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Energy and resource use assessment of graphene as a substitute for indium tin oxide in transparent electrodes

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ABSTRACT

One of the most promising applications of graphene is as material in transparent electrodes in applications such as liquid crystal displays (LCDs) and solar cells. In this study, we assess life cycle resource requirements of producing an electrode area of graphene by chemical vapor deposition (CVD) and compare to the production of indium tin oxide (ITO). The resources considered are energy and scarce metals. The results show that graphene layers can have lower life cycle energy use than ITO layers, with 3−10 times reduction for our best case scenario. Regarding use of scarce metals, the use of indium in ITO production is more problematic than the use of copper in graphene production, although the latter may constitute a resource constraint in the very long run. The substitution of ITO by graphene thus seems favorable from a resource point of view. Higher order effects may outweigh or enhance the energy use benefit. For example, cheaper, graphene-based electrodes may spur increased production of LCDs, leading to increased absolute energy use, or spur the development of new energy technologies, such as solar cells and fuel cells. The latter could potentially lead to larger absolute reductions in resource use if these new technologies will replace fossil-based energy systems.

1. Introduction

The carbon nanomaterial graphene offers a number of promising technical applications due to its unique electrical properties and high strength (Geim and Novoselov, 2007). One of the most promising applications is as a material in transparent electrodes (Berger, 2008; Blake et al., 2008). Such electrodes are used in liquid crystal displays (LCDs) for computers, smart phones and other electronic applications with transparent screens. To be suitable for such applications, a material must have sufficient conductivity and transparency. The current standard material for this purpose is indium tin oxide (ITO) produced by physical vapor deposition. Due to several reasons, research efforts have been undertaken toward finding substitutes to ITO. One reason is the current high price of ITO (Segal, 2009). Another is the scarcity and criticality of indium, which is partly due to the geopolitical situation with China being the dominating producer (Candelise et al., 2011). A third reason is the technical inadequacies of ITO, such as chemical instability (Blake et al., 2008). Graphene has been shown to have similar resistivity and similar optical transparency to those of ITO, which would make it a potential substitute (Blake et al., 2008; Emmott et al., 2012). Graphene-based electrodes have even been suggested to be technically superior to ITO-based electrodes due to their higher stability, which could increase durability (Blake et al., 2008).

Life cycle assessment (LCA) of substituting ITO-containing solar cells with ITO-free organic solar cells have been conducted, showing considerably shorter energy pay back times for ITO-free solar cells (Espinosa et al., 2012). That study considered the whole life cycle of the solar cells except end of life, and included production of graphene ink via Hummer's process for one type of solar cells. Graphene has also been assessed in LCA studies of the production processes chemical reduction of graphite oxide, ultrasonication of graphite (Arvidsson et al., 2014), and thermal reduction of graphite oxide (Pizza et al., 2014). For making graphene-based electrodes, however, the most technically feasible production process is chemical vapor deposition (CVD), since it can produce large areas of transferable thin layers of graphene with high quality (Sivudu and Mahajan 2012). Other processes do not produce graphene films of sufficient quality (e.g. chemical reduction of graphite oxide) or sufficiently large areas (e.g. nanomechanical cleavage) (Li et al., 2009b).

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CVD is an energy-intensive process, and graphene produced by this process has therefore been suggested to have high embedded energy (Emmott et al., 2012). This would be in accordance with an LCA study of carbon nanotubes produced by CVD, which has shown high energy use of approximately 500–1000 MJ/kg based on models of large scale production (Kushnir and Sandén, 2008). There may thus be high energy use related to CVD of graphene as well. In addition, it is clear that ITO production relies on the scarce metal indium (Andersson, 2000), which is becoming increasingly expensive due to increasing use in LCDs and limited availability (Berger, 2008; Segal, 2009). The exact magnitude of indium reserves is, however, very uncertain (Andersson, 2000; Candelise et al., 2011).

In this study, our primary aim is to assess resource requirements of producing 1 cm^2 electrode area of graphene by CVD and compare it to the production of ITO. The method for this assessment is life cycle energy analysis combined with an assessment of scarce metals used in the life cycle (i.e. LCA limited to two resource-based impact categories). This study is both prospective, since it studies an emerging product, and consequential, since it studies the resource consequences of substituting ITO for graphene. However, the consequences of material substitution may go beyond the linear effects of one-to-one replacement of materials (Sandén and Karlström, 2007). A lower cost per LCD device may, for example, lead to larger production volumes and new application domains. We therefore also discuss potential higher order effects (Sandén and Karlström, 2007) of a material substitution of ITO by graphene, and thus the impacts that material substitution may have on absolute reductions of resource use in society.

2. Materials and methods

The main method applied for investigating the consequences of material substitution in terms of resource use is LCA, which is an established method for assessing environmental and resource impacts of products and services along their life cycles (Baumann and Tillman, 2004; Hellweg and Milà i Canals, 2014; ISO, 2006). In LCA, environmental and resource impacts are quantified in terms of impact categories for a functional unit that describes the function of the product or service. This study is limited to two impact categories, which are energy use and use of scarce metals. Since one impact category is energy use, the study can also be seen as a life cycle energy analysis complemented with scarce metal use. Two ways of categorizing LCA studies are as attributional or consequential, and as retrospective or prospective (Sandén and Karlström, 2007). Since this study considers the substitution from ITO to graphene, and the consequences thereof, it is a consequential study. Since it considers an emerging product not yet available on the market, it is also a prospective study. In that sense, it is similar in scope to earlier prospective LCA studies, such as the assessment of biofuels by Hillman and Sandén (2008), the assessment of a silver-containing T shirt by Walser et al. (2011), and the assessment of graphene production by Arvidsson et al. (2014).

A quantitative assessment of the energy and scarce metal requirements of producing graphene is conducted, and its results are compared to those of ITO production. We include the linear, or first order (Sandén and Karlström, 2007), effects of complete substitution of material life cycles, rather than marginal substitution on a functional unit level. As noticed by Sandén and Karlström (2007), such a prospective, first order consequential study of the substitution is methodologically identical to a comparison between two prospective attributional studies. To make a relevant comparison of the two production systems, we model a future, mature, large scale production system of graphene electrodes.

2.1. Functional unit

The function of ITO and graphene are to serve as transparent conductors in LCDs or other flat, transparent applications. A layer with a surface area of 1 cm^2 was therefore chosen as functional unit in this study. In addition, there are two parameters that affect the function in terms of transparence and electrical conductivity, respectively: the optical transmission and the sheet resistance. For ITO, a typical sheet resistances are 30–80 Ω cm (Kholmanov et al., 2012), and the optical transmission of ITO is reported as 79–90% (Bae et al., 2010; Emmott et al., 2012; Kholmanov et al., 2012), although these numbers are influenced by layer thickness (Benoy et al., 2009). For a graphene monolayer, the optical transmission is typically reported as 97%, and the sheet resistance as 1.3–1.4 kΩ cm (Bae et al., 2010; Kholmanov et al., 2012). Note, however, that production process, substrate, and number of graphene layers influence these two parameters (Bae et al., 2010). For example, a four layer graphene sheet will have a sheet resistance of approximately 50 Ω cm, and an optical transmission of approximately 90% (Bae et al., 2010), which corresponds well to the ITO numbers. Although it has been reported that CVD results in predominantly monolayer graphene with some areas of multilayer graphene (Li et al., 2009a), it is not certain that large-scale production of graphene will always have such high quality. Consequently, despite claims of the technical superiority of graphene over ITO (Bae et al., 2010), we assume that 1 cm^2 of graphene layer can substitute 1 cm^2 of ITO layer based on currently available data.

2.2. System studied

The production system studied is shown in Fig. 1. Included in the system are the life cycle processes required to produce graphene, making this a so-called cradle-to-gate study. Note, however, that potential recycling of scarce metals is discussed in Section 4.3, since it is of crucial role to the scarce metal use.

2.3. Impact categories

There are two main concerns related to graphene production by CVD and production of ITO by physical vapor deposition: (1) high energy use for both processes (Emmott et al., 2012), and (2) use of the scarce metal indium in the production of ITO (Candelise et al., 2011). Consequently, we limit our study to two impact categories that address these concerns specifically: (1) life cycle energy use, and (2) life cycle use of scarce metals. In addition to being a relevant resource use impact category, the life cycle energy use (in terms of cumulative energy demand and cumulative fossil energy demand) has also been shown to be a good proxy indicator for many environmental impacts of products (Huijbregts et al., 2010, 2006). In this study, all energy use is recalculated into heat in order to allow for a comparison between the life cycle energy use of graphene and ITO production. This means that electricity use is divided by a heat-to-electricity conversion coefficient to get a thermal equivalent unit, denoted $J_{th\text{-}eq}$, which indicates that the electricity contribution has been weighted. Energy use already given as thermal energy, which includes chemical feedstock energy, is converted directly to thermal equivalents, without weighting. The contribution of electricity to thermal equivalent figures is specified to increase the transparency and usefulness of the figures. Energy figures are also specified as J_{el} or J_{th}, indicating electrical or thermal energy, respectively. This focus on secondary energy use makes the analysis more generally applicable, since the results can be combined with different heat and electricity production systems in future assessments, and is not only valid for a specific energy production system.

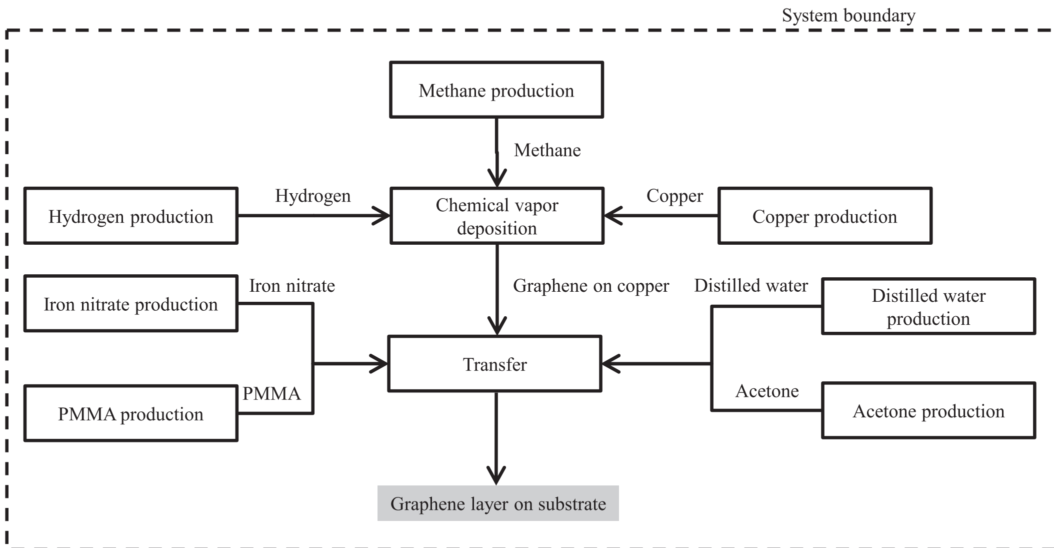

Fig. 1. Flow chart showing the studied production system for a graphene layer to be used in transparent electrodes.

For traditional, combustion-based power systems, the heat-to-electricity conversion coefficient is typically about 0.3 (Rydh and Sandén, 2005), which is used in the baseline scenario of this study. For systems that first generate electricity (such as systems dominated by wind and solar power), and only in a second step convert electricity to heat, it is reasonable to instead assume a conversion coefficient of 1 (Rydh and Sandén, 2005). The influence of this coefficient, reflecting different energy production systems, was tested in the sensitivity analysis.

The use of the scarce metal indium is a main driver for making the substitution of ITO by graphene (Berger, 2008; Segal, 2009). However, in the CVD process, copper is used as a catalyst for graphene formation (Li et al., 2009a). Even though copper is currently a common industrial metal, it is geochemically scarce, with low concentrations in the Earth's crust that can only be mined where concentrated into ore deposits that will one day become depleted (Ljunggren Söderman et al., 2014; Skinner, 1987). The same is true for the tin in ITO. There are thus uses of scarce metals in the life cycle of both materials, and therefore this impact category is interesting to assess. The scarce metal use per functional unit is assessed in two ways: (1) on a life cycle inventory level by comparison to current production rates and known reserves, and (2) with the EPS 2000 impact assessment method. In the EPS 2000 method, resource impacts are calculated based on the cost of restoring the resource (typical ore grade) from common rock (Steen, 1999).

Emission-based impact categories, such as global warming and acidification, are important and often included in LCA studies (Baumann and Tillman, 2004). The reason for not including emission-based impact categories in this study is that these impacts often mainly arise from background systems, such as electricity production and transport systems. Since graphene electrodes are only in an early stage of technological development, such systems may change before graphene electrodes are introduced on the market. Emission-based impact categories would thus mainly reflect assumptions about future energy production and transport systems, and would therefore risk hiding rather than highlighting inherent differences between the two technologies that are compared.

2.4. Data sources and sensitivity

The main data sources for the graphene production system were the studies by Li et al. (2009a, 2009b, 2010), and patent by Colombo et al. (2013). The patent was considered the most representative source of data on future large scale production of graphene, since patents generally contain processes that are believed to be technically feasible and considered to have economic value (Jaffe and Trajtenberg, 2002).

For established (non-emerging) products, the comprehensive LCA database Ecoinvent version 2.2, managed by the Swiss center for life cycle inventories (2010), has been frequently used for life cycle inventory data and other types of data. This database is subsequently referred to as the Ecoinvent database, and generally contains data for large scale production. Note that for copyright reasons, data from the Ecoinvent database cannot be provided unless aggregated. The detailed sources of input data are presented in Section 3.

This study departs from a baseline scenario, which is considered to be a likely scenario for future large scale production based on current knowledge. In addition to that, a scenario-based sensitivity analysis is conducted.

3. Calculations

3.1. Chemical vapor deposition

The graphene layer is formed during the CVD process. In this process, hydrocarbon gases are heated and form a graphene layer on a catalytic surface. This process is described in the articles by Li et al. (2009a, 2010), and in the patent by Colombo et al. (2013). The most common hydrocarbon gas of choice is methane. An excess of methane for creating an over-saturated environment is needed, so only a very minor fraction of the input methane actually ends up in the graphene product. In addition to methane, hydrogen gas is applied during the reaction in order to keep the atmosphere reducing and thereby avoid oxidation of the graphene. A number of metal catalysts can be used to enable the reaction, such as ruthenium, iridium, nickel and copper. However, difficulties of etching iridium, and high costs of iridium, ruthenium and nickel, make copper the most likely catalyst for large scale production (Li et al., 2009b). The reaction must take place at certain temperature and pressure. The CVD reaction, where methane forms graphene and hydrogen over a copper catalyst is chemically written as follows:

$$CH_4(g) \xrightarrow{Cu} C(s) + 2H_2(g) \quad \text{(R1)}$$

Note that the hydrogen produced in the reaction is negligible compared to the hydrogen required to keep the atmosphere reducing. Fig. 2 illustrates how the CVD may look like in an industrial setting, with baseline process parameter values shown.

To model the oven's energy requirement in the CVD process, we assumed a somewhat idealized model of an oven to represent a large scale continuous process and validated the result against smaller commercially available batch ovens. There are two components of the heating calculation: (1) heat losses through the oven walls, and (2) heating of the copper substrate, methane, and hydrogen.

The heat losses are the thermal transmission rate (r) (in W/m^2) of the oven wall insulation multiplied by the surface area of the oven. For a given oven width (w), operating on a copper substrate moving with velocity (v), for a residence time (t), the length of the oven is $v \times t$ and the surface area of the oven top and bottom will be $2 \times w \times v \times t$. The sidewalls of the oven with height (h) will have an area of $2 \times h \times v \times t$. If the height is expressed in terms of the width, $h = a \times w$, the surface area will be $2 \times w \times v \times \mathrm{t} \times (1 + a)$. The graphene product will have an area of $w \times v \times t$, so the oven surface per unit product area will be $2 + 2 \times a$. The thermal transmission is thus $r \times (2 + 2 \times a)$ in W per product area, and $r \times t \times (2 + 2 \times a)$ in J per product area. It is thus required to set a residence time, thermal transmission of the insulation and a height-to-width ratio for the oven. The result will be independent of the substrate width and velocity and thus of the scale of production.

The temperature at which the CVD takes place is approximately 1000 °C (Li et al., 2009a). The heat loss at that temperature is a property of the insulation. As baseline, we assume a commercially available aluminum oxide (Al_2O_3) and silica (SiO_2) ceramic wall modules with a transmission of 2.8–3.0 kW/m^2 at 950 °C and 500 Pa pressure (Heuer and Löser, 2012). To account for the higher temperature, we use the 3.0 kW/m^2 number.

The process residence time was set to 10 min in the baseline case (Li et al., 2009a), but varied down to 1 min in the sensitivity analysis considering different values found in the literature (Li et al., 2010). We assume a height-to-width ratio of 0.25 (e.g. 25 cm height for a 1 m width). The resulting value is 450 J lost per cm^2 graphene, regardless of production rate or oven size. This compares to an approximate range of 300–600 J/cm^2 calculated for existing commercial CVD ovens found on the online retail webpage Alibaba (2014). The higher number includes the vacuum pump, and the lower number is a highly insulated tube oven, which, while more geometrically efficient for small samples, would be inappropriate for wide sheets.

The energy for heating copper and input gases was calculated using the following equation:

$$E = m \times c_p \times \Delta T \quad (1)$$

where E is the energy use, m is the mass of the heated gas required per functional unit, c_p is the heat capacity of the material and ΔT is the temperature increase. The copper sheet has a thickness of 25 µm, an area of 1 cm^2 (same as the graphene area that is the functional unit of the study), a density of 8960 kg/m^3 and a specific heat capacity of 385 J/kg K. This results in a heating need of 8.5 J/cm^2. For methane and hydrogen, the numbers are 540 and 12 J/cm^2, respectively.

The heating of methane and oven heat losses thus contributes approximately half each to the overall energy use of the CVD process itself, while the contributions from heating copper and hydrogen are minor. Considering the magnitude of the sum of all these contributions, the value of 1.0 kJ/cm^2 for heating was applied in the baseline case. All CVD process heating is assumed to use electric elements for precise temperature control. The range of reducing or increasing the 1 kJ$_{el}$/cm^2 number by a factor of two (i.e. a range of 0.5–2 kJ$_{el}$/cm^2) was tested in the sensitivity analysis.

The required methane to produce high-quality graphene layers is typically 35 cm^3/min for 1 cm^2 graphene according to Li et al. (2009a). However, considerably higher application rates are possible as well (Colombo et al., 2013; Li et al., 2010). An exact relationship between methane application rate and layer quality is lacking, although application rates below 35 cm^3/min have been shown to give low-quality graphene (Li et al., 2010). In order to account for this variation, the methane application rate was thus varied between 35 and 350 cm^3/min in the sensitivity analysis. In addition, the feedstock heat value of methane (57 MJ$_{th}$/kg) was included as energy use. However, considering that most methane is not consumed in R1 but used to obtain the oversaturated environment, recovery of the heat value of methane is possible. The influence of doing so was tested in the sensitivity analysis.

The methane used in the CVD process needs to be of high purity, and we assumed that 99.9% purity was required. The energy use of the required purification step is highly dependent on the feed gas. While some natural sources of methane do have that purity, the vast majority will require purification. The energy carrier used in methane production and purification was assumed to be electricity. On the upper end of the scale, for feeds with low methane concentration such as biogas, commercial units achieve efficiencies of roughly 2.5 MJ$_{el}$/kg methane to achieve 99.9% purity levels. For more purified fossil feedstock, a regenerating adsorbent bed with a pressure swing of 30 psi is generally sufficient. Assuming an isothermal compression at 75% efficiency, the required energy is 0.21 MJ$_{el}$/kg methane. The 0.21–2.5 MJ$_{el}$/kg range was tested in the sensitivity analysis.

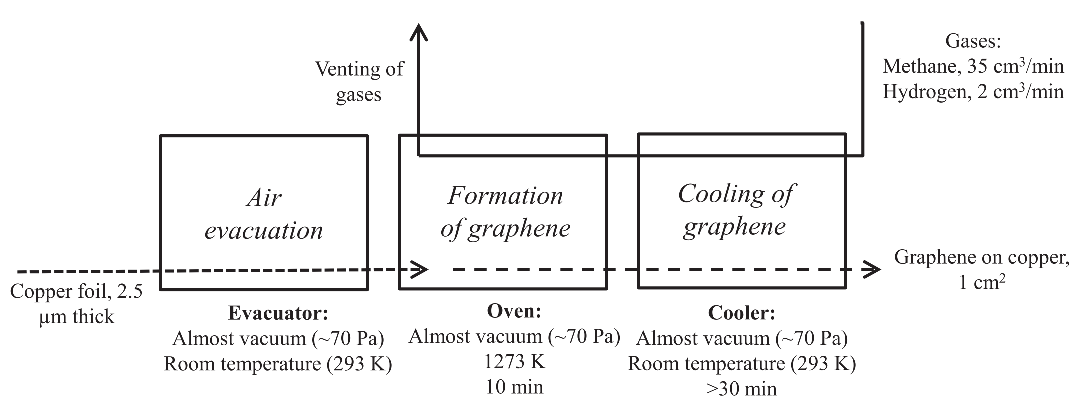

Fig. 2. Graphical illustration of the chemical vapor deposition process.

The 2 cm^3/min hydrogen required for 1 cm^2 graphene in the CVD requires a high purity of >99.9% (Li et al., 2009a). This purity can be obtained by electrolysis of water into hydrogen and oxygen (Ursúa et al., 2012):

$$2H_2O(l) \rightarrow 2H_2(g) + O_2(g) \quad \text{(R2)}$$

This reaction requires considerable amounts of electricity to take place, ranging from 180 to 300 MJ_{el}/kg (Ursúa et al., 2012), consisting entirely of electricity used for hydrolysis. The lower value of 180 MJ_{el}/kg was applied for the baseline scenario, and the range up to 300 MJ_{el}/kg was tested in the sensitivity analysis. In addition, considering that the hydrogen does not take part in any reaction, and is thus not consumed, it would be possible to use the heating value of the used hydrogen for other purposes. The heating value of the hydrogen (140 MJ_{th}/kg) could thus be recovered. The influence of doing so was also tested in the sensitivity analysis.

The copper catalyst required is typically 25 μm thick (Li et al., 2009a). From this value and the copper density (8690 kg/m^3), the required amount of copper was calculated. The energy requirement of copper production was assumed to be 22 $MJ_{th\text{-}eq}$/kg in the baseline scenario based on average energy use reported by Northey et al. (2013). This number is in good agreement with Ayres et al. (2002) and the Ecoinvent database. Based on different values reported in these three sources, the range of 10–70 $MJ_{th\text{-}eq}$/kg was tested in the sensitivity analysis. According to the Ecoinvent database, electricity contributes roughly 75% of the thermal equivalent value.

3.2. Transfer

After the CVD, a graphene layer has been created on copper. But in order to be a part of a transparent electrode, the graphene layer must be transferred onto a transparent substrate. According to Li et al. (2009b), this is done in the following steps:

1. Deposit poly(methyl methacrylate) (PMMA) onto the graphene as support.
2. Etch away the copper with iron nitrate.
3. Wash away residue iron nitrate with distilled water.
4. Place on transparent substrate.
5. Possibly add additional PMMA to stabilize and prevent cracks in the graphene layer.
6. Wash away PMMA with acetone.

In the articles describing this process, there is no reporting of the amounts of PMMA used. It is clear that a surface of 1 cm^2 of PMMA is required for 1 cm^2 of graphene, but the thickness of the PMMA layer is not specified in available literature. Based on interviews with a researcher producing graphene with CVD, the PMMA thickness was assumed to be 500 nm thick for the baseline scenario (Sun, 2014), and a range of 250–1000 nm was tested in the sensitivity analysis. A recent LCA of PMMA reports an energy use of 85 MJ_{th}/kg for PMMA production (Kikuchi et al., 2014). Chemical feedstock and heat contributes effectively 100% of the value. This is close to the energy use reported by Rydh and Sun (2005) for thermoplastics in general.

The amount of iron nitrate is not reported in the articles on graphene production either. We have thus assumed a stoichiometric amount required to dissolve the copper in the baseline case, representing an optimized large scale production. The etching occurs according to the following electrochemical reaction:

$$2Fe^{3+} + Cu(s) \rightarrow 2Fe^{2+} + Cu^{2+} \quad \text{(R3)}$$

The influence of doubling the stoichiometric amount was tested in the sensitivity analysis. No direct energy use data for iron nitrate has been found. The energy use from producing iron nitrate was assumed to take place by reacting iron with nitric acid:

$$2Fe(s) + 8HNO_3(aq) \rightarrow 2Fe(NO_3)_3(aq) + 2NO(g) + 4H_2O(1) \quad \text{(R4)}$$

The required amounts of iron and nitrous acid were then calculated based on stoichiometry. The iron in R4 was assumed to be sinter iron, for which energy use data was obtained from the Ecoinvent database. The energy use of nitric acid was also obtained from the Ecoinvent database. The final value used for iron nitrate was 11 $MJ_{th\text{-}eq}$, with 99% from thermal and feedstock energy.

The amount of distilled water required to wash away the iron nitrate was not reported either, but was assumed to be the same volume as the iron nitrate. The volume of the iron nitrate could be calculated since Li et al. (2009a) reported an iron nitrate concentration of 0.05 g/ml. The influence of doubling this amount was tested in the sensitivity analysis. The energy use of distilled water was obtained from the Ecoinvent database. This energy is in the form of electricity.

For acetone as well, no amounts are reported. However, Baker (2010) reported the solubility of PMMA in acetone to be 24 g/liter. From this, the lowest possible amount of acetone required to dissolve the PMMA was calculated in order to represent large scale production. Again, a doubling of this number was tested in the sensitivity analysis. The energy use of acetone was obtained from the Ecoinvent database with 99% of the energy used in the form of heat.

3.3. ITO production

ITO typically consists of indium oxide (In_2O_3) and tin oxide (SnO_2) at mass concentrations of 90% and 10%, respectively (Yang, 2012). ITO is typically produced as a powder and then deposited onto a transparent substrate by physical vapor deposition. The difference between chemical and physical deposition is that no chemical reaction takes place during physical vapor deposition. Emmott et al. (2012) report the life cycle energy use of ITO to be 7.2–27 kJ/cm^2. Based on data from the Ecoinvent database, the energy for producing ITO was assumed to be one third heat and two thirds electricity. This results in a range of 18–68 $kJ_{th\text{-}eq}$/cm^2 ITO. The arithmetic mean of 43 $kJ_{th\text{-}eq}$/cm^2 was used for comparison to the graphene baseline scenario, but ranges were shown as well.

Regarding use of scarce metals, the thickness of an ITO film is typically 150 nm (Yang, 2012). The amount of indium was calculated from the volume of the indium tin oxide (1 cm^2 × 150 nm), its density (7140 kg/m^3), and the indium content (74%). The use of tin was calculated in the same way as for indium, but with a 7.9% content.

3.4. Transports

Since the energy use of transports varies due to future modes of transport and process locations, which are currently unknown, transport energy use was not included in the baseline case. The potential influence of transport energy use was instead assessed in the sensitivity analysis.

4. Results and discussion

4.1. Energy use results

Fig. 3 shows the energy use results for graphene in the bar to the left. As comparison, energy use values for ITO production are also included to the right. As can be seen, the graphene baseline

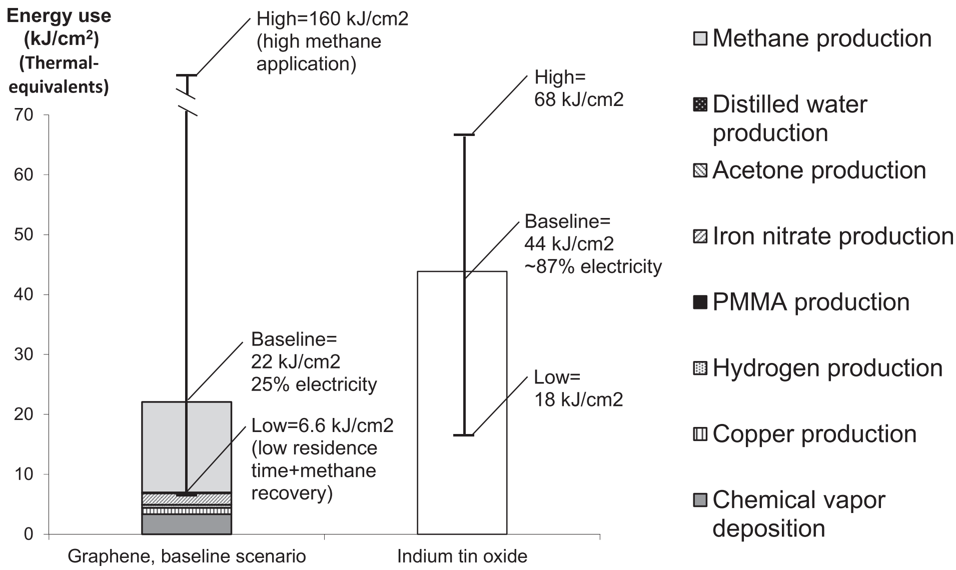

Fig. 3. Energy use results for the baseline scenario for graphene layer, with contributions from different processes shown. Results from the low and high scenarios of the sensitivity analysis are also shown. Energy use results for an indium tin oxide is included for comparison from Emmott et al. (2012).

scenario has an energy use similar to the lowest ITO energy use value. The energy use for the baseline scenario of graphene production is about three times lower than that of the highest energy use of the ITO production. In Fig. 3, the processes that contribute the most to the high energy use of graphene layers can be also identified. These are methane production (68%), the CVD process itself (15%), iron nitrate production (9%), copper production (5%), hydrogen production (2%) and acetone production (1%). Contributions from other processes are negligible. Methane is thus the main contributor to the energy use of the graphene, and most of this energy use is the feedstock heat value of methane. Most of the energy use (91%) is related to the CVD step, while the contribution of the transfer step is lower (9%). Approximately 75% is thermal energy and 25% is electricity.

4.2. Scarce metal use results

The resource use indicators applied to indium, copper, and tin are presented in Table 1. If compared on a life cycle inventory data level, that is in terms of kg per functional unit, the copper use in graphene production is about 300 times higher than the use of indium and tin in ITO production. However, indium and tin are arguably scarcer than copper given current prices and production systems. Global copper reserves (i.e. what is known and economically feasible to extract at current prices) are estimated at 690 million metric tonnes and the annual production in 2013 was almost 18 million metric tonnes (Brinistool, 2014). Indium production in 2013 was less than 800 metric tonnes. Current global reserves of indium are unknown, in the sense that there are no officially available estimates (Tolcin, 2014a). Tin reserves are estimated at 4.7 million metric tonnes, and annual production is 230 thousand metric tonnes (Tolcin, 2014b), placing it between copper and indium in relative scarcity. The annual copper production is thus 20,000 times higher than that of indium (and about 80 times higher than that of tin). Although current reserves of indium are not disclosed in any published documents, the numbers on annual production indicate that indium use in ITO presents a resource scarcity issue of a higher dignity than copper use in graphene production (Table 1).

The EPS 2000 method takes a long term view on metal resource scarcity. When compared according to this method, the resource impact of copper in graphene production is very similar to that of indium in ITO production (Table 1). The EPS 2000 characterization factor for indium is approximately 200 times higher than that of copper, reflecting the differences in average concentrations in the Earth's crust. Both copper in graphene production and indium in ITO production are hundreds of times higher than those of tin in ITO production when compared with EPS 2000. The implication of this is that while copper availability is unlikely to present any real constraint on graphene production in the foreseeable future, current copper use in society cannot continue forever, and therefore copper use is a valid long-term concern.

4.3. Sensitivity analysis

The following parameters in the graphene production were identified as uncertain: Heat-to-electricity conversion coefficient, energy use of copper, methane application rate, residence time,

Table 1
Results from the assessment of scarce metal use for ITO and graphene production. ELU stands for environmental load units.

Metals used	Metal use per electrode area [g/m^2]	Annual metal production rates[a] [ktonnes/year]	Resource constrained electrode area production [Gm^2/year]	EPS 2000 results [ELU/m^2]
ITO production				
Indium	0.80	0.8	1	39
Tin	0.084	230	2700	0.10
Graphene production				
Copper	220	18,000	82	47

[a] Production rates here refer to mine production for tin and copper and refinery production for indium.

Table 2
Parameter values tested in the sensitivity analysis.

Parameter	Low scenario	Baseline scenario	High scenario	Unit	Electricity contribution (%)
Heat-to-electricity conversion coefficient	0.3	0.3	1	–	–
Energy use of copper	10	22	70	$MJ_{th\text{-}eq}/kg$	50%
Methane application rate	35	35	350	cm^3/min	–
Residence time	1	10	10	min	–
Vacuum oven energy requirement	500	1000	2000	$J_{th\text{-}eq}/cm^2$	100%
Energy use of methane production	0.7	4.6	8.4	$MJ_{th\text{-}eq}/kg$	100%
Recovery rate of methane	0	0	1	–	–
Energy use of hydrogen	590	590	990	$MJ_{th\text{-}eq}/kg$	100%
Recovery rate of hydrogen	0	0	1	–	–
PMMA layer thickness	250	500	1000	nm	–
Iron nitrate use	170	170	340	mg/cm^2	–
Acetone use	2	2	4	mg/cm^2	–
Use of distilled water	3.4	3.4	6.8	g/cm^2	–

vacuum oven energy requirement, energy use of methane production, recovery rate of methane, energy use of hydrogen, recovery rate of hydrogen, PMMA layer thickness, iron nitrate use, acetone use and use of distilled water (Table 2). By applying different values for these parameters, 18 scenarios (including the baseline scenario) were developed and analyzed. Of these scenarios, most had a small influence on the energy use results, ranging from 19 to 25 $kJ_{th\text{-}eq}/cm^2$. Only three scenarios had a more considerable influence on the results: The high methane application rate scenario, the low residence time scenario, and the high recovery of methane energy scenario. All these scenarios affect methane energy use, which is not surprising considering the dominance of methane production in the graphene production energy use (Fig. 3).

The high methane application rate scenario, with 350 cm^3/min instead of 35 cm^3/min, gave an energy use of 160 $kJ_{th\ eq}/cm^2$, which is almost a factor of four higher than the baseline scenario and higher than the energy use of ITO production (Fig. 3).

The low residence time scenario and the recovery of methane energy scenario both gave a result of 8.0 $kJ_{th\ eq}/cm^2$, which is almost a factor of three reduction in energy use and considerable lower than the energy use of ITO production (Fig. 3). Production of graphene layers have been shown to be possible at 1.5 min residence time (Li et al., 2010), making this a reasonable scenario for large scale production, and a potential improvement from an energy use point of view. Applying both these scenarios at the same time gives an energy use of 6.6 $kJ_{th\ eq}/cm^2$, which can be seen as a best case scenario result. This suggests that the comment by Emmott et al. (2012), saying that graphene could have similarly high energy use as ITO, is not necessarily true.

In addition to the 18 scenarios discussed above, the potential energy use of including transport was also investigated. Although future transport distances are difficult to predict, it can be concluded that the exclusion of transports did not have a considerable influence on the results. Water and gaseous input materials are typically transported via pipes or produced on site, which has comparably negligible transport energy use. Other input materials, that is copper, PMMA, iron nitrate and acetone, could be transported by ship or truck. Sea transport typically has energy uses of 0.2 kJ_{th}/kg km, and truck transport typically 0.7 kJ_{th}/kg km (Baumann and Tillman, 2004). A transport distance of the total mass (approximately 0.19 g/cm^2) of these materials of 10,000 km would, in the baseline scenario, only increase energy requirements by 2% for ship and 6% for truck.

Regarding scarce metals, recycling indium from LCD screens is possible (Nakamura and Sato, 2011; Yang, 2012) and occurs in Japan and South Korea (Tolcin, 2014a). Recycling of indium would reduce the requirement of virgin indium per functional unit, although at an energy cost. Recovery of copper may also be possible. A recently developed alternative to the traditional transfer process is hydrogen bubbling (de la Rosa et al., 2013), which potentially could be conducted in such a way that the copper foil can be reused over and over again. In this process, the creation of hydrogen bubbles via water electrolysis between the graphene-PMMA cluster and the copper separates these layers, leaving the copper intact. This process can thus make copper a ‘true’ catalyst, since a true catalyst should not be consumed during the process. This process would also avoid the use of iron nitrate, which contributed 9% to the energy use of graphene in the baseline scenario, but instead require electricity for the electrolysis. Even with the current transfer process, it should be possible to recycle the copper from the etched copper and iron nitrate solution by electrolysis (Choi and Kim, 2003), although at an energy cost.

In addition to metal recovery, thinner ITO and copper layer thicknesses would lower the use of scarce metals in the two cases. For ITO, this would negatively affect the technical performance of the layer, thereby affecting the comparability of the two products. For graphene, a copper foil thickness half the size in the baseline scenario (12.5 μm) seemed to work well (Li et al., 2009a), so some reduction in copper use seems possible. It is, however, unclear how thin the copper foil can be without affecting the graphene layer adversely, and this should therefore be further investigated.

4.4. Higher order effects discussion

Beyond the linear, physical flow-based, first order effects of substituting one material life cycle for another, a substitution could also have non-linear, higher order effects, which are mainly governed by socio-economic mechanisms (Sandén and Karlström, 2007). Marginal market effects from substituting one functional unit for another have been dealt with in the literature on consequential LCA (Halog and Earles, 2011; Zamagni et al., 2012). Increased demand from substitutions resulting in efficiency improvements have been considered in the literature on rebound effects (Chitnis et al., 2013; Sanne, 2000). In both these literature streams, effects are mainly discussed in terms of an offset in environmental gains, and results typically show that the gains of a substitution is not as large as the first order linear model would indicate. The discussion on rebound effects has typically revolved around effects related to energy savings in the use phase of products, and that energy savings also lead to cost savings. These cost savings could lead to increased consumption of the same product and/or other products.

The reason for this focus on offsets in environmental gains in these literature streams is that they take an equilibrium view of the economy as starting point, where any disturbance in balance would create a counterforce trying to reestablish the balance. Such effects can be important for the absolute environmental and resource impact of a product or service.

A material substitution can also lead to more structural changes in society, with time frames beyond one decade. These may be even more important than equilibrium effects for emerging technologies, and can cause an initial environmental gain to become magnified (Sandén and Karlström, 2007). For example, starting producing a product could lead to increased learning and efficiency over time (Grübler, 1998).

The results of this study show that graphene has a lower energy use than ITO provided that no large amounts of methane are used (best case and baseline scenarios in Fig. 3). In addition, metal scarcity is less of an issue for graphene than for ITO (Table 1). In other words, there are potential gains from a substitution. There could, however, be higher order effects that reduce or magnify these first order effects.

Below, we highlight two possible higher order effects with different implications for absolute reductions in energy use: (1) the rebound effect, and (2) effects of technology spill-over due to learning. These are two of the higher order effects outlined by Sandén and Karlström (2007), which could be particularly relevant in this case.

The most common product in which transparent electrodes are used at present is LCDs. Considering the current high cost of ITO electrodes, it could be that graphene will enable cheaper electrodes, and consequently cheaper displays. Such a lower price on screens could result in increased consumption in terms of more or larger screens, which is an example of a rebound effect (reduced price of a commodity leads to increased consumption of that commodity). Our sensitivity analysis shows that given reasonable optimizations (our low estimate in Fig. 3), energy use could be reduced by almost two thirds over the lower ITO case (from 18 $kJ_{th\text{-}eq}/cm^2$ for ITO to 6.6 $kJ_{th\text{-}eq}/cm^2$ for graphene). Thus, if graphene enabled three times or larger screen area to be manufactured and purchased, the rebound effect would offset the energy saving per functional unit, and absolute energy savings would not occur. By eliminating the key constraint (indium) on total LCD production, graphene could result in more energy use for LCDs in society, despite enabling a lower energy use per functional unit. This mechanism works as follows: increased use of graphene in LCDs → cheaper LCDs → more LCDs → higher absolute energy use.

However, the increased use of a new technology could create knowledge and experience that can be used in other technological areas (Sandén and Karlström, 2007), which can be referred to as technology spill-over. In this case, the substitution of ITO by graphene in transparent electrodes could occur not only in LCDs, but also in solar cells (Emmott et al., 2012; Espinosa et al., 2012). In addition, the increased use of graphene in transparent electrodes could lead to increased use of graphene in other areas. One important such area is electricity production, where graphene produced by CVD has been suggested as an alternative to platinum as catalyst in fuel cells (Brownson et al., 2011). This mechanism works as follows: increased use of graphene in LCDs → increased use of graphene in other applications → higher or lower absolute energy and resource use. Whether such other applications of graphene will be beneficial from an energy and resource use perspective will depend on the exact applications. Since studies have indicated that ITO constitutes a bottleneck for diffusion of organic solar cells (Emmott et al., 2012), and that organic solar cells can have very low energy payback time (Espinosa et al., 2012), such a technology spill-over could very well contribute to an overall reduction in energy and resource use (provided that copper remains of lower resource concern than indium).

It is impossible to tell now whether the rebound effect from cheaper LCDs, or reductions in energy and resource use due to technology spill-over, will dominate. The net effect will depend on a range of decisions in society, which are beyond the scope of this study to investigate.

5. Conclusions

This study has shown that the energy use of graphene production could be lower than that of ITO production. Considering this, a substitution of ITO by graphene could be beneficial from an energy point of view. The feedstock heat value of methane is the main contributor to the energy use of graphene. This energy use could be reduced by shortening the residence time, or by recovering the heat value of unreacted methane by combustion. Excessive methane application rates should be avoided, since it can cause the energy use of graphene to exceed that of ITO. Regarding scarce metal use, although indium use is arguably of larger concern for ITO than copper use is for graphene, processes that reduce net copper use are nevertheless advisable. Such processes seem to be under development. In addition, moving from ITO to graphene may have a range of higher order effects. These may lead to net increase or decrease of energy use in society depending on whether the substitution will mainly cause effects such as increased use of LCDs, or contribute to the development of new, energy- and resource-efficient graphene-based technologies.

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