1. Introduction

Thermoelectric materials generate electric power directly from heat by converting temperature differences into electric voltage due to their high electrical (σ) and low thermal conductivity (k). 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 (ΔT) 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 (ΔT) via the Seebeck coefficient, S, (i.e., V = SΔT). 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 μV/K and 300 μV/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 vehicles. 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 tracker (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 tetraethylsilane (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 aqueous 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 semiconducting 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).

\[
\frac{Q}{R_{total}} = \frac{T_{in} - T_{out}}{R_{conv.1} + R_{cond.1} + R_{conv.2} + R_{cond.2} + R_{cond.3} + R_{cond.4}}
\]

where, Q is the exhaust heat, T_{in} is the exhaust temperature, k is the conductivity, h is the heat transfer coefficient for convection. Based on the Fig. 1.
1(b). A is the surface area of the hollow part of cylindrical generator, \( A_s = 2\pi L (r_2 - r_1) \); \( A_{sl}(s) \) the area of SiO\(_2\) layer, \( A_{sl}(s) = 2\pi L (r_1 + r) \), \( A_{sl}(s) \) the area of the layer of P-type SC material, \( A_{sl}(sl) = 2\pi L (r_2 - r_1) \), \( A_{sl}(tl) \) the area of the layer of N-type SC material, \( A_{sl}(tl) = 2\pi L (r_4 - r_3) \), and \( A_{sl}(c) \) the area of the coolant jacket, \( A_{sl}(c) = 2\pi L (r_3 - r_2) \). The heat flux due to conduction (\( Q_{cond} \)) can be formulated as:

\[
Q_{cond} = q_cT = \left( -k \frac{dT}{dr} (2\pi L) \right) \frac{dT}{dr} = \frac{C}{r}
\]

where, \( (r_2-r) \) is the radial distance of the layer of SiO\(_2\), P-type, ZnO/SiO\(_2\) and N-type. Temperature affects the properties of electronic systems. The most fundamental of properties is the energy band gap, \( E_g \), which is affected by temperature according to the Varshni (1967) Eq. 2:

\[
E_g(T) = E_g(273K) + \left[ \frac{\alpha E_g}{2} \right] (T - 273K)
\]

(2)

where, \( E_g(273K) \) 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\(_2\) 6.47 eV (Chelikowsky and Schlueter, 1997) assuming based on the concentration (ZnO 10%), \( \alpha_s(6 \mu V/K) \) and \( \beta_s(900\mu V/k) \) 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),

\[
E_{cond} = E_\text{Fermi}(0) + \frac{n_e e^{-\frac{\phi}{kT}}}{N_{cond}} \text{ with } E_\text{Fermi}(0) = E_\text{valance} + \frac{\phi e^{-\frac{\phi}{kT}}}{N_{valance}}
\]

(3)

where, \( n_e \) is the electron density, \( h \) is the hole density, \( N_{cond} \) is the density of states in the conduction band, \( N_{valance} \) is the density of states in the valence band, \( E_{cond} \) is the conduction band energy level, \( E_{valance} \) is the valence band energy level, \( E_{\text{Fermi}} \) is the Fermi energy level (the top of the available electron energy levels at low temperatures), k=1.38-10^{-23} J/K is the Boltzmann constant, \( E_{cond} \) 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 \( E_{av} \) per electron can be determined (Eq. 4):

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

(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, \( E_{\text{Fermi}} = (1/2) m_e \gamma^2 \), where \( m_e \) is the mass of electron (9.1 x 10^{-31} kg) and \( \gamma \) is the drift velocity, \( V = \mu e V \) 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\(^2\)s), with the carrier densities defined as Eq. 5:

\[
J = \left[ (N_n \mu_n + N_p \mu_p + N_e \mu_e) E + \left(D_n \frac{\partial N_n}{\partial x} + D_p \frac{\partial N_p}{\partial x} + D_e \frac{\partial N_e}{\partial x} \right) \right]
\]

(5)

where, ‘n’ represents N-type, ‘p’ for electrolyte and ‘h’ 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 \( N_e \) 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) (\( V_n=dn_n/dx, V_p=dn_p/dx, V_e=dn_e/dx, \rho_n=-N_n e, \rho_p=-N_p e, \rho_e=0, \rho_{\text{rel}}=\rho_{\text{rel}} \)), \( \rho_{\text{rel}}=\rho_{\text{rel}}=N_n e \) and \( e = 1.6 x 10^{-19} \)C). The diffusion coefficient is estimated by using Einstein equation, \( D=\mu kT/q \), \( k \) 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, \( \mu_e = 1350 \text{ cm}^2/\text{V.s}, \mu_h = 750 \text{ cm}^2/\text{V.s} \) (assuming based on the concentration of GO), and the hole mobility, \( \mu_h = 480 \text{ cm}^2/\text{V.s} \) (Jeon and Burak, 1989). Based on Ohm’s law, the current density also can be defined as, \( J = \sigma E \) where \( \sigma \) is the conductivity of semi-conductive elements of the generator (S/m), \( \sigma = (N_{\text{free}} + N_{\text{free}} + N_{\text{free}})(e) \), 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, \( E = |q|/(4\pi\epsilon_0) \), \( d \) is the thickness of the electrolyte and \( \epsilon \) is electrical permittivity of the semi-conductive material, \( \epsilon = \epsilon_r \epsilon_0 \) where \( \epsilon_0 \) is free space permittivity, \( \epsilon_r = 8.85 x 10^{-12} \text{F/m}, \) and \( \epsilon_r \) is relative permittivity of electrolyte (\( \epsilon_r = 2.5 \) considered for the electrolyte of the generator which is made with ZnO 30 vol.% and 70 vol.% of SiO\(_2\)), total charge, \( Q = \rho_{\text{rel}} dV \). 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, \( \mu = \frac{u}{E} \), 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 \( \mu_{ph} \), surface roughness scattering \( \mu_{sr} \), bulk charge Columbic scattering \( \mu_{cb} \), and interface charge Columbic scattering \( \mu_{ic} \) (Chain et al., 1997). Each of these scattering parameters is related to the temperature of the composite (ZnO/SiO\(_2\)) 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):

\[
d = \frac{\varepsilon_0 A_s}{C} \text{ with } C = \frac{2\pi \varepsilon_0 L}{L n(r_d/r)}
\]

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 (\( \varepsilon_0 = \text{8.85x10}^{-12} \text{F} \)). The charging time of the P-type and N-type is computed by using the equation,

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

where, \( D \) is the diffusion coefficient and \( \lambda_d \) is the Debye length, \( Z_e = q \) is the mobile ion charge, \( e \) 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:

\[
I = \left[ (N_p h_n + N_p h_e + N_h h_n) E + (D_h \frac{\partial h_n}{\partial x} + D_e \frac{\partial h_e}{\partial x} + D_h \frac{\partial h_e}{\partial x} \right] e A_s
\]

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

\[
P = E J dV = Q_{ex}
\]

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 \( \rho_{ve} \) (\( \rho_{ve} = \rho_{vnt} + \rho_{vne} \)) and \( \rho_{vh} \). The emf develops can be estimated as,

\[
V = \frac{(T_e - T_C)}{R_{total}}
\]

where, \( V \) is the emf, \( T \) is the exhaust temperature, \( T_C \) 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 had 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/SiO$_2$ composite electrolyte in terms of conduction energy and voltage due to the increment of carrier parameters such as $\mu$, D, and E. The conduction energy level ($E_g$) has decreased in nonlinearly 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/SiO$_2$) 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/SiO$_2$-SC generator have 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.

The development of ZnO/SiO$_2$ TEG, which is an alternative approach, overcomes some of the practical challenges associated with long, thin silicon-nano-wire (SiNW) TEG. This is 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 $\kappa$ and so TE performance might be less for nano-films than it is for SiNWs.

References

Anedda R, Cannas C, Musinu A, Pinna G, Picaulaga G, and Casu M (2008). A two-stage citric acid–sol/gel synthesis of ZnO/SiO$_2$ nanocomposites: study of precursors and final products. Journal of Nanoparticle Research, 10(1): 107-120.

Cannas C, Musinu A, Peddis D, and Piccaluga G (2006). Synthesis and characterization of CoFe$_2$O$_4$ nanoparticles dispersed in a silica matrix by a Sol–Gel auto-combustion method. Chemistry of Materials, 18(16): 3835-3842.

Chain K, Huang JH, Duster J, Ko PK, and Hu C (1997). A MOSFET electron mobility model of wide temperature range (77-400 K) for IC simulation. Semiconductor Science and Technology, 12(4): 355–358.

Chelikowsky JR and Schlüter M (1977). Electron states in α-quartz: A self-consistent pseudopotential calculation. Physical Review B, 15(8): 4020-4029.

Conklin JC and Szybist JP (2010). A highly efficient six-stroke internal combustion engine cycle with water injection for in-cylinder exhaust heat recovery. Energy, 35(4): 1658-1664.

Dolz V, Novella R, García A, and Sánchez J (2012). HD Diesel engine equipped with a bottoming Rankine cycle as a waste heat recovery system. Part 1: Study and analysis of the waste heat energy. Applied Thermal Engineering, 36: 269-278.

Hatazawa M, Sugita H, Ogawa T, and Seo Y (2004). Performance of a thermoacoustic sound wave generator driven with waste heat of automobile gasoline engine. Transactions of the Japan Society of Mechanical Engineers, 70(6998): 292–299.

Homm G and Klar PJ (2011). Thermoelectric materials—Compromising between high efficiency and materials abundance. Physica Status Solidi (RRL)-Rapid Research Letters, 5(9): 324-331.

Jeon DS and Burk DE (1989). MOSFET electron inversion layer mobilities—a physically based semi-empirical model for a wide temperature range. IEEE Transactions on Electron Devices, 36(8): 1456-1463.

Mang A and Reimann K, and Rübenacke ST (1995). Band gaps, crystal-field splitting, spin-orbit coupling, and exciton binding energies in ZnO under hydrostatic pressure. Solid State Communications, 94(4): 251-254.

Rahman A, Abdul Razak F, Hawlader MNA, and Rashid M (2013). Nonlinear modeling and simulation of waste energy harvesting system for hybrid engine: Fuzzy logic approach. Journal of Renewable and Sustainable Energy, 5(3): 1-13.

Rahman A, Razzak F, Afroz R, Mohiuddin AKM and Hawlader MNA (2015). Power generation from waste of IC engines. Renewable and Sustainable Energy Reviews, 51: 382-395.

Reitz RD (2012). Reciprocating internal combustion engines. Engine research center, University of Wisconsin-Madison. Available online at: https://www.researchgate.net/profile/Rolf_Reitz/publication/265804679_Reciprocating_Internal_Combustion_Engines/links/5630d3d808ae0530378cddc5.pdf

Sabnis AG and Clemens JT (1979). Characterization of the electron mobility in the inverted- 100> Si surface. In the International Electron Devices Meeting. IEEE, Washington, USA: 18-21. https://doi.org/10.1109/IEDM.1979.189528

Saidur R, Rahim NA, and Hasanuzzaman M (2010). A review on compressed-air energy use and energy savings. Renewable and Sustainable Energy Reviews, 14(4): 1135-1153.

Stabler F (2002). Automotive applications of high efficiency thermoelectrics. In the DARPA/ONR/DOE High Efficiency Thermoelectric Workshop. San Diego, USA: 1-26.

Stobart RK, Wijewardane A and Allen C (2010). The potential for thermo-electric devices in passenger vehicle applications. In the SAE 2010 World Congress & Exhibition, Detroit, USA.

Varshni YP (1967). Temperature dependence of the energy gap in semiconductors. Physica, 34(1): 149-154.

Yang J (2005). Potential applications of thermoelectric waste heat recovery in the automotive industry. In the 24th International Conference on Thermoelectrics (ICT 2005), IEEE, Clemson, USA: 170-174. https://doi.org/10.1109/ICT.2005.1519911

Yu C and Chau KT (2009) Thermoelectric automotive waste heat energy recovery using maximum power point tracking. Energy Conversion and Management, 50(6): 1506-1512.