Nano materials for renewable energy economy

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***Abstract*—Renewal energy economy relies on a range of novel materials for efficient production, distribution and consumption of energy. It is argued that nano materials are going to play increasingly important role in the economy. Examples are given following the original research on materials for the infrastructure and basic devices of the renewable economy, with focus on the transmission of energy. The attention is paid to nano-modified superconductors and novel thermo-insulators. A forecast of the future activity is suggested that is expected to lead to better materials, for example, superconductors with higher critical temperature and/or higher critical current density. The processes and equipment to handle nano-materials are also discussed.**

Keywords—nano materials; renewal energy economy; energy transmission; superconductors.

I. INTRODUCTION

The growing demand for energy, restricted amount of fossil fuels and an attempt to reduce CO_2 emissions set in motion a unique process of re-structuring energy economy. There is growing understanding that energy economy should eventually be renewable and fossil fuels-independent. Achieving this goal, however, is far from easy in the world heavily dependent of the fossil fuels accounting for more than 85 % of total energy supply. According to International Energy Agency, over the last 40 years, the contribution of renewables to world total primary energy supply was quite stable, showing 13.8% in 2014, and three quarters of this supply comes from solid biofuels (mainly wood) [1]. Although the situation starts changing, it is too early to speak about substantial rise of renewables.

In electricity generation, the share of renewables is slightly better. From the report of International Renewable Energy Agency's 2017, in 2015 renewables provided an estimated 23.5% of all generated electricity [2]. But again, one component only, namely hydropower, dominates the generation and there is no possibility to increase this component without significant damage to the environment.

These numbers show that renewable energy economy may forever remain a dream and that further uncontrollable use of fossil fuels may inevitably lead to ecological disaster and collapse of civilization. Such reasoning, however, does not take into consideration power of technological progress and scientific achievements. While scientific and technological development is rather complicated and not free from mishandling and errors, it is quickly changing world around and gives hope for solving problem of renewability.

One of success stories is the development of nano-science and nano-technology. While it is also not free from errors or unreasonable expectations; its steady move already created a basis, which could be used to transform energy sector. There are several areas, where nanotechnology is successful in energy applications. First of all, it is in generation of energy, where, for example, efficient solar panels are developed by introducing nanoparticles into the energy harvesting elements [3] or nano-composite materials are used to improve strength of blades in wind power generators [4]. In the energy conversion, nanoparticles are used to increase the efficiency of membranes and electrodes in fuel cells [5]. The use of nanoparticles significantly improves process of hydrogen production by electrolysis of water [5] and creates a range of solid-state hydrogen storage devices [6]. The nano-materials are also essential in transmission of energy, which is in the focus of this paper.

In most countries, the level of electrical energy renewability is different from the level of renewability of total primary energy. The extreme example is Norway, where electrical energy is 100% renewable, but the total energy is not. Moreover, economy of Norway as most of other countries is strongly oil dependent, as shown in figure 1. In this figure, the correlation between growth domestic product per capita and consumption of oil in 2013 is shown for a range of countries. To achieve full renewability in electrical energy generation in all countries and extend it to other sectors of energy economy, a unified approach is necessary.

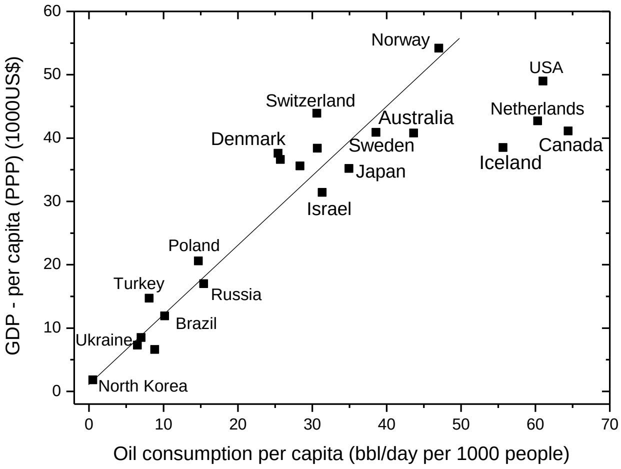

Fig. 1. Correlation between growth domestic product per capita and consumption of oil in 2013 for a range of countries.

A good start would be in building energy distribution network in form of Smart Superconducting Grid (Supergrid)

[7-9] switching at the same time to renewable generation of energy. The concept of Supergrid is based on the hydrogen cycle and combines simultaneous generation and delivery of electricity and liquid hydrogen as fuel and coolant. The loss-free delivery of electricity assumes extensive use of superconducting materials in the energy infrastructure. To achieve this, superconducting materials should have high critical temperature, high critical current density; and the techniques for their processing, thermal stabilization and safe operation should be developed. This is possible provided the resources from fossil fuels are redirected in this development investing in the renewable future.

In this paper, the adaptation of superconducting materials for Supergrid is discussed. The most effective way to do it appears to be through the nano-technology. The materials of choice for Supergrid are currently MgB_2 and $YBa_2Cu_3O_{7-x}$ (YBCO), but the efforts are under way to adopt new superconducting materials also. A nano approach to thermal insulation is an additional trend in relation to Supergrid.

II. EXPERIMENTAL METHODS

While considering and analyzing general approach to renewability, the paper is focused on experimental research of materials suitable for Supergrid. The materials preparation techniques include traditional pulsed laser deposition [10], hot isostatic pressing [8] as well as less used spark plasma sintering [11], spin-coating [12] and paint covering [8].

The samples characterization techniques include traditional technique used in nano-characterization: polarized optical microscopy, scanning electron microscopy, transmission electron microscopy, atomic force microscopy, conductance scanning probe microscopy, x-ray diffraction, magnetization techniques based on superconducting quantum interferometry and vibrating sample magnetometry, techniques for recording current-voltage characteristics, temperature dependence of resistance, and magnetic field and angle dependence of critical current.

Less wide-spread in research laboratories is magneto-optical imaging technique proved to be very useful in renewal energy applications [13,14]. It is a relatively simple technique suitable for magnetic and superconducting materials and allowing, by using polarized light, mapping distribution of magnetic field in the sample. This technique, together with resistance measurements, is most important for current work.

III. RESULTS AND DISCUSSION

Fig. 2 shows magneto optical images of three MgB_2 samples prepared by spark plasma sintering [8] with different nano-additions at temperatures of a) 20, b) 35, c) 39.4 and d) 186 K. The nano-additions in the samples were (from left to right) liquid hydrocarbon, SiC and Al_2O_3. The latter two were thoroughly dry-mixed with MgB_2 powder in the form of nanoparticles, while the liquid hydrocarbon chains were naturally evenly spread by wetting the powder. Using such chemically inert liquid is probably the most effective way of incorporating nano additions into MgB_2.

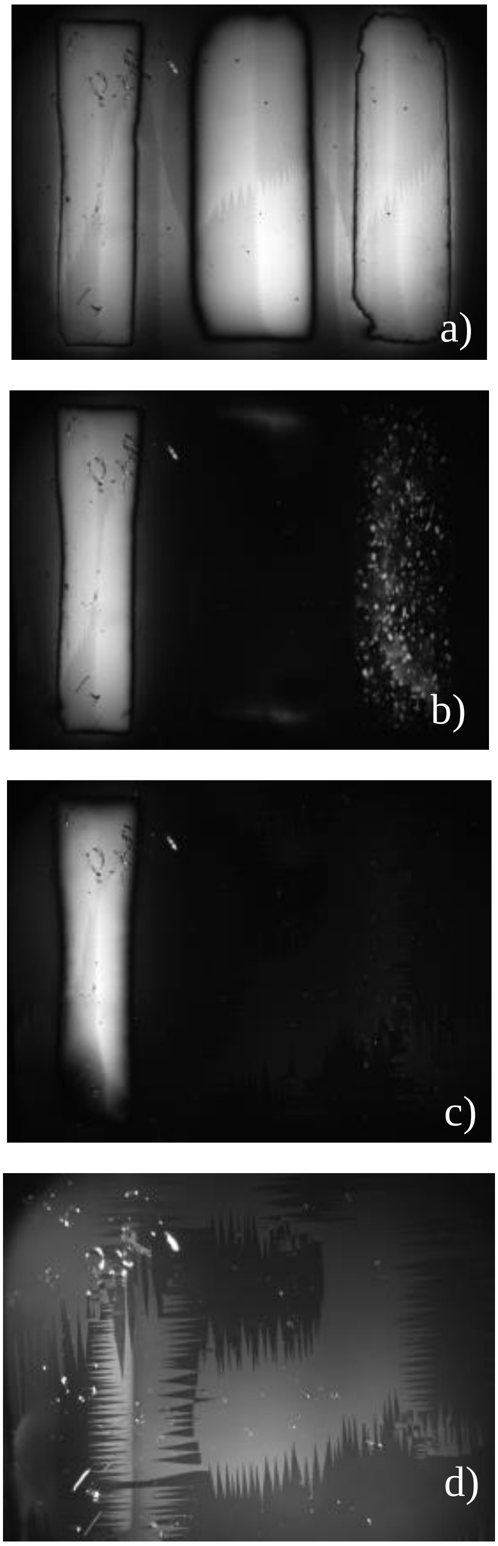

Fig. 2. Magneto optical images of three MgB_2 samples with different nano-additions at a) 20, b) 35, c) 39.4 and d) 186 K.

The effectiveness of liquid nano-addition is reflected in MOI images of Fig. 3. While at temperature of 35 K (Fig. 3b) superconducting response from the sample with SiC nanoparticles is nearly absent (middle sample) and the sample with Al_2O_3 nanoparticles (sample to the right) superconductivity survives just in few grains, the response of the sample with hydrocarbon inclusions (sample to the right) is still very good. At 39.4 K (Fig. 3c), it is the only sample with superconducting response. Moreover, an intriguing feature of seemingly superconducting response, although very week, is also observed in this sample at higher temperatures (Fig. 3d), up to the room temperature.

Finding room-temperature superconductivity would resolve important issue for the infrastructure of the renewable energy economy, which is cooling material to low temperature and heat-insulating it from the environment. The cheapest possible solution so far is to use $YBa_2Cu_3O_{7-x}$ spin-coating [15] and employ non-vacuum heat insulation in form of aerogel [16,17]. However, it is still requires large investments, and any possibility to increase critical temperature of superconductors above room temperature should be properly explored. Therefore, it is worth to further discuss the properties of the sample obtained with the addition of hydrocarbons.

The incorporation of organic polymer chains into matrix of another material is an unusual approach. It is well known that due to strong fluctuations of the order parameter, superconductivity as a conventional long-range phenomenon should not be possible in two, one and zero-dimensions [18,19]. However, topological order still can exist in two dimensions at reduced temperatures [20]. Moreover, quasi two-dimensional systems like $YBa_2Cu_3O_{7-x}$ exhibit significantly higher critical temperature (T_c) than their conventional three-dimensional counterparts. Following this rule, one could expect even higher T_c in quasi-one dimensional systems. Indeed, in 1964 Little predicted unusually high T_c of ≈2200 K in linear organic chains linked with certain molecular complexes [21].

Although superconductors with critical temperature higher than room temperature were never found, some observations, for example, confirmation of superconductivity at 203 K in H_2S at high pressure [22] or superconductor-like current-voltage characteristics in brain tissues [23] continue stimulating activity in the area. It is interesting that both observations were in materials containing light chemical elements that typically compose organic materials. Addition of carbon-hydrogen polymer chains to MgB_2 follows the same pattern.

In Fig. 3, temperature dependence of resistance is shown for the material with added hydrocarbons recorded at currents of 10 (a) and 1 mA (b), left axis, black points. The measurements has been done in four probe configuration to avoid effect of possible heating from current leads, and both current and potential contacts were made by pressing indium to the sample. In measurements, it is important to monitor simultaneously current flowing through the sample as some effects of the absence of voltage suggestive of zero resistance may be due to current stopping flowing through the sample.

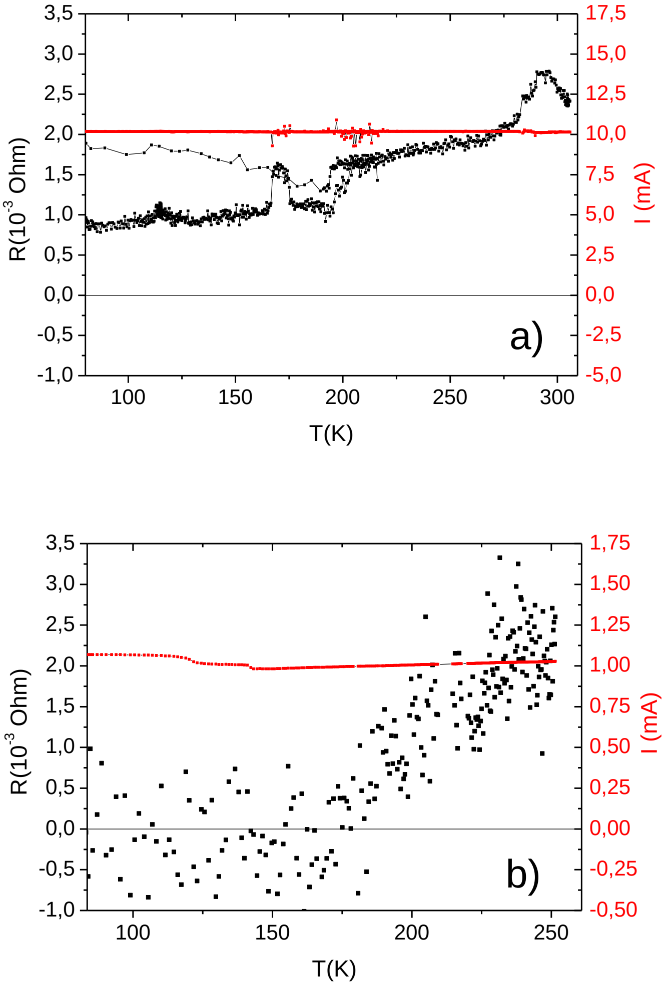

Fig. 3. Temperature dependence of resistance for MgB_2 with added hydrocarbons recorded at currents of 10 (a) and 1 mA (b), left axis, black points.

The value of the current flowing through the sample is shown in Fig. 3 by red points (right axis). The current remains nearly constant during the measurements, but the data scattering for the resistance is very large. There are also transitions between different states and irreversibility of the data with decrease and increase of temperature. Still, at both current, upon decrease of temperature, resistance starts decreasing from the same value at room temperature of about 2 10^{-3} Ohm (resistivity ≈10^{-6} Ohm m) and while it is still high at about 100 K for current of 10 mA, the resistance at 1 mA already showing fluctuation around zero below ≈180 K. Suggesting that this effect comes from fluctuating superconductivity, such a behaviour would be in agreement with diamagnetic response in Fig. 2. Another arguments in favor of superconductivity is relatively small, but steady increase of current in the circuit due to decrease of the resistance of the sample showing additionally sharp step-like features between 150 and 100 K (red curve in Fig. 3b). The large scattering in resistance is either instrumental effect or intrinsic property of the system.

In Fig. 4, current-voltage (IV) characteristics of the sample are plotted at several temperatures. Again, scattering of data points is large, even on the background of expected robust superconductivity in MgB_2 matrix at 4.2 K. A constant voltage shift of the curves to the right from zero to about 4 μV is also seen, which is likely to be of a thermo-electric nature.

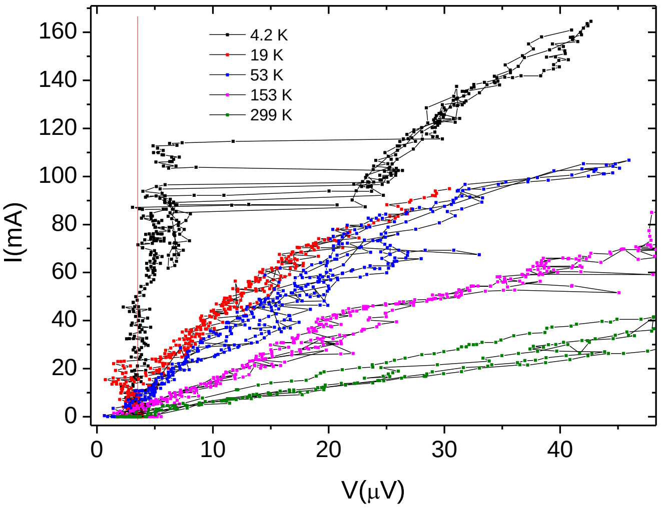

Fig. 4. Temperature dependence of resistance for MgB_2 with added hydrocarbons recorded at currents of 10 (a) and 1 mA (b), left axis, black points.

Apart from that, IV curve are strongly non-linear at low temperatures and there are voltage fluctuations around vertical red line in the superconducting state. These fluctuations are well seen at temperatures of 4.2 and 19 K (black and red points, respectively), but there is also accumulation of blue and magenta points around red line at low current that correspond to temperatures of 53 and 153 K, which are obviously above critical temperature of MgB_2 (≈ 40 K). Green points at room temperature show no visible accumulation of points around the vertical line.

The obtained IV curves could be used to estimate the value of critical current. At 153 K (magenta points), it is about 5 mA, which is again in agreement with data of Fig. 3b that show apparent zero resistance below ≈180 K in the curve recorded at current of 1 mA.

The presented data are strongly fluctuating, which does not make them conclusive. The resistivity of material at room temperature is also not competitive with resistivity of copper ≈1.7 10^{-8} Ohm m or even pure MgB_2 (≈ 10^{-7} Ohm m). Still, optimization of preparation conditions may change situation in the future. On this stage, it is principally important to prove that superconductivity or Bose-Einstein Condensation (BEC) of charged particles is possible at room temperature. Additional to multiple indications that it is actually possible, among which are results of [22,23], there is progress in experimental confirmation of a room-temperature superfluidity phenomenon [24]. Even if it was found that superconducting material could not provide high critical current density at room temperature, they could be used in superconducting electronics.

From what is said, it is clear that applications of superconductivity in energy sector, in particular for delivering of loss-free current and fuel (liquid hydrogen) would currently need to operate at low temperatures. MgB_2 is reasonably good choice of material for these purposes, since its critical temperature is twice above boiling temperature of liquid hydrogen, it is light (nearly three times less heavy than stainless steel) and relatively non-expensive.

Main techniques for processing of MgB_2 are already suggested and partially tested [8,9,11,13]. There is, however unexpected return to YBCO in recent years. Following impressive progress in spin-coating technics, it is possible now to spray a metal-organic solution on curved surfaces that after thermal treatment forms superconducting cover with critical current density approaching that in pulsed laser deposited films [15].

One can now use metal pipes for carrying liquid hydrogen with specially prepared surface, to which a layer of YBCO is deposited by the metal-organic technique. The advantage of $YBa_2Cu_3O_{7-x}$ compared with MgB_2 is its much higher critical temperature. This reduces requirements for thermal insulation, and aerogel [5,6] could be used, at least partially, instead of vacuum. Furthermore, established nano-techniques [10] could be used to improve critical current density in YBCO cover.

IV. CONCLUSIONS

Nano materials are going to play important role in development of renewable energy economy. They are already in intensive use in generation, distribution and use of energy, and in future use of nanomaterials is expected to be even on greater scale. In distribution of energy, a concept of Smart Superconducting Grid is currently under consideration as the basic infrastructure for renewal energy economy. The grid will be based on superconducting pipelines simultaneously delivering loss-free electricity and liquid hydrogen that supposed to be main CO_2 emissions-free fuel in industry, transport and household. Nanomaterials would allow increasing current capacity of the grid. There are also attempts to increase by nano-additions critical temperature of superconducting materials, which may lead to pipelines operating at room temperature. The nano-approach to heat insulation is also resulting in novel materials, like aerogel that can insulate pipelines if there eventually will be necessary to operate at low temperatures.

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