as anodes for aluminium or lithium smelting which do not require the intense treatment to produce pure graphite.

Pure graphite is produced by heating the baked article to over 3000°C such as in an electrically heated furnace invented by Acheson in 1895 or an induction furnace to the same temperature. This is possibly the highest temperature used in an industrial process of commercial significance. Slowly heating from ambient to 3000°C accomplishes almost total graphitisation and purification of the graphite. The sublimation point of graphite is over 3600°C and because all of the impurities (including mineral matter) sublime well below 3000°C, the major portion of impurities are expelled from the formed article.

For high purity graphite (used for example in nuclear reactors) volatile halogen compounds are added during the furnace heating. These can be as sodium fluoride or gases such as sulphur hexafluoride, note the very high greenhouse potential (23,900 x CO₂) of the latter. These additives convert impurities to more volatile halides and reduce the impurity level to very low levels (e.g. total ash < 100ppm for nuclear uses of graphite).

Graphite electrodes are produced by machining the formed graphite articles to the dimensions required.

The natural mineral graphite occurs in various forms depending on how formed. Most current interest is in the flake type of mineral and especially the so-called jumbo-flake. The structure of natural graphite is in two forms - hexagonal and rhombohedral. Natural graphite has some properties which distinguish it from synthetic graphite, for instance higher density. Natural graphite is favoured over synthetic for some uses - for instance bushes for DC motors. It is not clear if natural graphite is preferred over synthetic for the production of lithium battery carbon anodes.

Of course natural graphite will contain mineral matter. Most of this can be removed by floatation at the mine site. For high purity uses and total graphitisation of the carbon present, high temperature furnace treatment like synthetic would be required.

Since its discovery in 2004, graphene is now the subject of major study and development across a broad range of fields; there are currently over 1000 US patents and over 2600 US patent applications containing the word graphene in the abstract. Theoretically graphene could offer the optimum capacity for holding oxygen in a lithium/air battery cathode.

There are two forms of graphene currently being widely used which are produced from graphite - non-oxidised and oxidised. In the non-oxidised version, graphite sheets are exfoliated by mechanical means or intense ultrasonication to produce a graphene slurry which is subsequently processed. In the oxidised version, the edges of the graphite are oxidised by strong usually acidic oxidising agents (sulphuric/nitric acid, chromic acid etc.) which after ultrasonication produces graphene in which the edges have pendent oxygen or hydroxyl groups. If necessary the oxidised form can be reduced or the oxygen groups used beneficially to synthesis larger sheets or attach the graphene as a ligand onto another substrate such as a carbon fibre.

From the present state-of-the-art, it is not clear if natural graphite offers significant advantages over synthetic form. However, of note is the very high value of jumbo-flake graphite which can command prices over three times that of other flake graphite. However, this may be because this form can produce very large graphene sheets which has uses in other fields (micro electrical components) rather than being used for battery anodes.

Compared to lithium side of the battery, the optimum technology for the graphite/graphene cathode and its manner of production, from the basic starting materials to the final product, is poorly defined. This offers many opportunities for Australian researchers to make their mark in this rapidly developing field.

Although the optimum technology for graphite use in lithium batteries remains unclear, what is evident is the high energy intensity of producing graphite of high purity and the likely high cost (relative to other commodity chemicals) of producing graphene if that is what is required. Again like lithium, we are likely to see Australia producing only relatively low valued mineral graphite to be exported to manufacturing intensive countries - Australia does not produce either petroleum coke or anthracite which are preferred feedstock for synthetic graphite.

The high energy intensity of producing both lithium and graphite/graphene supports the argument advanced by John Morgan (*Chemistry in Australia*, August 2014, p. 22) that battery storage for solar is, in the long term, an unsustainable option for powering a country such as Australia.

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