Energimyndigheten

Datum
20191218

Dnr

Projektnr
35509-2

Energimyndighetens titel på projektet – svenska Termoeletriska polymerer	
Energimyndighetens titel på projektet – engelska Polymer thermoelectrics	
Universitet/högskola/företag Linköping University	Avdelning/institution Laboratory Organic Electronics
Adress Bredgatan 34, Norrköping	
Namn på projektledare Xavier Crispin	
Namn på ev övriga projektdeltagare	
Nyckelord: 5-7 st organic electronics, thermoelectrics, electrochemistry, electrolyte	

Förord

The project has been financed mostly by the Swedish Energy Agency. However, due to the multidisciplinary character and the width of the project, part of the researchers involved in the project have been financed by The European Research Council, and the Advanced Functional Material Center at Linköping University.

Innehållsförteckning

Sammanfattning

Solen är vår största förnyelsebara energikälla, tillräckligt stor för att kunna svara upp mot världens allt större behov av elektricitet (cirka 13TW år 2012, cirka 26 TW år 2050). Instrålningen vid jordytan uppgår till cirka 105 TW varav 600 TW kan utnyttjas i praktiken. Den effektivast möjliga omvandlingen av solenergi till elektricitet, via solvärmeanläggningar eller solceller, beräknas ligga på 40 procent, vilket innebär att en stor mängd värmeenergi förblir oanvänd. Termoelektriska generatorer kan dock omvandla en del av denna värme till elektricitet.

Box 310 • 631 04 Eskilstuna • Besöksadress Kungsgatan 43
Telefon 016-544 20 00 • Telefax 016-544 20 99
registrator@energimyndigheten.se
www.energimyndigheten.se
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Idag sker en stor del av elproduktionen från fossila bränslen och kärnkraft, medan mängden elektricitet producerad från solenergi är i det närmaste försumbar. Omvandlingen av primära energikällor till el eller mekaniskt arbete, i form av transport, elproduktion eller processindustri, innebär i samtliga fall stora förluster av värme, upp till 60 procent. Omkring 50 procent av spillvärmen lagras i stora volymer varma vätskor (under 250°).

De termoelektriska generatorerna skulle kunna erbjuda en kostnadseffektiv lösning på Rankinecykeln. I dagens termoelektriska generatorer för lågtemperaturomvandling används dock legeringar av vismut, antimon och tellur. De är alla grundämnen som är sällsynta i naturen och som därmed är dyra och ofta också skadliga för miljön. Med dagens teknik är en storskalig användning av termoelektriska generatorer därför otänkbar.

Med min forskning, har vi hittat effektiva organiska termoelektriska material och därmed också kunna utveckla termoelektriska generatorer som omvandlar såväl solvärme som spillvärme till el. De organiska materialen kan också syntetiseras i lågtemperatur- och/eller lösningsbaserade tillverkningsprocesser till relativt låga kostnader, vilket gör de organiska termoelektriska generatorerna väl lämpade för massproduktion.

Summary

At the moment, there is no viable technology to produce electricity from natural heat sources and from 50% of the waste heat stored in large volume of warm fluids ($T<200°C$). To extract heat from large volumes of fluids, the thermoelectric generators (TEGs) need to cover large areas in heat exchangers, but no efficient thermoelectric materials exist with atoms of high natural abundance and low manufacturing cost.

As a result of the previous two granted projects, the applicant has made two breakthroughs: Firstly, conducting polymers constitute a new class of thermoelectric materials. Secondly, conducting polymers can be semimetallic and this is a prerequisite to be good thermoelectric polymers. The solution processability, mechanical flexibility and intrinsic low thermal conductivity of conducting polymers motivated us to explore further the potential of polymers in thermoelectric applications.

The results are divided in four parts: (i) the ionic Seebeck effect; (ii) the electronic Seebeck effect, (iii) thermoelectric effect in mix electron-ion conductors, (iv) the thermogalvanic effect. These investigations have provided various strategies to further improve the thermoelectric efficiencies of polymers, as well as allow us to propose new device concepts such as thermoelectric supercapacitors, all-polymer thermogalvanic cells.

Inledning/Bakgrund

The sun is the largest readily available renewable energy source potentially capable of meeting the growing worldwide demand in electricity (~13TW in 2012, ~26TW in 2050). Its irradiating power at the surface of the earth is ~ 105 TW, 600 TW of which could be practically used. The maximum conversion efficiency of solar energy into electricity via solar thermal plants or solar cells is estimated at 40%, whereas a large amount of energy in the form of natural heat remains unused. Heat can be transformed into electricity quietly and environment friendly through thermoelectric generators (TEGs). TEGs are electronic devices without mechanical parts to wear out. In years to come, depending on the population growth and climate conditions, the integration of solar cells and TEGs technologies shall be considered as one of the essential parts of more efficient global energy conversion. As for now, the electricity production largely relies on fossil fuels and nuclear energy, while the fraction of electricity produced by solar energy is negligible. The transformation of these primary energy sources into electricity or mechanical work (transport, electricity production, process industries) accompanied by substantial heat loses (~60%). About 50% of the waste heat is stored in large volume warm fluids (T<250°C) and as yet no viable technology exists to produce electricity from this low energy density heat. Thermoelectric generators could offer a complimentary solution to Rankine cycles. Today's thermoelectric materials of choice for low temperature energy conversion are bismuth antimony telluride alloys. The constituting atomic elements have a low natural abundance and therefore expensive. Additionally, low natural abundance goes hand in hand with some level of toxicity for the environment. Thereby, in today's scenario it is unthinkable to enable a widespread use of thermoelectric installations for waste heat recovery. The overall goal of my research is to find efficient organic thermoelectric materials and device concepts to harvest electricity form solar heat and waste heat. The synthesis of organic materials can be readily scale-up for mass production of organic thermoelectric devices at relatively low-cost via low-temperature and/or solution-based manufacturing processes.

Genomförande- Resultat

We have gathered a team covering the interdisciplinary aspects: solid state physics, polymer chemistry, theoretical modelling, device physics, electrochemistry. We have built up appropriate experimental set-up that are not on the market. People involved: Xavier Crispin, Dan Zhao, Zia Ullah Kahn, Hui Wang, Anna Håkansson, Ujwala Ail, Kosala Kosala Wijeratne.

-Electronic Thermoelectric Generators: The power factor of conducting polymers has been optimized through control of the oxidation level, through control of the morphology and crystallinity, through control of the chemical structure. We optimize both n-doped and p-doped polymer thermoelectrics. We get world record values for power factor both n- and p-doped polymers. We discover a relationship between Seebeck coefficient and the degree of molecular order in the polymer. We succeed to create a strategy to get thick layer of highly conducting polymer generator with record high value in power per area.

Combined Electronic and Ionic Thermoelectrics: We demonstrate the peculiar effect of combined thermodiffusion of electron and ion in conducting polymers. We show that following the thermovoltage versus time is a good method to distinguish of the nature of the conductor: electron-only, ion-only or mixed ion-electron. Such an effect has been used within another project to create unique polymer thermoelectric aerogels that are sensors for temperature, humidity and pressure.

Electricity generation from thermodiffusion of ions: We demonstrate a giant Seebeck effect with ions in polymer electrolyte. We use that advantageously to charge a supercapacitor with heat, to send heat signal transformed in electric signal through a transistor, to create ultra-sensitive ionic thermopile. This is a unique new technology that we have patented.

Polymer thermogalvanics: We have demonstrated that it is possible to use a polymer electrode in thermogalvanic cells, which are electrochemical device that generated constant electrical power under a temperature gradient. This led us to study the fundamentals of the electron transfer from a polymer electrode and a redox molecule in a solution. We identified that the electron transfer at the electrode-electrolyte interface is governed by the density of percolation paths for the electronic transport in the bulk of the electrode.

Diskussion

The electronic thermoelectric effect in polymers is still scrutinized and that research field is increasing significantly with new world record every years. It is thus encouraging and it will certainly lead to new technologies. The first technologies that will be created are powering with heat the electronics of internet of everything. Also, our demonstration of ionic thermopile led to the world most sensitive sensor for heat fluxes and temperature. It has the potential to replace commercial pyroelectric sensors. Now, the most exciting part is related to the observation of giant ionic Seebeck effect in polymer electrolyte. We do not yet understand fully the mechanism, but it is unexpected. This leads to new possibility to harvesting solar energy and charge energy storage device. In this project, we demonstrated that with charging a supercapacitor but we are now considering charging batteries with heat. This is thus very complementary to solar cells since charging can be during daytime and discharging during nights. I think we are just touching the top of the iceberg in this new research field. Beside that the thermogalvanic cells are easy to manufacture but their efficiency is difficult to defend compared to other thermoelectric technologies.

Publikationslista

1-10

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11. Thesis: Conducting Polymer Electrodes for Thermogalvanic Cells, by Kosala Wijeratne, 2018, ISBN 978-91-7685-156-2

Bilagor

- *Administrativ bilaga*

Energimyndigheten

Datum
20191219

Dnr

Projektnr
35509-2

Projektledare
Xavier Crispin
Projekttitel
Polymer thermoelectrics

Administrativ bilaga till Slutrapport

Uppföljning av måluppfyllelse och nyttiggörande

I samband med att ni lämnar in slutrapport för ert projekt ska också denna blankett fyllas i och läggas som bilaga till slutrapporten.

Denna blankett riktar sig till Energimyndigheten, och visas *inte* i vår externa projektdatabas.

Syftet med blanketten är att följa upp projektets måluppfyllelse enligt Energimyndighetens beslutsdokument, eventuella avvikelser i projektets måluppfyllelse och genomförande samt vad projektet har gjort/kommer att göra för att projektets resultat ska komma till gagn för övriga samhället. Samtidigt följer vi också upp ett antal generella indikatorer som Energimyndigheten följer för de projekt vi stödjer.

Detta dokument ska skickas in som en bilaga till slutrapporten via E-kanalen.

1. Projektets måluppfyllelse

a) Vilka var projektets mål (enligt Energimyndighetens beslutsdokument)?

To investigate the possibility to convert heat into electricity with polymer thermoelectrics and new concepts of thermoelectricity.

The thermal energy wasted in the form of heat from burning fossil energy is 60% of the source of energy. Only 40% is used for mechanical work or electricity production. Hence, the amount of waste heat is enormous. Moreover, there is another heat source of importance: the sun. So, if it is possible to create use only few percent of that heat unused into electricity, this could have some impact. Here we investigate the possibility to use abundant organic materials for converting heat into electricity.

Box 310 • 631 04 Eskilstuna • Besöksadress Kungsgatan 43
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b) Hur förhåller sig projektets resultat till projektets mål?
För vart och ett av projektets mål, redovisa de viktigaste resultaten och bedöm i vilken utsträckning och/eller på vilket sätt dessa bidrar till att projektets mål uppnåtts eller kan komma att uppnås. (Exempel: Om projektets mål var att fram en prototyp av ett visst slag som sparar x kWh jämfört med en viss annan teknik, berätta hur många kWh som faktiskt sparas med den teknik som tagits fram inom projektet jämfört med den referensteknik som angavs i målet).

We discovered that organic polymers display thermoelectric properties when conducting either electrons or ions. We developed two strategy to harvest the electricity: a generator producing constant power as long as there is a temperature different between hot and cold electrode of the device; and an non-constant producing device that can be appropriate for intermittent heat sources such as the sun: day and night cycles. The thermoelectric figure of merit found with our material is modest ZT=0.25 at room temperature, which means maybe 1% of conversion from heat to electricity at decent temperature gradient that can sustain those materials. From the beginning of our project, we have inspired a whole research community to search for new organic thermoelectric materials, so it will be interesting to see what will happen in the coming years. But at the moment, we are in the percent of energy conversion with those materials. Other more expensive materials, such as BiTe alloys, are more efficient but the limited natural abundance of those materials does not make possible any major implementation of that technology. In contrast, our proposed materials are composed of atomic elements of high abundance and thus very cheap. So, even if the conversion efficiency is lower, it might be viable to make business out of it.

To project that in numbers, the production of electricity from Sweden is mostly from nuclear power (75TWh/y) and hydro (70TWh/y) and little from fossil energy (4TWh/h). From non-renewable energy sources, waste heat for electricity production (average efficiency about 60%) amounts 118TWh/y. Although efforts are made to use the waste heat for co-generation of electricity, efficient installations are not common over the country and low temperature waste heat is still difficult to use (besides local district heating). Although, the actual energy lost in waste heat for Swedish nuclear plants are not easy to find, it could be at least 60TWh/y.

In Sweden, the industrial waste heat is produced mostly from process industries (50% from the paper industry, 20% from the chemical industries, 20% from refinery). The association of "Svensk Fjärrvärme" has delivered a report in which low temperature industrial waste heat is estimated to be about 8 TWh/y. Note that Fjärrvärme system has an issue during the summer that the water cannot be cooled down since no buildings need heating. Hence cooling could be achieved via heat exchangers functionalized with TEGs.

Another major source of waste heat is from transportation. In an engine 60% of the fossil energy (oil, biofuel, etc…) is lost in heat in the exhaust pipes and radiators. The Swedish oil consumption is 328100 bbl/day (=192 TWh/y), 50% is used for transportation. Hence the waste heat from transportation is 56TWh/y (30% in exhaust pipe, 20% in radiator).

Hence, a first estimate of an order of magnitude for the total waste heat in Sweden amounts at least 100TWh/y. Hence, assuming we produce massively and implement the polymer thermoelectrics everywhere there is waste heat, we can expect a production of electricity of 1 TWh/y extra from that waste heat. Of course, this does not consider if the challenge to implement the technology.

2. Kommentera eventuella betydande avvikelser i projektets måluppfyllelse och/eller genomförande i förhållande till Energimyndighetens beslut om stöd till projektet

Om projektet inte nått målen eller om betydande förändringar gjorts i projektets genomförande jämfört med projektbeslutet, motivera detta. Beskriv också vad som har gjorts för att motverka dessa avvikelser.

The project has reached the goal.

3. Spridning och nyttiggörande av resultatet i samhället

a) Hur har projektet arbetat för att sprida projektets resultat och/eller på andra sätt se till att det kommer till nytta? Vilka eventuella ytterligare aktiviteter kommer att göras framöver?
Beskriv projektets genomförda och planerade kommande aktiviteter för att sprida projektets resultat och/eller på andra sätt se till att det kommer till nytta i samhället. Berätta också om ni har förslag på resultat som ni eventuellt skulle vilja kommunicerades genom Energimyndighetens kanaler (genom nyhet, information riktad till Energi – och klimatrådgivare etc), och föreslå i så fall gärna hur detta skulle kunna göras.

Conferences, scientific publications, press releases. We have contributed significantly to the creation of a new research community for “organic thermoelectrics”. This community is growing and has its own conferences and symposium in major conferences (such as E-MRS, MRS, …).

b) Har eller planeras projektet resultera i några patent eller andra bevis på rättigheter till resultat, eller några ansökningar om detta? Om bevis på rättigheter till resultat tagits ut eller ansökningar planeras, vem äger/har nyttjanderätt till dessa?
Beskriv detta i så fall här.

Thermoelectric device

Patent number: 10211385

THERMOELECTRIC DEVICE

Publication number: 20130276851

THERMOELECTRIC DEVICE

Publication number: 20130276850

4. Eventuella bilagor till rapporten som inte ska visas i Energimyndighetens externa projektdatabas

a)	Innehåller slutrapporteringen bilagor som inte ska visas i Energimyndighetens externa projektdatabas? Slutrapporten ska alltid kunna visas i Energimyndighetens externa projektdatabas. Däremot visas inte denna Administrativa bilaga i projektdatabasen. Innehåller slutrapporteringen andra bilagor som inte ska visas i Energimyndighetens externa projektdatabas? ☐ Ja ☒ Nej
b)	Om ”Ja” i frågan ovan, vilka bilagor gäller det? Skriv filnamnen på eventuella bilagor till slutrapporten som inte ska publiceras externt här. Bilagor som inte ska publiceras externt ska märkas upp genom att ”KÄNSLIG INFORMATION” skrivs in i dokumentets rubrik. Alternativt kan dokumentet vattenstämplas med ” KÄNSLIG INFORMATION”. Dessutom ska i filnamnet läggas in orden ” KÄNSLIG INFORMATION”.