Physics of ZnO/SiO$_2$ electrolyte semi-conductive thermal electric generator

Ataur Rahman*, Kyaw Myo Aung, Khalid Saifullah, Mizanur Rahman

Department of Mechanical Engineering, Faculty of Engineering, International Islamic University Malaysia, 50728 Kuala Lumpur, Malaysia

**Abstract**

Thermoelectric generator generates electrical power from heat based on the temperature gradient. The total energy (fuel) supplied to the engine, approximately 30 to 40% is converted into useful mechanical work, whereas the remaining is expelled to the environment as heat through exhaust gases and cooling systems, resulting in serious greenhouse gas (GHG) emission. The technologies reported on waste heat recovery from exhaust gas of internal combustion engines (ICE) are thermo electric generators (TEG) with finned type, Rankine cycle (RC) and Turbocharger by the different researchers. The deficiency and acclimatization of existing TEG emphasis this study to develop a nanomaterial zinc oxide (ZnO)/Silicon di-oxide (SiO$_2$) electrolyte based semi-conductive thermal electric generator (TEG) to generate electricity from the IC engine exhaust heat. This technology produces electricity from the exhaust heat due to the thermal motion, carrier drift and carrier diffusion. The ZnO/SiO$_2$ simulated result based on the 60% of exhaust heat of IC engine shows that its electrical energy generation is about 80% more than conventional TEG for the exhaust temperature of 500°C due to its higher thermal and electric conductivity and higher surface area both in radially and longitudinally. The ZnO/SiO$_2$ electrolyte semi-conductive technology develops 524W to 1600W at engine speed 1000 to 5000 rpm, which could contribute to reduce the 10-12% of engine total fuel consumption and improve emission level by 20%.

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1. Introduction

Thermoelectric materials generate electric power directly from heat by converting temperature differences into electric voltage due to their high electrical ($\sigma$) and low thermal conductivity ($\kappa$). Having low thermal conductivity ensures when one side is made hot, the other side stays cold, which helps to generate a large voltage for temperature gradient ($\Delta T$) causes are drift and diffusion. The measure of the magnitude of electrons flow in response to a temperature difference across that material is given by the Seebeck coefficient ($S$). The resulting voltage ($V$) is proportional to the temperature difference ($\Delta T$) via the Seebeck coefficient, S, (i.e, $V = S \Delta T$). By connecting an electron conducting (N-type) and hole conducting (P-type) material in series, a net voltage is produced that can be driven through a load. A good thermoelectric material has a Seebeck coefficient between 100 $\mu$V/K and 300 $\mu$V/K; thus, in order to achieve a few volts at the load, many thermoelectric couples need to be connected in series to make the thermocouple device to make the thermoelectric device. The large amount of energy from the stream of exhaust gases could potentially be used for waste heat recovery to increase the work output of the engine (Stobart et al., 2010). Hatazawa et al. (2004), Stabler (2002), Yang (2005), and Yu and Chau (2009) stated that the waste heat produced from thermal combustion process generated gasoline could get as high as 30-40% is lost to the environment through exhaust pipe. Conklin and Szybist (2010) investigated that the percentage of fuel energy converted into useful work only 10.4% and also found that 27.7% energy lost through exhaust pipe. Dolz et al. (2012) reported that the value of exhaust gases is 18.6% of total combustion energy. The IC engine waste energy of IC engine can be recovered about 15% by using waste energy harvesting coolant based (weHS) and exhaust based (weHS*) as an integrated unit (Rahman et al., 2013; 2015). Thermoelectric...
materials can capture some of this heat, and produce electricity. Stobart et al. (2010) explored the possibility of thermoelectric generator (TEG) in vehicles in which they found that the 1.3 kW output of thermoelectric device could potentially replace the alternator of small vehicle. Therefore, the load on the engine is reduced thereby improving fuel efficiency by as much as 10% and requires the temperature gradient at least 500°C. An increase of 20% of fuel efficiency can be easily achieved by converting about 10% of the engine waste heat into electricity (Saidur et al., 2010; Yang, 2005). Yu and Chau (2009) have proposed and implemented an automotive thermoelectric waste heat recovery system by adopting a maximum power point tracking (MPPT) controller as tools for power conditioning and transfer. Homm and Klar (2011) have compared several classes of TEG materials in terms of efficiency and material abundance, including the base materials of Bi₂Te₃, PbTe, SiGe, Fe₃Si, and ZnO etc., and concluded that ZnO related oxide materials are ideal for stationary mass production and applications due to their large earth abundance (thereby low cost) and environmental friendliness.

The aim of this study is to develop a waste heat energy conversion technology with zinc oxide (ZnO) and silicon dioxide (SiO₂) electrolyte sandwiching by boron doped silicon (N-type) and phosphorus doped silicon (P-type) semi-conductive elements to increase the engine efficiency by 10-15%.

2. Methodology

2.1. Preparation of ZnO / SiO₂ composite electrolyte

ZnO/SiO₂ nano-composite electrolyte has been prepared based on the combination of the nitrate / citrate sol/gel self-combustion technique (Cannas et al., 2006; Amedda et al., 2008). Two separate solutions have been prepared. 1st solution, 10 ml of ethanol (96%) and 10 ml of tetrathoxysilane (TEOS) (98% Aldrich) were mixed and stirred for 10 min in a beaker and kept in oven at 50°C for 16h. 2nd solution, 1.039 g of citrate acid (99%, Aldrich) in 2 ml water. The molar ratio equals to 3:2 and adjusting the pH at 4.0 by addition of ammonia (30%, Carlo Erba). The amount of zinc nitrate and TEOS were chosen so as to get 10 wt% of ZnO in the nano-composite. In the second step, the aquous solution was slowly added to the TEOS-ROH sol, together with 6 ml of ethanol at 50°C for 24 h. All the gel was heated with 350°C for 1 h and the heat treatment in the range of 500 – 700°C for 2 h. The final product was collected as the ZnO/SiO₂ nano composite electrolyte.

2.2. Model of the ZnO/SiO₂ energy generator

The main focus of this study is to generate electricity by converting heat energy of exhaust. The hollow cylindrical ZnO/SiO₂ electrolyte semi-conductive energy conversion technology has been developed Fig.1(a) from this study, which consists of a single cylindrical thin layer of P-type (phosphorus doped silicon) and N-type (Boron doped silicon) semi-conductive material that are connected with an ultra-capacitor. A coolant jacket with the generator uses to increase the temperature gradient. Heat carries the majority electron through the ZnO/SiO₂ composite P-type to N-type semiconductor surface and produces electrical power due to the drift and diffusion. The ZnO/SiO₂ electrolyte is considered as electron contributor based on its ionic and thermal properties due to the diffusion of interstitial G0, which is expected to enhance the ionic and thermal conduction of the technology.

2.3. Mathematical model

The geometry Fig. 1(b) shows the example of the exhaust pipe system with the thermoelectric generator with ZnO/SiO₂ based nanomaterial-thermal-diffusive-electrolyte based super-capacitive materials phosphorus and boron doped silicon.

Consider steady, one dimensional heat flow through walls in series, which are exposed to convection on both. The heat flux for the generator can be formulated as (Eq. 1).

\[ Q = \frac{T_1 - T_2}{R_{total}} = \frac{T_1 - T_2}{R_{cond,1} + R_{cond,2} + R_{cond,3} + R_{cond,4} + R_{conv,2}} \]

where, \( Q \) is the exhaust heat, \( T_2 \) is the exhaust temperature, \( k \) is the conductivity, \( h \) is the heat transfer coefficient for convection. Based on the Fig. 1 model of ZnO/SiO₂ composite electrolyte semi-conductive generator.

![Diagram of ZnO/SiO₂ composite electrolyte semi-conductive generator](image-url)
1(b). A is the surface area of the hollow part of cylindrical generator, \(A_a = 2\pi L(r-a)\), \(A_{1(g)}\) the area of SiO\(_2\) layer, \(A_{5g} = 2\pi L(r_1-r)\), \(A_{5g}\) the area of the layer of P-type SC material, \(A_{3g} = 2\pi L(r_2-r)\), \(A_{3}\) the area of the ZnO/SiO\(_2\) composite, \(A_{0} = 2\pi L(r_3-r)\), \(A_{4g}\) the area of the layer of N-type SC material, \(A_{4g} = 2\pi L(r_4-r_3)\), and \(A_{5g}\) the area of the coolant jacket, \(A_{5g} = 2\pi L(r_4-r_3)\). The heat flux due to conduction (\(\text{cond}\)) can be formulated as:

\[
Q_{\text{cond}} = q_r A \left( -k \frac{dT}{dr} (2\pi L) \right) w/\text{yr} \frac{dT}{dr} = \frac{C}{r}
\]

where, \((r_x-r)\) is the radial distance of the layer of SiO\(_2\), P-type, ZnO/SiO\(_2\) and N-type. Temperature affects the properties of electronic devices. The most fundamental of properties is the energy band gap, \(E_g\), which is affected by temperature according to the Varshni (1967) Eq. 2:

\[
E_g(T) = E_{g(30K)} + E_{g(0)} - \frac{\alpha g_e^2}{\tau e}\frac{T^2}{r_m}
\]

(2)

where, \(E_{g(30K)}\) is the band gap energy (3.17 eV) at 273 K, \(E_{g(0)}\) is the band gap energy of electrolyte with ZnO concentration (6.16 eV) by considering the \(E_{g(0)}\) for ZnO 3.37 eV at 273K (Mang et al., 1995) and SiO\(_2\) 6.47eV (Chelikowsky and Schlüter, 1997) assuming based on the concentration (ZnO 10\%), \(\alpha\) (6 \(\mu\)V/K) and \(\beta\) (90oV/k) are material-specific constant. Carrier densities affect electrical and thermal conductivity, and are a function of the effective densities of states in the appropriate band (conduction for N-type, valence for P-type), the Fermi energy level in the material (which is a function of temperature and dopant concentrations), and the temperature can be given as (Eq. 3),

\[
\begin{align*}
E_{\text{cond}} &= E_{\text{Fermi(0)}} + \frac{n_e e^{-\Delta x} x_{\text{cond}}}{\hbar^2} \\
E_{\text{Fermi(0)}} &= E_{\text{valance}} + \frac{n_e e^{-\Delta x} x_{\text{valance}}}{\hbar^2}
\end{align*}
\]

(3)

where, \(n\) is the electron density, \(h\) is the hole density, \(x_{\text{cond}}\) is the density of states in the conduction band, \(x_{\text{valance}}\) is the density of states in the valence band, \(E_{\text{cond}}\) is the conduction band energy level, \(E_{\text{valance}}\) is the valance band energy level, \(E_{\text{Fermi}}\) is the Fermi energy level (the top of the available electron energy levels at low temperatures), \(k=1.38\times10^{-23}\) J/K is the Boltzmann constant, \(E_{\text{cond}}\) the conduction band energy level (at higher temperatures a finite number of electrons can reach the conduction band and yield current, \(I\) and \(T\) temperature in K. The average energy \(E_{\text{avg}}\) per electron can be determined (Eq. 4):

\[
E_{\text{avg}}(T) = \frac{3}{5} E_{\text{Fermi(0)}} \left[ 1 + \frac{5\pi^2}{12} \left( \frac{kT}{E_{\text{Fermi(0)}}} \right)^2 \right]
\]

(4)

where, \(E_{\text{Fermi(0)}}\) distribution extends with increasing the temperature which is much more higher at the contact of the exact and lower at out surface of the generator. Since it is assumed that due to the presence of higher concentration of ZnO, the conduction electron in the generator surface is free. In this case the electron energy also called Fermi energy can be defined as, \(E_{\text{Fermi}} = (1/2) m^* v^2\), where \(m^*\) is the mass of electron (9.1 x 10^-31 kg) and \(v\) is the drift velocity, \(v = \mu E\) where \(E\) is the electric field intensity (V/cm) and \(\mu\) is the electron mobility (m^2/V.s), \(V\) indicates volt. The electron mobility gives rise to a conduction current of the generator, which is due to the movement of both electrons and holes of the semi-conductive elements. Consequently the more energy electrons in the hot end diffuse toward the cold region until a potential difference \(\Delta V\) is built up which prevents further diffusion. The temperature dependence of the carrier concentrations, mobility and diffusion coefficient affects the temperature behavior of the current densities \(J\) (Coulomb/m^2s), with the carrier densities defined as Eq. 5:

\[
J = \left[ \left( N_n \mu_n + N_p \mu_p + N_\alpha \mu_\alpha \right) E + \left( D_n \frac{\partial n}{\partial x} + D_p \frac{\partial p}{\partial x} + D_\alpha \frac{\partial \alpha}{\partial x} \right) \right]
\]

(5)

where, \('n'\) represents N-type, \('\alpha'\) for electrolyte and \('p'\) for P-type, \(\mu\) is the electron mobility of composite, \(D\) the diffusion coefficient and \(\rho\) the charge per unit volume (C/m^3), \(N_n\) and \(N_p\) are the number of free electrons of the N-type and electrolyte and \(N_\alpha\) is the number of free holes for P-type (hole) per unit volume, \(V\) is the concentration gradient (if there is no concentration gradient, there is no diffusion) \(V_n=dn_n/dx, V_p=dn_p/dx, V_\alpha=dn_\alpha/dx, \rho_n=+ Ne_n, \rho_p=- Ne_p, \rho_\alpha=N_\alpha e\) and \(e = 1.6 \times 10^{-19}\)C). The diffusion coefficient is estimated by using Einstein equation, \(D=\mu k T/q\), \(k\) is the Boltzmann’s coefficient, \(T\) is the temperature, \(k\) is the Boltzmann’s constant, and \(q\) is the charge. In room temperature about 300K, the electron mobility of Si, \(\mu_e = 1350\) cm^2/V.s, \(\mu_h = 750\) cm^2/V.s (assuming based on the concentration of GO), and the hole mobility, \(\mu_h = 480\) cm^2/V.s (Jeon and Burk, 1989). Based on Ohm’s law, the current density also can be defined as, \(j e = \sigma e\) where \(\sigma\) is the conductive of semi-conductive elements of the generator (S/m), \(\sigma = (N_n \mu_n + N_p \mu_p + N_\alpha \mu_\alpha)(e)\), where \(e\) is the absolute charge of single electron or hole. While, based on Coulomb’s law, electric field \(E\) induces by an isolated charge \(q\) at any point of the generator, \(E = q/(4\pi d^2)\), \(d\) is the thickness of the electrolyte and \(e\) is electrical permittivity of the semi-conductive material, \(e = e_t e_0\) where \(e_0\) is free space permittivity, \(e_t = 8.85 \times 10^{-12}\)F/m, and \(e_t\) is relative permittivity of electrolyte (\(e_t = 2.5\) considered for the electrolyte of the generator which is made with ZnO 30 vol\% and 70 vol\% of SiO\(_2\)), total charge, \(Q = j F e\) dv. In equation (6), the 1st part, the current density of the generator due to the drift velocity and 2nd part, the current density due to the diffusion caused by exhaust heat. Electron mobility is one of the main factors of electricity generation resulting in the temperature gradient.
The carrier mobility, $\mu$ (cm$^2$/V·s), describes the drift velocity of a particle in an applied electric field. Under small to moderate electric fields, $\mu = u/E$, where $u$ is the drift velocity, and $E$ is the electric field. Electron mobility has very complex temperature dependence, defined by the interplay of the four scattering parameters: phonon scattering $\mu_p$, surface roughness scattering $\mu_b$, bulk charge Columbic scattering $\mu_c$, and interface charge Columbic scattering joint (Chain et al., 1997). Each of these scattering parameters is related to the temperature of the composite (ZnO/SiO$_2$) and semi-conductive material and the effective transverse electric field, which is approximated (Sabnis and Clemens, 1979). The electric field $E$ for continuous charge distribution along the can be estimated by using Coulomb’s Law (Eq. 6):

$$E(L) = \frac{q}{4\pi \epsilon_0 r}$$

where, $E$ is the electric field in V, $q$ is charge (1.6x10$^{-19}$ Coulomb), and $r$ (or $r = r^2$) of the generator as stated in equation (1). The distance or the thickness of electrolyte (d) between the P-type and N-type semi-conductive component can be computed as (Eq. 7):

$$d = \frac{\varepsilon_0 A_s}{C} \text{ with } C = \frac{2\pi \varepsilon_0 L}{\ln(r_d/r)}$$

where, $C$ is the capacitance in F, $A_s$ is the surface area of the P-type and N-type component, $d$ is the distance between P-type and N-type and $\varepsilon_0$ is vacuum permittivity (8.85x10$^{-12}$F). The charging time of the P-type and N-type is computed by using the equation,

$$\tau_{DL} = \frac{\lambda_D d}{2D} \text{ with } \lambda_D = (\varepsilon \varepsilon_0 kT/Z^2 e^2 n_a)^{1/2}$$

where, $D$ is the diffusion coefficient and $\lambda_D$ is the Debye length, $Z_e = q$ is the mobile ion charge, $\varepsilon$ is the electron charge (1.6x10$^{-19}$ Coulomb), $\varepsilon$ is the relative dielectric permittivity and $n_a$ is the electron concentration. The Debye length is found approximate ~1 nm and $\tau_{DL} \ll 10^{-2}$ seconds. The current and emf develops by the generator due to the drift velocity and diffusion:

$$I = \left[ (N_p\mu_n + \mu_n\mu_e + N_p\mu_e)E + (D_n \frac{\partial n_p}{\partial x} + D_e \frac{\partial n_e}{\partial x} + D_h \frac{\partial n}{\partial x} \varepsilon_{Ah} \right]$$

Power dissipated in a conducting medium in presence of electric field $E$ based on Joule’s law,

$$P = E J dv = Q$$

where, $Q$ is the heat energy due to exhaust heat is modeled by Eq. 1, $J$ is the current density is model by Eq. 6. The medium contains of free electrons (N-type SC element and electrolyte) and hole with volume charge densities $\rho_{ve}$ ($\rho_{ve} = \rho_{ve} + \rho_{voe}$) and $\rho_{vb}$. The emf develops can be estimated as,

$$V = \frac{(R_x - T_{ex} R_{total})}{(N_p\mu_n + \mu_n\mu_e + N_p\mu_e)} E + (D_n \frac{\partial n_p}{\partial x} + D_e \frac{\partial n_e}{\partial x} + D_h \frac{\partial n}{\partial x} \varepsilon_{Ah})$$

where, $V$ is the emf, $T$ is the exhaust temperature, $T_0$ is the outlet temperature of the generator, and $R_{total}$ is the thermal resistance of the generator.

3. Result and discussion

A simple mechanical APDL coding series has been developed for the simulation. The coding has been used for all conditions of the concentration of ZnO/SiO$_2$ composite. The maximum composite thickness for the simulation has been considered 2 mm based on the thickness of the conventional TEG. The simulation study on the effect of engine speed (rpm) to the heat transfer in cylinder wall and the volumetric efficiency has been conducted by using GT-suite software. Combustion occurs about the same engine rotation at all speeds, so the time of intake and combustion is less at higher speeds. The less time for intake and ignition and less time for heat transfer per cycle, causes the engine runs hotter. Therefore, the wall of the cylinder becomes hotter which might affect the fuel lost. Conclusion is supported by Reitz (2012) who reported that up to 30% of fuel energy is lost to the wall heat transfer. Therefore, the exhaust temperature will be high and it could be in the range of 300 – 900°C. By observing the result of the electrical generate from the thermoelectric generator, we have determined the concentration of ZnO in the ZnO/SiO$_2$ composite to produce more electrical energy. The heat flux, thermal conductivity and electric conductivity for the ZnO/SiO$_2$-SC generator has been studied with considering the electrolyte (ZnO/SiO$_2$ composite) thickness in the range of 0.2-2mm thickness. The result shows that the heat flux and thermal conductivity has decreased significantly with increasing the thickness of the composite for the same concentration of GO. Heat flux decreases drastically when the thickness of the composite changes from 0.2 mm to 1.0 mm, which is about 390% while heat flux decreases smoothly about 101% when the electrolyte thickness has changed from 1 mm to 2.0 mm as shown in Figs. 2 and 3. The effect of cooling system has a major contribution on the generation of electricity by making the temperature gradient. Simulation result shows that the air cooling has higher contribution than the engine coolant.

Fig. 4 shows the temperature gradient of ZnO/SiO$_2$ at room temperature of 24°C for the air, R43a and liquid cooling approach. Fig. 5 shows the thermal conductivity of composite for the different percentage of ZnO. Results show higher percentage of ZnO has provided higher thermal conductivity.
Figs. 6 and 7 show the performance of ZnO/SiO₂ composite electrolyte in terms of conduction energy and voltage due to the increment of carrier parameters such as σ, D, and E. The conduction energy level (E_g) has decreased in non-linearly due to the increment of exhaust, which kept the enhancement of electron mobility. While the output of the generator in terms of voltage (V) increases with the increment of exhaust temperature and current density. The voltage increases with the increment of temperature could be due to the drift of electron and diffusion.

4. Conclusion

The following conclusion has been made based on the contents of the manuscript:

- The electrolyte (ZnO/SiO₂) causes of electrons contributor to the P-type due to the diffusion with the exhaust heat.
- The heat flux, thermal conductivity and electric conductivity for the ZnO/SiO₂-SC generator have been studied with considering the electrolyte (ZnO/SiO₂ composite) thickness in the range of 0.2-
2mm thickness. The result shows that the heat flux and thermal conductivity has decreased significantly with increasing the thickness of the composite for the same concentration of GO.

The development of ZnO/SiO2 TEG, which is an alternative approach, overcomes some of the practical challenges associated with long, thin silicon-nano-wire (SiNW) TEG. This more robust, has better area coverage and could be manufactured in a more scalable process than SiNWs. However, the major drawback until now has been that the nano-film geometry is far less effective at reducing κ and so TE performance might be less for nano-films than it is for SiNWs.

References


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