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Energimyndighetens titel på projektet – svenska	
Nytt termiskt energilagerkoncept utvärderas i en fullskalig demonstrator	
Energimyndighetens titel på projektet – engelska	
New thermal energy storage concept evaluated in a full-scale demonstrator	
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Förlustfri, Energität energilagring, Skalbar, Kostnadseffektiv	

Förord

Projektet har finansierats av Sunflake Technologies, Energimyndigheten och ETC El i Katrineholm. Ahlstrom-Munksjö Paper AB och Sigma har ingått i referensgruppen.

Innehållsförteckning

Sammanfattning

Den snabbt växande medvetenheten om klimatkrisen innebär en stark marknadsdrift att använda energi som inte ger skadliga CO_2-utsläpp. Förnybar energi och återvinning av industriellt avfallstermisk energi uppfyller dessa villkor. De tillgängliga metoderna för fossilfri energiproduktion, som spillvärme, sol- och vindenergi, är dock intermittenta på grund av dess beroende av väder och industriella förhållanden. En lösning på det intermittenta problemet är att lagra energin när den är tillgänglig. Energilagring är därför nyckeln till att hitta sätt att hantera den allt större andelen avfall, sol- och vindkraft i energisystem. Sunflake Technologies AB har utvecklat en ny TESM som kan masstillverkas med industriell roll-to-roll-utrustning. Vårt nya och grafeninkapslade granulerade

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kalciumhydroxidmaterial kan användas för termisk energilagring för uppvärmning och elproduktion vid behov. Grafeninkapslingsmetod med låg skjuvspänning utvecklades och verifierades som en ytterligare förbättring av patentet (US9459026B2). Metoden är skalbar och kostnadseffektiv. Den optimala grafensammansättningen bestämdes via direkta mätningar av hydratiserings-/ångabsorptionsdynamiken. Power in/power out-mätning visade att grafeninkapsling resulterade i 25 % förbättring av power in/power out-kapacitet. Svepelektronmikroskop och BET-analyser stödde att cyklad TESM avslöjar ytterligare förbättring av hydreringsdynamiken. Dessutom gjorde TESM-kompetensuppbyggnad det möjligt att hitta teoretiska förklaringar av grafenförbättring. ”The rodmap” till massproduktion av det nya grafeninkapslade lagringsmaterialet för termisk energi togs fram. Nyckelpartner, intressenter och potentiella kunder fastställdes. Pilotprototypen för lagring av värmeenergi byggdes, utvärderades och levererades till kunden.

Summary

The rapidly growing awareness of the climate crisis implies a strong market drive to use energy that does not produce harmful CO2 emissions. The renewable energy and recuperation of industrial waste thermal energy fulfils these conditions. The available methods for fossil-free energy production, like waste heat, solar and wind energy, are however intermittent due to its dependence on weather and industrial conditions. A solution to the intermittent problem is to store the energy when available. Energy-storages are therefore key in finding ways to handle the ever-larger percentage of waste, solar and wind power in energy systems. Sunflake Technologies AB has developed novel TESM that can be mass produced using industrial roll-to-roll equipment. Our novel and graphene encapsuled granulated calcium hydroxide material can be utilized for thermal energy storage for heating and electricity generation when required. Low shear stress graphene encapsulation method was developed and verified as a further progress improvement of the patent (US9459026B2). The method is scalable and cost effective. The optimum graphene composition was determined via direct measurements of hydration/steam absorption dynamic. Power in/power out measurement revealed that graphene encapsulation resulted in 25% improvement of power in/power out capacities. Scanning electron microscopy and BET analyses supported that cycled TESM reveal further improvement of hydration dynamic. Moreover, TESM competence building made it possible to find theoretical explanations of graphene enhancement. The road map for mass production of the novel graphene encapsuled thermal energy storage material was taken forth. Key partners, stake holders and potential customers were determined. The thermal energy storage pilot prototype was built, evaluated, and delivered to the customer.

Inledning/Bakgrund

The rapidly growing awareness of the climate crisis implies a strong market drive to use energy that does not produce harmful CO_2 emissions. The renewable energy and recuperation of industrial waste thermal energy fulfils these conditions. The available methods for fossil-free energy production, like waste heat, solar and wind energy, are however intermittent due to its dependence on weather and industrial conditions. A solution to the intermittent problem is to store the energy when available. Energy-storages are therefore key in finding ways to handle the ever-larger percentage of waste, solar and wind power in energy systems. The project group of Sunflake Technologies AB (SFT) and Ahlstrom-Munksjö Paper AB (AM) has developed and patented a novel method to integrate energy storage material (calcium hydroxide) into fibre material that make it possible to store thermal energy as long as required. Small scale test (performed by Sunflake team) revealed that this composite energy storage material is sustainable at least during 150 cycles and does not degrade. During previous joined project (2019-2020) we have as well demonstrated that this energy storage composite material can be produced using AM industrial line. The tested material was based on powder type calcium hydroxide that created production and environmental challenges like powder leak during conveyer fabrication, the powder created dusty pollutions of air and difficulties with recuperation of unused materials. Therefore, a new and novel approach is under urgent demand.

The overall goal and expected result for this project is to successfully produce graphene encapsuled granulated calcium hydroxide as energy storage material, to build a demonstrating pilot plant with heating power of 6 kW and energy storage potential of 20 kWh, prove the sustainability of this novel energy storage composite material, and integrate the pilot into Energy House at ETC/ Katrineholm at our customer facility.

This pilot plant will be used as a demonstrator as energy storage potential for energy entities like SSAB, Vattenfall, Vestas and other potential partners from industry and energy sector, determine conditions for mass production of the novel graphene encapsuled material. The development in this proposal will provide the foundations to materialize our long-term vision and impact not just in development and technology, but also in society economy and in the partners' future leadership.

The dissemination and exploitation of our concept will catalyse the transfer of knowledge to industries and sectors with an appetite for innovation, creating an impact on development and technology, paving the way to a new technology that breaks with the established energy storage conventions. It brings a solution for energy storage renewable integration and adapts to fulfil the required needs of the selected application such as building, solar energy or industry.

Impact on society, this project is framed on a social duality, triggering society awareness of humankind contribution to climate change and, simultaneously, driving a solution to help transition to a low carbon economy by implementing our novel approach. The new energy storage diversified market will transfer into the end user at the same time the opportunity and the responsibility of selecting the energy source. This system will push together with the rest of driving forces to meet the energy consumption and CO_2 emissions reduction targets (Paris agreement and the EU action 2030 Climate and energy framework). This new technology will strengthen European industrial technology and specifically address the social challenge of “Secure, Clean and Efficient Energy” where advanced energy technologies are a crucial element of climate change mitigation and secure energy supply.

Impact in economy, the project will deploy a technology able to store heat and transform resources into energy-profitable revenues. The industrial and environment relationship: - The sustainable thermal energy storage (STES) will convert electricity to heat and heat to heat or electricity when required. The storage period is not limited. - Both solar/wind energy and waste heat can be stored and subsequently used for example for district heating or electricity production.

Genomförande

I. 200 kg of granulated calcium hydroxide were produced in collaboration with Nordkalk AB with the following properties: average particle size: 3,0±1,0 mm; material density: 856,6 kg/m^3, energy storage capacity: 354,4 kWh/m^3. Graphene was supplied by 2Dfab. Graphene encapsulation of granulated calcium hydroxide was successfully accomplished with low shear stress method that had been developed as a further progress and improvement of the patent: Dmitri Glebov & Göran Bolin US9459026B2. This method is fully scalable and cost effective. The optimum graphene encapsulation composition was experimentally determined and verified via cycling (hydration/dehydration) of samples and measurement of steam absorption dynamic. The steam absorption dynamic is directly related with heating power of the material: power in/power out. The greater steam absorption rates will practically result in greater power output in thermal energy storage application. Steam absorption rates measurements, scanning electron microscopy and BET analyses revealed that graphene encapsuled samples demonstrated 25% greater steam absorption rates compared with graphene-free reference material. Furthermore, cycled samples demonstrated an improvement of steam absorption rates both for graphene encapsuled and graphene-free samples. *Further competence building* made it possible to explain the mechanism of graphene encapsulation enhancement and supported by scanning electron microscopy and BET analyses.

The integration of graphene encapsuled granulated calcium hydroxide at Ahlstrom-Munksjö AB production is planned during Q4 2022.

II. The thermal energy storage pilot prototype was built, and the following steps were accomplished:

- Technical calculations: energy- and mass- balances, heat transfer dynamic, hydraulic calculations and pressure drop
- Piping and Instrumentation diagram (P&ID)
- Bill of materials (BOM list)

- Specification and delivery of components
- Specification and delivery of measuring equipment
- CAD-drawings and 3D CAD-models
- Electric specification and control box assembly
- Assembly of the pilot
- Insulation
- Components tests
- Power in/power out tests
- Delivery to the customer (ETC AB /Katrineholm)

The pilot has energy storage capacity of 18,5 kWh and 4,8 kW average discharge power.

III. The road map for mass production of our novel and graphene encapsuled TESM was taken forth. Strategic partners and customers (stake holders) were determined:

Nordkalk (partner company): is a global supplier of different lime products.
Ahlstrom-Munksjö (collaboration and strategic partner): is a global company manufacturing tailor-made composite materials.
Sigma Energy (collaborative partner): is a leading Swedish consulting company with experience in CAD-drawings, CAD-models, electric layouts, mechanical design, and safety.
MAVAB (collaborative and strategic partner): is a Swedish leading manufacturing company of customer-ready containerized equipment.
2Dfab (collaborative and strategic partner): is a Swedish leader in graphene supplier.
Absolicon (strategic partner and customer): is a European leader in manufacturing of solar driven and green solutions for thermal energy management.
ETC El (strategic customer): is a Swedish leading company for construction of residential houses integrated with green thermal energy storage solutions.
Pluss Advanced Technologies India (collaborative and strategic partner): is Indian leader in manufacturing of thermal energy storage materials for different temperature ranges and applications.

Sunflake Technologies AB has carried out an intensive work to determine companies that will supply key-components for thermal energy storage systems. The core business idea is to use standard components that don't require an extra development work.

Resultat

- Low shear stress encapsulation method was developed and verified as a further progress improvement of the patent (US9459026B2). The method is scalable and cost effective. The optimum graphene composition was determined via direct measurements of steam absorption rates and supported with BET analyses and SEM. The measurements of hydration rates reveal 25% improvement for graphene encapsuled materials compared to graphene-free reference.
- Further competence building in thermal energy storage material made it possible to explain the mechanism of enhancement associated with graphene encapsulation.
- The thermal energy storage pilot prototype was built, verified, and delivered to the customer.
- The road map for mass production of thermal energy storage material was taken forth. Key partners, stake holders and potential customers were determined. Key-components delivery network was developed.

Diskussion

The reversible reaction of calcium oxide hydration to calcium hydroxide has since more than 20 years been a candidate for thermal storages due to the abundance of the material, its low cost and high energy density,

$$CaO \;+\; H_2O \leftrightarrow Ca(OH)_2 \;+\; 109{,}48\, kJ/mole \qquad (1)$$

corresponding to 354,4 kWh/m^3 of calcium hydroxide. The energy storage capacity is more than two times greater compared to electric batteries but at much lower cost.

Generally, thermochemical energy storage materials have a specific energy that is approximately eight to ten times higher than sensible heat storage an energy density from five to ten times higher than PCMs. The main technical challenge to deploy thermochemical energy storage material on industrial scale is that the material agglomerates after number of cycles. The agglomeration of the reactants not only leads to a high-pressure drop in a directly operated reactor but also affects the heat and mass transfer performances in the reaction bed, which leads to a reduction in the energy conversion and the cyclability, and hence a lower performance.

Our novel and breakthrough approach is based on the idea of graphene encapsulation of granulated material instead of using powder type substance. Graphene encapsulation of granulated calcium hydroxide was successfully accomplished with low shear stress method that had been developed as a further progress and improvement of the patent: Dmitri Glebov & Göran Bolin US9459026B2. The method is fully scalable and cost effective. Digital microscope USB X1600 was used to investigate the surface structure of test samples. Microscopic investigation of the surface structure revealed that graphene encapsulation is uniform over entire granulate surface.

The optimum graphene composition was determined experimentally by direct measurements of hydration rates / steam absorption rates. *Hydration dynamic directly corresponds to heat power out / power in for every test sample.* Grater values of steam absorption rates correspond to greater heat production (power out / power in) in industrial applications as well. It was experimentally proven that graphene encapsuled samples revealed 25% greater steam absorption rates than graphene-free reference material.

Further thermal energy storage material competence building made it possible to explain the mechanism of graphene encapsulation enhancement. The hydration process consists of number of stages. At the first stage steam molecules should reach the surface of calcium oxide. This stage is driven by steam convection and therefore not limited. At the second stage the steam molecules diffuse via cracks and small capillaries and micro/nano pores inside the granulated particles and then react with calcium oxide, forming calcium hydroxide according to chemical formula (1). The diffusion of steam molecules via small sized channels (<< 1 micron) is driven by collisions between the molecules and channel boundaries rather than between like and unlike gas molecules. This free molecule flow, or Knudsen diffusion[2], is much slower than diffusion in cracks where the steam flow is still driven by convection. The permeability of steam inside calcium oxide particles is faster via cracks than via micro channels, therefore the diffusion of steam inside micro channels is not determining for hydration process and large channels and cracks took over the hydration process dynamic.
Graphene, due to its atomic properties, is obviously more "attractive" for infrared waves that are responsible for heat transfer by radiation[3]. The heat transfer dynamic inside graphene encapsuled samples is greater due to greater radiative heat transfer. Graphene encapsulation triggers the formation of cracks therefore enhancing the hydration dynamic. *More intensive temperature rise for graphene encapsulated sample will result in more effective power in/ power out dynamic that is important for thermal energy storage applications.*

The integration of graphene encapsulated TESM into fibre-based composite at Ahlstrom-Munksjö production facility in PontEvêque (France) is planned to start Q4 2022. A-M was not able to deliver the material during Q4 2021 due to pandemic situation in France. The thermal energy storage pilot prototype was built, tested, and delivered to the customer during Q1-Q2 2022 despite of challenges caused by global pandemic situation.

The pilot has energy storage capacity of 18,5 kWh and 4,8 kW average discharge power. The road map for mass production of thermal energy storage material was taken forth. Key partners, stake holders and potential customers were determined. Key-components delivery network was developed. Sunflake Technologies AB has carried out an intensive work to determine companies that will supply key-components for thermal energy storage systems. The core business idea is to use standard components that don't require an extra development work.

Publikationslista

Inga kommande publikationer

Referenser, källor

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2. Knudsen flow through a porous medium, J. The Physics of fluids, 11, 2544 (1968).
3. Aksel L. Lydersen "Fluid flow and heat transfer" 1979.