BRIEFING No. 26

CHEMISTRY & MATERIALS

Addressing critical commodity scarcity

A number of non-energetic commodities are particularly relevant to specific high tech products and crucial for future socio-economic mega-trends such as mobile computing or sustainable energy. Supply shortages represent an increasing challenge for Europe and its economy. Limited availability and monopolistic production structures contrast with a strongly increasing consumption. Optimizing resource efficiency is one of the major challenges of the future and nanotechnology offers a number of possible solutions.[1]

Background

The European raw materials initiative assessed 41 "non-energy minerals and metals". 14 raw materials have been identified as particularly critical for Europe´s economy[2] (***Figure 1*** and ***Table 1***). Meanwhile China has grown to be a major and partially monopolistic supplier for a number of these materials.

Substitution of scarce by abundant materials has been recognised as a key possibility to address upcoming shortages and to prepare for possible economic threats. However, this entails new challenges for R&D. Nanotechnology offers potential solutions in this respect and increasing research effort is being spent on nano-enabled approaches for substitution and enhanced efficiency[3].

This BRIEFING will specifically focus on indium and rare earths for which nanotechnology may offer valuable alternatives. However, most of the activities are still in the research state.

Indium (ITO)

Indium is of extraordinary importance as constituent of "Indium-Tin-Oxide" (ITO) which is comprehensively utilised for transparent electrodes. These are indispensable particularly in two strongly developing market areas; flat panel displays (FPD) and photovoltaics (PV).

However, Indium is scarce, increasingly expensive, and the EU is fully dependent on imports. Moreover, ITO is brittle and inappropriate for flexible products, neither in the display- nor the PV-sector. Considerable research is underway to develop alternatives and nano-enabled approaches may be crucial and include:

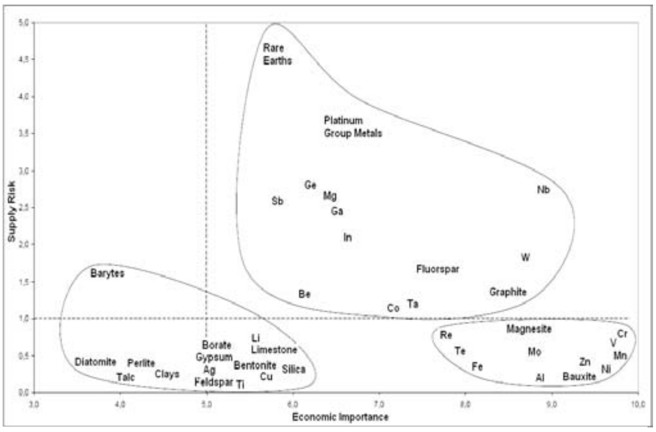

Figure 1*: Criticality of raw materials as following from "economic importance" and "supply risk".*

- **Indium free sub-micron transparent conductive oxide (TCO) films** under investigation are mostly based on ZnO and variants. Other approaches use TiO_2. Some require doping or compounding with other scarce elements (e. g. Ga or Nb) in low amounts. Others are manufactured using solely abundant materials[4]. The performances are not yet fully comparable with ITO. However, many material parameters remain to be further optimized and promise future potential. Moreover, they are suitable for large-area coating techniques and are quite resistant to chemicals.
- **Transparent conductive polymers** are inherently flexible. They allow for cost efficient large scale coating by printing techniques. The most widely utilised organic base form is "PEDOT". However, its UV stability remains an issue and its conductivity still ranges far below that of ITO. Substrate coating is established but remains to be further optimized. Research is underway to combine PEDOT with Single-Wall-Carbon nanotubes (SWNT)[5].
- **Carbon nanotubes (CNT):** CNT thin films – SWNT-films in particular - have been investigated for transparent electrodes. They are flexible and substrate coating may be achieved by printing and spraying techniques or by nano imprint lithography. CNTs have experienced a significant cost reduction. However, issues remain concerning growth control, dispersion homogeneity and the optimization of electro-optical properties. Industry is still reluctant, although transparent conducting CNT films are promising in particular for flexible applications, where ITO fails[6].
- **Graphene** is also promising for transparent flexible electrodes. Research groups recently succeeded in transferring graphene films to PET substrates. However, despite achieving good optical transmittances, electrical sheet resistances remain too large. Doping of graphene layers with various metals is currently being

investigated and looks moderately promising. Large scale processing and roll-to-roll fabrication seem possible in the long term[7].

- **Metallic nanowires** are further promising ITO-substitutes. Mostly silver is investigated, and to a lesser extent, copper, nickel, gold and indium. Single metallic wires are highly conductive and flexible. Both top-down processing and bottom-up approaches are applied, to coat mostly polymer foils (PET) with nano sized metallic transparent conductive layers. First companies succeeded in transferring these towards large area roll-to-roll fabrication; however, still at a high cost[8]. Further issues remain e. g. with inhomogeneous mesh formation, the material's high bulk resistance, its substrate adhesion and high processing temperatures. However, recent research achieved highly conductive, transparent layers, compatible with a wide range of substrate materials[9].

Rare Earths

Rare earths (RE) include 17 elements exhibiting specific properties, which are key to numerous technologies. They may be applied as phosphors in electronic displays and fluorescent lamps, compound in advanced glasses, alloy components in battery technology, catalysts, polishing paste in glazing processes, contrast agent in NMR-tomography to mention just a few.

The greatest importance; however, arises from the outstanding magnetic properties of some RE-elements such as praseodymium, samarium, holmium and, almost importantly neodymium (Nd) and dysprosium (Dy). Due to their electron structure, appropriate RE-admixtures cause iron-bearing materials to keep their magnetization and to fortify the bulk alloy against external demagnetisation. Neodymium-iron-boron (NdFeB) magnets are the strongest conventional magnetic materials currently known[10].

High power permanent magnets, are crucial for E-engines and electric generators such as those utilised in wind turbines. Hence, with E-mobility and sustainable energy two future megatrends outline a strongly increasing demand for specific REs.

The utilization of REs in magnets is hard to replace and there is unfortunately only a limited chance for alternatives. However, within nanotechnology effort is spent to minimizing RE-consumption.

One approach utilises nanoscale Nd, Fe and B instead of bulk materials[10]. The goal is to mix the nanoparticles in a way to achieve comparable magnetization with less neodymium. However, larger scale fabrication of the nanoparticles and their embedding into bulk solids remain issues.

Raw Materials	Main Producers (2008, 2009)	EU Import Dependency	Recyling Rate
Antimony	China 91 % Bolivia 2 % Russia 2 % South Africa 2 %	100%	11%
Beryllium	USA 85 % China 14 % Mozambique 1 %	100%	
Cobalt	DR Congo 41 % Canada 11 % Zambia 9 %	100%	16%
Fluorspar	China 59 % Mexico 18 % Mongolia 6 %	69%	0%
Gallium	NA	strong fluctuations	0%
Germanium	China 72 % Russia 4 % USA 3 %	100%	0%
Graphite	China 72 % India 13 % Brazil 7 %	95%	0%
Indium	China 58 % Japan 11 % Korea 9 % Canada 9 %	100%	0,30%
Magnesium	China 56 % Turkey 12 % Russia 7 %	100%	14%
Niobium	Brazil 92 % Canada 7 %	100%	11%
Platinum Group Metals	South Africa 79 % Russia 11 % Zimbabwe 3 %	100%	35%
Rare Earths	China 97 % India 2 % Brazil 1 %	100%	1%
Tantalum	Australia 48 % Brazil 16 % Rwanda 9 % DR Congo 9 %	100%	4%
Tungsten	China 78 % Russia 5 % Canada 4 %	73%	37%

***Table 1:** List of critical raw materials*

Within the Japanese "Rare Metal Substitute Materials Development Project" a research team including large industries such as Toda Kogyo, Toyota and Honda has succeeded in the fabrication of several tens of grams of a highly magnetic material without REs[11]. They produced an ultra-fine powder of nano-scale iron-nitrogen-particles. However, upfront to applications the powder has to be transferred to a bulk solid in critical and finally upscaled processes. Commercialization is not expected before 2023.

Other scarce materials

Critical scarcities are present for numerous other commodities (***Figure 1***) and considerable effort will continue to be spent in finding alternatives. Challenging goals have been formulated[12] including:

- Reduction of tungsten e. g. in carbide tools;
- Reduction of cerium in polishing pastes;
- Reduction of Te and Eu in fluorescent lamps;
- Reduction of platinum group metals (Pt, Pd, Rh etc.) in catalytic converters;
- Substitution/Reduction of Ga, Ge, In, Sb in opto-electronics, LED-technology and PV; and
- Substitution/Reduction of Li in batteries.

A variety of application dependent nano-based approaches such as the utilization of quantum dots, nano-antennas, targeted biotemplating and many more are currently under investigation or even close to market entry. However, a more detailed analysis is beyond this BRIEFING's scope.

Impacts

Economic/industrial

There is a considerable and increasing demand for critical commodities which are crucial to numerous key emerging technologies within ICT, electronics, energy, automotive or chemical engineering and Europe is highly dependent on external supply (***Table 1***).

Technological research tries to face this challenge by substituting scarce with abundant materials. Nanotechnology also contributes to these efforts and has shown encouraging approaches. However, many of these are still in the research state. Hence, the economic impact of nano-enabled alternatives is currently still limited.

The display area has experienced a transition towards flat panels. LCD and plasma displays dominate the markets and novel OLED-, touch displays or field emission devices entered or are in advanced states. In parallel even photovoltaics (PV) considerably expanded matching the trend towards sustainability and green energy. In addition to well established Si-solar cells a pipeline of promising novel developments such as CIGS, thin film silicon or organic PV is standing in the wings to address new markets[13]. All these applications boosted the markets for transparent electrodes and caused an increasing demand for Indium. However, only a few countries dominate the world supply and Europe is fully dependent on imports.

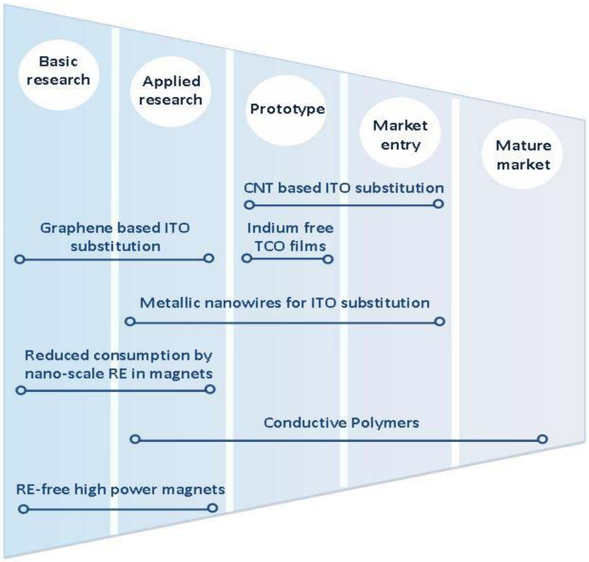

Figure 3: *Technology readiness levels for some nano-enabled critical resource solutions.*

The global transparent electronics market will continue to grow. Inorganic materials serving this sector accounted to a volume of $74 billion in 2010 and are expected to grow to more than $100 billion in 2015[14].

In the transparent electrode sector ITO is a widely established material and continues to be economically crucial. Even if alternatives were mature they would require considerable upfront investment.

Rare earths are crucial for a variety of key technologies (see above). Prices have dramatically increased and the global market was expected to grow from €2.4 billion in 2008 to €27 billion in 2011[15]. Reasons for this extreme rise are both a strongly increasing demand and the quasi monopolistic position of China. Besides, REs have

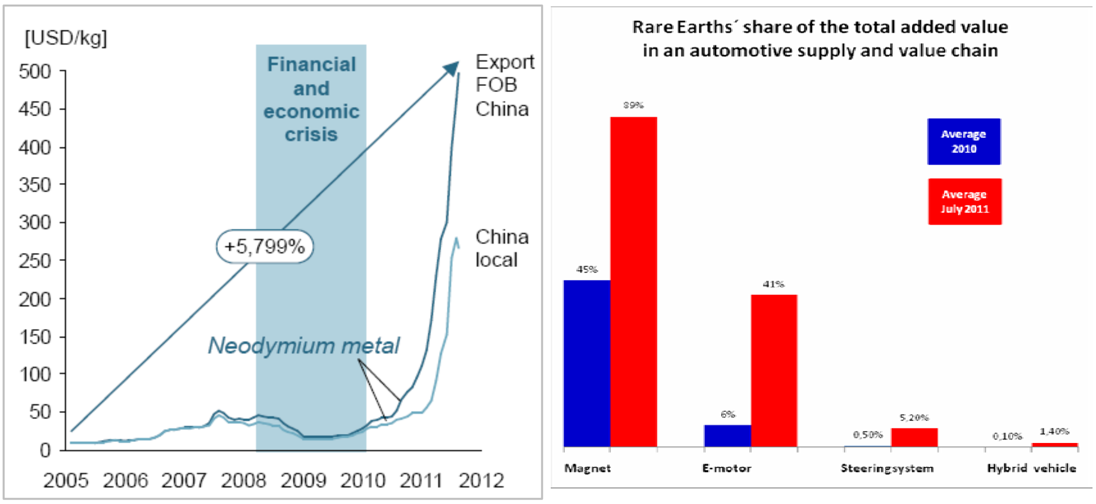

Figure 2: *left: Price of neodymium metal shipped from China until August 2011. right: RE´s share of an automotive value chain (hybrid car).*[15]

Increasingly turned towards objects of financial speculation. All this negatively influences high tech companies´ profitability. Research driven minimization of RE-consumption is thus highly desirable.

The continuing global economic deceleration has seen slight price relaxations of some critical materials. However, experts expect further price rises, although below the exaggerated level of the past two years.

Societal

Nano-enabled rare mineral substitution is expected to negatively impact the economies of countries that are highly dependent on exports of these materials e.g. less developed countries such as DR Congo, Mozambique, Rwanda and Zambia[16]. It could decrease employment especially among the poorest segments of the population.

Health, safety and environmental

The nanomaterials under consideration as possible alternatives for indium and rare earth elements are varied. These include both high volume production materials (e. g. metal oxides), as well as new materials (e.g. CNT, graphene). Excessive exposure has the potential to result in risks to health and the environment. For many of these nanomaterials, use of appropriate exposure control measures is likely to provide sufficient protection against potential harm. However, for some materials (e.g. CNT & nanowires), a potential for much greater toxicity has been observed. For all of these, particular attention should be given to controlling exposure to those particles which are utilised in powder form or sprayed (and therefore likely to become airborne). Appropriate occupational health and safety mechanisms should therefore be in place. Life cycle assessments, including recycling processes, are also required to prevent long-term environmental implications.

Challenges

Much effort is currently spent to replace scarce high tech commodities or to minimize their consumption; however, challenges remain. For example in transparent electrodes the degradation of sensitive layers by intense UV-illumination or exposure to oxygen remains an issue. Hence, encapsulation stays crucial and represents a major challenge particularly for flexible products.

In high performance magnets possibilities for alternatives are even more rare and at much earlier R&D stages. Up-scaled production of substitutes as well as solid state formation remain major issues.

EHS aspects should be carefully considered, and occupational health and safety controls put in place in line with the precautionary principle.

EU´s Competitive Situation

Numerous critical raw materials are crucial for Europe’s technology oriented economic sectors; however, Europe is highly dependent on imports. Current R&D to face this challenge seems qualitatively on par with that in the US, Japan and Korea. Numerous research groups address specific topics of substitution and consumption reduction. Appropriate funding is now underway also on the EU-level[3]. However, Japan and Korea with their specific economic focus on electronics, spend considerable effort. A quantitative comparison of European research effort with these countries as well as with the US and other world regions remains to further analysis.

Summary

- 14 non-energetic raw materials have been identified to be particularly crucial for key emerging technologies.
- Europe is highly dependent on imports.
- China is a dominant supplier.
- Much R&D-effort is spent on alternatives.
- Nanotechnology offers substitution potential.
- Manifold approaches for indium (ITO) replacement in transparent electrodes are under investigation.
- ITO will likely remain the “gold standard” for rigid surfaces in displays and PV
- ITO-substitutes get increasingly significant for flexible displays/PV
- Possibilities for rare earths substitution are limited and currently in earlier R&D-states.
- European R&D is competitive in this area.

Contact Information

Leif Brand, VDI Technologiezentrum GmbH, brand@vdi.de

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