

Modeling Degradation Using Thermodynamic Entropy

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ABSTRACT

Manufacture transforms raw materials into finished components. Ageing and degradation of components, driven by dissipative processes, irreversibly alter material structures. The second and third laws of thermodynamics assert that these dissipative processes must generate entropy. This entropy is a fundamental quantity to describe ageing and degradation.

This recognition led to a Thermodynamic Degradation Paradigm encapsulated in a Degradation Entropy Generation (DEG) Theorem, wherein the rate of degradation was related to the irreversible entropies produced by the underlying dissipative physical processes that age and degrade components. This paradigm and theorem permit a structured approach to modeling degradation of any kind. If properly applied, the DEG Theorem leads to a differential equation in a variable that describes the degradation. The equation depends on the operational and environmental variables that characterize the system. Integration of the equation accumulates the degradation over time. This approach has led to accurate models for progression of and failure by wear, fatigue, and battery degradation that are consistent with prior models.

This article will review the Thermodynamic Degradation Paradigm and Degradation Entropy Generation Theorem, and apply these to formulate predictive models of wear, fatigue, and battery degradation, i.e., differential equations that govern the degradation or ageing. The article will conclude with a discussion on how to use these governing degradation equations for machine prognosis.

1. THERMODYNAMIC DEGRADATION PARADIGM AND DEGRADATION ENTROPY GENERATION THEOREM

Doelling, Ling, Bryant, and Heilman (2000) originally proposed the Thermodynamic Degradation Paradigm

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(TDP), which states that the irreversible entropy produced as a consequence of degradation can become a fundamental variable to quantitatively describe the degradation. For boundary lubricated sliding of copper on steel, they measured wear and the concomitant entropy produced at the sliding interface, and showed wear proportional to entropy. For dry sliding of bronze on stainless steel, Bryant and Khonsari (2008) also showed wear proportional to entropy.

Degradation manifests via a mechanism of dissipative processes. Dissipative processes that damage tribology interfaces include adhesion, surface plastic deformation, fracture, chemical reaction, material phase changes, viscous dissipation, heat dissipation, and material mixing, among others (Bryant, 2009).

Bryant, Khonsari, and Ling (2008) encapsulated the Thermodynamic Degradation Paradigm into the Degradation Entropy Generation (DEG) Theorem. Suppose degradation of whatever form can be measured by a variable w , which is a non negative, monotonic function $w=w\{p_i\}$ of the energies p_i associated with the $i = 1, 2, \dots, n$ dissipative processes that comprise the degradation mechanism. Suppose also that the processes $p_i = p_i(\xi_i^j)$ depend on time dependent phenomenological variables $\xi_i^j = \xi_i^j(t)$. Here i indexes all the dissipative processes of a degradation mechanism, and j indexes the phenomenological variables within a dissipative process. Altogether, $w=w\{p_i(\xi_i^j)\}$. According to thermodynamics laws 2 and 3, the dissipative processes *must* produce irreversible entropy $S' = S'\{p_i(\xi_i^j)\}$ dependent on the same energies and phenomenological variables. Via the chain rule, rates of entropy and degradation are (Bryant et al, 2008)

$$\begin{aligned} \frac{dS'}{dt} &= \sum_{i,j} \left(\frac{\partial S'}{\partial p_i} \frac{\partial p_i}{\partial \xi_i^j} \right) \frac{\partial \xi_i^j}{\partial t} = \sum_i \frac{dS'_i}{dt} \quad (1) \\ \frac{dw}{dt} &= \sum_{i,j} \left(\frac{\partial w}{\partial p_i} \frac{\partial p_i}{\partial \xi_i^j} \right) \frac{\partial \xi_i^j}{\partial t} \\ &= \sum_{i,j} \left[\frac{\partial w / \partial p_i}{\partial S' / \partial p_i} \right] \left(\frac{\partial S'}{\partial p_i} \frac{\partial p_i}{\partial \xi_i^j} \right) \frac{\partial \xi_i^j}{\partial t} \end{aligned}$$

$$= \sum_i B_i \frac{dS'_i}{dt} \quad (2)$$

In the foregoing, indices i, j beneath summation signs refer to a sum over both variables. The similar dependence structures in $w = w\{p_i(\xi_i)\}$ and $S' = S'\{p_i(\xi_i)\}$ led to the similar factors inside the sums in Eqs. (1) and (2). Terms in the first line of Eq. (2) were multiplied by unity in the form $(\partial S'/\partial p_i)^{-1}(\partial S'/\partial p_i)$ to give the terms in the second line of Eq. (2). Coefficients

$$B_i = \frac{\partial w}{\partial p_i} \left(\frac{\partial S'}{\partial p_i} \right)^{-1} = \frac{\partial w}{\partial S'} \Big|_{p_i} \quad (3)$$

which arise from the terms inside the square bracket of Eq. (2) are material properties that represent the increment of degradation incurred per increment of entropy generated by activity of process p_i . The B_i can be measured or related to other material properties. If p_i is the energy dissipated by a dissipative process, definition of entropy suggests $\partial S'/\partial p_i = 1/T_i$, where T_i is a temperature associated with p_i . The other terms in the second line of Eq. (2) are then dissipated power components $dp_i/dt = (\partial p_i/\partial \xi_i)(\partial \xi_i/\partial t)$.

The final line of Eq. (2) asserts that rate of degradation can be expressed as a linear combination of the rates of production of irreversible entropy by the underlying dissipative processes of a degradation mechanism. As suggested in the prior paragraph, when a process dissipates power dp_i/dt the irreversible entropy S' generated and the degradation w depend on process temperature T_i , generalized force $(\partial p_i/\partial \xi_i)$ and generalized velocity $(\partial \xi_i/\partial t)$.

Also used will be laws 1 and 2 of thermodynamics (Kondepudi & Prigogine, 1998)

$$dE = dQ - dW + \sum \eta_k dN_k \quad (4a)$$

$$dS = dS' + dS_e \quad (4b)$$

that conserve energy (internal energy E , heat Q , work W and energy in chemical potential η_k and molar mass N_k) and entropy (entropy flow S_e associated with heat flow, entropy generated S' , and system entropy S).

2. APPLICATIONS

The DEG theorem presented in the prior section will be applied to sliding wear, fatigue, and battery degradation.

2.1. Sliding Wear

Figure 1 depicts a slider sliding on a counter surface. Bodies that rub and slide shed particles that accumulate as wear, measured as volume w of material lost. Friction force $F = \mu N$ sliding through distance x dissipates work $p = Fx$, where μ is friction coefficient and N normal load. For steady

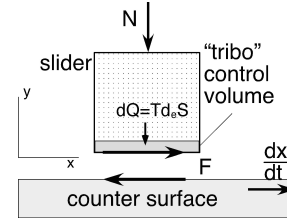


Figure 1. Slider on counter surface.

sliding at speed dx/dt the process is stationary, rendering $dE = dS = 0$ which simplifies Eqs. (4). Also, since the internal energy lost with a wear particle is small, the final term in Eq. (4a) can be neglected compared to other terms. The entropy produced arises from the friction work p dissipated within the tribo control volume (Fig. 1) that encompasses the sliding interface and nearby surface layers within slider and counter surface. Via Eq. (1), friction generates entropy at rate

$$\frac{dS'}{dt} = \left(\frac{dS'}{dp} \frac{dp}{dx} \right) \frac{dx}{dt} = \frac{F}{T} \frac{dx}{dt}, \quad (5a)$$

where contact temperature T arose via $dS'/dp = 1/T$. Applying Eq. (2),

$$\frac{dw}{dt} = \frac{BF}{T} \frac{dx}{dt} = \frac{B\mu}{T} N \frac{dx}{dt}. \quad (5b)$$

Archard's (1953) wear law $w = kNx/H$ relates w to N and x , via wear constant k and hardness H of the softer of the material pair. With N and T constant, Archard's law gives

$$\frac{dw}{dt} = \frac{k}{H} N \frac{dx}{dt}. \quad (5c)$$

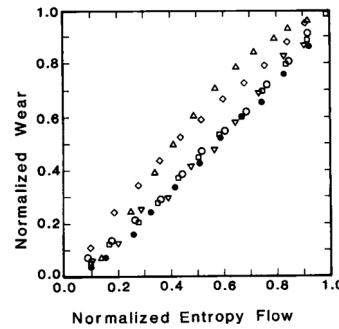


Figure 2. Wear vs. entropy flow, with axes normalized by max values. Symbols show six trials. Load $N = 9.9$ kg, speed $dx/dt = 3.3$ ms⁻¹. From Doelling et al (2000).

Comparing (5c) to (5b),

$$k = \frac{B\mu H}{T}. \quad (5d)$$

Doelling et al (2000) estimated $B = dw/dS'|_p$ under boundary lubricated sliding of copper on steel using the Fig. 2 graph of normalized wear versus normalized entropy flow.

Doelling calculated entropy flow $S_n = \sum \frac{\Delta Q^{(n)}}{T^{(n)}}$, where

$\Delta Q^{(n)}$ is the heat input to the slider during the n th time interval, and $T^{(n)}$ is the corresponding average absolute surface temperature of the stationary copper slider rubbing the rotating steel cylinder. Via Eq. (4b) and a stationary process wherein $dS = 0$, $dS_e = -dS'$, leading to $B = dw/dS_e$. Averages over the six data trials of Fig. 2 led to $B = 4.0 \times 10^{-10} \text{ m}^3/(\text{JK}^{-1})$ and $k=1.01 \times 10^{-4}$. For the same metals sliding under poor or similar lubrication, Rabinowicz (1980) measured $k=1.0 \times 10^{-4}$. The k estimated by (5d) and Fig. 2 arose from measured wear, temperatures and forces; Rabinowicz's k via Archard (1953) arose from measured wear, forces and distance.

A different sliding configuration (bronze ring against 4140 stainless steel) under *dry rubbing* with different load 226.8 kg (500 lb), speed, temperature, and materials was performed (Bryant & Khonsari, 2008). Friction coefficient, wear, and temperature were measured similar to Doelling et al (2000). Results also yielded a remarkably accurate wear coefficient compared to Rabinowicz (1980).

Measurements of very different quantities rendering k values identical to within a few percent suggests validity of the entropy/degradation hypothesis, and Eq. (2). Note that integration of Eq. (5b) would accumulate the degradation by wear. Since energetics of degradation and friction are embedded in the entropy-wear statement of (5b), friction and wear are treated as related, not separate. Archard's wear law is a subset of the thermodynamic entropy formulation. As shown in Bryant et al (2008), Eqs. (2) and (3) can describe other modes of wear (abrasive and fretting among others) if the entropy generated can be formulated.

2.2. Metal Fatigue

Amiri & Khonsari (2012), Naderi & Khonsari (2010), and Amiri, Naderi & Khonsari (2011) have shown that fatigue of metals and other materials such as composites (Naderi & Khonsari, 2012) obey the Thermodynamic Degradation Paradigm and the Degradation Entropy Generation (DEG) Theorem. Collectively, these references experimentally correlate the cumulative effects of fatigue damage with the entropy produced in a fatiguing member.

Fatigue is driven by the energy dissipated by plasticity and fracture. Amiri et al (2011) formulated an expression for the irreversible entropy S' generated during progression of fatigue based on the Clausius-Duhem inequality (Lemaitre & Chaboche, 1990). But since the expression was very complicated—the expression included the complex plastic strain and stress fields, the thermal heat transfer, and the strain hardening effects—they instead pursued entropy flow S_e as a substitute for S' under a stationary process

approximation $dS = 0$. As discussed in section 2.1, this leads to $dS_e = -dS'$, which allows use of entropy flow in the DEG theorem, to describe degradation. Naderi, Amiri, & Khonsari (2010) determined the entropy flow via temperature measurements over a cantilevered member undergoing reverse bending, using an infra-red camera in conjunction with thermal finite elements. Finite elements calculations of stress and heat transfer induced by plastic work estimated flows of heat and entropy over the fatigued member. The elasto-plastic-thermal finite element model was excited by mechanical loads similar to those applied to the specimen, and 2709 ten-node quadratic tetrahedral finite elements connected via an appropriate mesh. The temperatures estimated were consistent with the infra-red measured temperature distribution.

Naderi et al (2010) found that during an initial phase of the first hundred cycles or so temperatures increased due to heat generated by plastic work dissipation. During a second phase of thousand of cycles, temperatures stabilized at approximately constant levels set by equilibrium between heat transfer and heat generated. Finally, near the end of the component's fatigue life, temperatures abruptly increased. Naderi et al (2010) proposed that temperature can be used to predict progression of fatigue and fatigue failure.

Defining degradation measure w as rupture strength S_R (i.e., the maximum load the specimen can sustain) the DEG theorem gives $dS_R/dt = -BS'$ where the minus sign denotes diminishing. When integrated, Eq. (2) becomes

$$S_R = S_{R0} - B \int S' dt, \quad (6a)$$

where subscript 0 refers to the initial rupture strength. When sufficient entropy accumulates, fatigue strength S_R equals the applied load, and the specimen ruptures.

Similar to Fig. 2, Amiri, Naderi, & Khonsari (2011) found that a plot of normalized number of cycles M/M_f vs. normalized entropy flow S_e/S_f yielded an approximately linear function, up to the catastrophic rupture of the component. Their plot can be visualized by replacing normalized wear on the ordinate axis of Fig. 2 with normalized number of cycles. Amiri et al (2011) normalized S_e and M with counterparts S_f and M_f at rupture, since these were maximum values. Since the plot had unity slope, similar to Fig. 2, Amiri et al (2011) concluded

$$\frac{S_e}{S_f} \approx \frac{M}{M_f} \quad (6b)$$

which suggests that once a fatiguing member generates a critical amount of entropy S_f (which Eq. (6) correlates to a critical number of cycles M_f), rupture occurs. This is consistent to Eq. (6a) accumulating enough entropy to reduce the strength to critical levels. Indeed, others tests (Amiri et al, 2011) under different loading conditions such

as torsion showed the persistence of the same amount of critical entropy to rupture. Finally, Naderi & Khonsari (2010) showed that the damage parameter used extensively to characterize fatigue can be obtained from entropy.

2.3. Battery Degradation

In this section, a battery ageing model will be constructed from a model of the operational dynamics of a battery, by blindly applying the DEG theorem of Eq. (2) to those elements in the batteries’ operational system dynamics model that generate entropy. The ageing model will be shown to be qualitatively consistent with known characteristics and traits of battery ageing.

Batteries store energy electrochemically. Popular battery types include lead acid and lithium ion batteries. Batteries consist of anode and cathode electrodes, electrolyte, separator, and terminals. Batteries have finite lifetimes, which are usually limited by manufacturing defects and ageing effects. This section will focus on ageing effects on battery life. Battery health is often measured in terms of capacity \mathcal{C} (Ah), the amount of charge in ampere-hours a battery can deliver when discharged at a rated current, or growth of internal cell impedance Z (ohms), see (Broussely, Biensan, Bonhomme, Blanchard, Herreyre, Nechev & Staniewicz, 2005). Ageing reduces capacity \mathcal{C} and increases impedance Z . Cycles of charging and discharging age a battery. Battery cycle life is rated as the number of complete charge-discharge cycles a battery can perform before 1) capacity \mathcal{C} falls below 80% of initial rated capacity and/or 2) the internal resistance Z increases 1.3 to 2 times initial value.

Wohlfahrt-Mehrens, Vogler & Hammouche, 2005). Most prevalent are:

- (a) Number of charge-discharge cycles experienced by the battery: more cycles diminish remaining life.
- (b) Depth of discharge (DOD- the percent of battery capacity discharged during a charge-discharge cycle): a larger DOD reduces cycle and increases the increment of energy dissipated per cycle.
- (c) Electrolyte decomposition enhanced by high temperature and Li plating.
- (d) Electrode plating by Li, which increases resistance and fades capacity, is exacerbated by lower temperature.

A battery operational model in bond graph form from Ménard, Fontès, & Astier (2010) models the dynamic electrochemical phenomena in a Li-ion battery. The bond graph of Ménard et al (2010) was copied and is presented as Fig. 3. A bond graph is a map of where and how power flows in a physical system. A bond graph also shows where energy is stored, dissipated, and transformed. The half arrows in Fig. 3 indicate the direction of positive power flow in the Li ion battery. In a bond graph, potential energy is stored in capacitance elements C , kinetic energy is stored in inertance elements I , and power is dissipated in resistance elements R . From a completed bond graph, the differential equations that govern the physics and dynamics of a system can be extracted (Brown, 2006 and Karnopp, Margolis, & Rosenberg, 2000).

The bond graph of Fig. 3 has additional labels to indicate where in the battery system is “energy storage”, “diffusion phenomena”, “electrochemical conversion”, “electrochemical phenomena”, and “ohmic phenomena”. On the far right of Fig. 3 are battery terminal voltage V_{bat} and current I , which pertain to the voltage and current across the physical terminals of a physical battery. Chemical capacitance $C_{storage}$ found in the “energy storage” sector stores the battery’s energy via electrochemical charge separation involving Li^+ ions and electrons. Gibbs free energy $-\Delta G_{storage}$ (J) and molar flow of lithium ions J (mol/sec) appear as effort and flow on multiple bonds, indicating the chemical thermodynamics embedded in this bond graph. The minus sign on $-\Delta G_{storage}$ refers to energy leaving the main storage $C_{storage}$. In “diffusion phenomena”, capacitance C_{diff} and dissipative resistance R_{diff} together set a time constant which controls the slow dynamics of Li^+ ion diffusion in the electrolyte, which transports charge through the electrolyte. Transformer TF: nF in electrochemical conversion has modulus of the Faraday constant F ($9.649 \times 10^4 \text{ C mol}^{-1}$) and the number of moles of electrons n exchanged for each mole of lithium ions involved in the electrochemical reaction at the electrodes. This transformer, which converts electrochemical power to electrical power, bridges the electrochemical and electrical domains. Effort source $-\Delta G^0$ establishes a reference thermodynamic potential

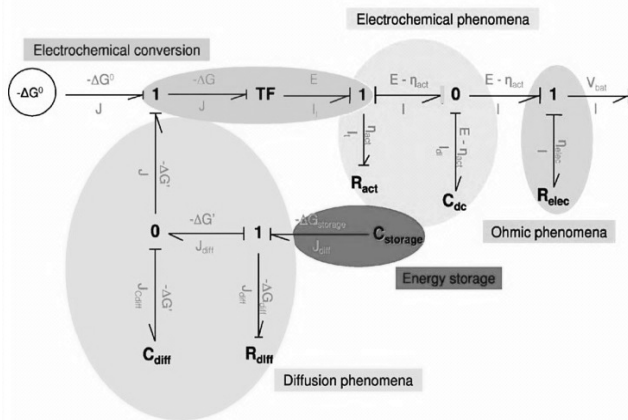


Figure 3. Bond graph systems dynamic model of a Li ion battery, from Ménard et al (2010).

Battery life, typically 500 to 1200 charge discharge cycles, depends on many factors (Broussely et al, 2005 and Vetter, Novak, Wagner, Veit, Moller, Besenhard, Winter,

within the bond graph. The power needed to activate electrochemical reactions at the electrode–electrolyte interfaces imposes resistance R_{act} . This activation power is not stored, but dissipated. Capacitance C_{dc} is due to a layer of charge (electrons and lithium ions Li^+) that forms about the electrode–electrolyte interface. Low mobility of Li^+ ions through the electrolyte relative to electron flows in the battery causes ohmic resistance R_{elec} .

In electric circuits, electric resistances dissipate power VI , where V and I are the voltage drop across and current through the physical resistor. The electric resistance R_{elec} in Fig. 3—which represents the Thevenin equivalent impedance seen across the battery terminal—has voltage drop η_{elec} and current I . Similar to an electrical resistance, the power dissipated by other resistances is the product of the labeled quantities (which are equivalent to voltages and currents) on the half arrow bonds. In the bond graph of Fig. 3, generalized resistances R_{elec} , R_{diff} , and R_{act} dissipate powers $\eta_{elec} I$, $-\Delta G_{diff} J_{diff}$, and $\eta_{act} I_t$ respectively.

The entropy S' generated is the dissipated power divided by a temperature associated with the dissipative process. Thus, via Eq. (1),

$$\frac{dS'}{dt} = \frac{-\Delta G_{diff} J_{diff}}{T_{diff}} + \frac{\eta_{act} I_t}{T_{act}} + \frac{\eta_{elec} I}{T_{elec}} \quad (7a)$$

By way of Eq. (2), the battery degradation is

$$\frac{dw}{dt} = B_{diff} \frac{-\Delta G_{diff} J_{diff}}{T_{diff}} + B_{act} \frac{\eta_{act} I_t}{T_{act}} + B_{elec} \frac{\eta_{elec} I}{T_{elec}}, \quad (7b)$$

where degradation measure w can be battery capacity \mathcal{C} and/or internal impedance Z . Temperatures T_{diff} , T_{act} , and T_{elec} are associated with the diffusion, activation, and electric domains of the battery. Equation (7b) relates rate of capacity or impedance change (Erdinc, Vural & Uzunoglu, 2009) to power dissipated, and sums dissipative effects from Li-ion diffusion into/out of electrodes, the energy of activation of Li/Li-ions at electrodes, and ohmic effects associated with mobility of Li ions in electrolyte. The sum over effects in Eq. (7b) is consistent with Vetter et al (2005), who reviewed ageing mechanisms in Li-ion batteries and stated that diverse “effects can be considered as additive”. Equation (7b) is consistent with item (b) of the list, since a larger depth of discharge yields larger power dissipations from all effects, with greater per cycle changes in w , and with Broussely et al (2005) who found capacity faded and impedance increased with more charge-discharge cycles¹. In

Eq. (7b), coefficients B_{diff} , B_{act} , and B_{elec} should be adjusted to reflect the relative importance of each entropy term on the degradation. For w being \mathcal{C} or Z , these coefficients must be negative or positive, respectively, to model capacity fade or impedance increase. Equation (7b) can be posed in terms of phenomenological variables via constitutive relations of Eqs. (14) and (17) of Ménard et al. (2010), wherein

$$-\Delta G_{diff} J_{diff} = \frac{RT_{diff}}{\alpha F I_{lim}} I_t, \quad \eta_{act} I_t =, \quad \eta_{elec} I = R_{elec} I^2 \quad (8a)$$

giving

$$\frac{dw}{dt} = B_{diff} \frac{RT_{diff}}{\alpha F I_{lim}} \frac{I_t}{T_{diff}} + B_{act} \frac{RT_{act}}{\alpha F I_o} \frac{I_t^2}{T_{act}} + B_{elec} \frac{R_{elec} I^2}{T_{elec}} \quad (8b)$$

Here R is the molar gas constant, $\alpha = 1/2$, and I_{lim} and I_o are diffusion currents dependent on number of lithium ions. The first two terms of Eqs. (8b)—pertaining to electrolyte diffusion and electrode–electrolyte interface activation— increase influence of temperature on the electrolyte diffusion and activation terms of Eq. (7b), consistent with item list (c). The last term of Eq. (8b) retains T_{elec} in the electric term of Eq. (7b), suggesting more influence from this term at lower temperature, consistent with item list (d). Finally, since I_t increases with state of charge Ménard et al. (2010), a higher state of charge results in a higher, which increases the first two terms of Eqs. (7b) and (8b).

3. DISCUSSION

Prognostics tries to predict future behavior of systems, to assess performance. Models of a machine’s physical operation, consisting of the machine system’s governing differential equations, can accurately mimic machine behavior if the model has sufficient fidelity (i.e., the model includes the critical physics and has sufficient dynamic states), is given inputs similar to that of the real machine, and if the numerical values of the model’s parameters accurately reflect the real machine’s condition. Parameters can be tuned from data measured off the real machine. As equipment degrades or ages via processes such as wear, fatigue, and others such as those involved in battery ageing, the system’s operational behavior can change, causing the machine to lose tolerance and not perform its function. Often this degraded machine behavior can be mimicked by the machine system’s operational models (the governing differential equations), but with certain parameters associated with the ageing given revised numerical values. As a system ages, those parameters associated with the

produced, via the second law of thermodynamics. As cycles accumulate, the entropy produced accumulates, and list item (a) suggests battery life diminishes with increased entropy accumulation.

¹ With each increment of energy dissipated during each charge-discharge cycle an increment of entropy must be

ageing will change with time. As presented in this article, physical ageing is driven by dissipative processes, and the ageing behavior can be predicted by solving differential equations posed in terms of a variable w that measures the degradation.

If degradation changes a certain parameter P_k then $P_k = P_k(w)$, and via the chain rule $dP_k/dt = dP_k/dw (dw/dt)$. Substitution of Eq. (2) then gives

$$\frac{dP_k}{dt} = \sum_{i=1}^n \left(B_i \frac{dP_k}{dw} \right) \frac{dS'_i}{dt} = \sum_{i=1}^n B_i^* \frac{dS'_i}{dt} \quad (9)$$

where dP_k/dw was grouped with the “old” constants B_i to form new constants B_i^* . Values for these constants can be derived by measurements of the ageing phenomena on a machine. Once tuned, governing differential equations can forecast the changes in parameters far into the future. These forecasted parameter values can then be used in the operational machine model to simulate future behavior of the aged or degraded machine.

4. CONCLUSION

The method presented derives differential equations that govern system degradation from an assessment of the irreversible entropy produced by operation of the system. Equation (2), which states the simple result of the DEG theorem, was applied to degradation venues of wear, fatigue, and battery ageing. When applied to wear, the DEG theorem and Eq. (2) related wear to friction and accurately described multiple forms of wear that do and do not obey Archard’s wear law. When applied to fatigue, the DEG theorem and Eq. (2) accurately described fatigue, for reversed bending, torsion, and combinations, and led to a method of predicted fatigue life by measuring temperatures. Finally, when the DEG theorem and Eq. (2) were blindly applied to a system dynamics model of a battery, an expression for battery ageing Eq. (8b) was obtained that qualitatively agreed with existing observations of Li ion batteries.

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NOMENCLATURE

| | |
|---------------|-------------------------|
| B_i | degradation coefficient |
| \mathcal{C} | battery capacity (Ah) |
| C | generalized capacitance |
| E | internal energy |

| | |
|-------------|--|
| F | friction force |
| $-\Delta G$ | Gibbs free energy for electrochemical cell |
| J | molar flow of lithium ions (mol/sec) |
| k | wear coefficient |
| M | number of fatigue cycles |
| N | normal force |
| p_i | energy of i th dissipative process |
| Q | heat |
| R | generalized resistance |
| S_e | entropy flow |
| S' | irreversible entropy generated |
| S | system entropy |
| S_f | critical entropy at failure |
| t | time |
| T | temperature |
| w | degradation |
| W | work |
| x | distance slid |
| Z | battery internal impedance |
| η | internal voltage drop in battery |
| μ | friction coefficient |
| ζ | phenomenological variable |

REFERENCES

- Amiri, M., Naderi, M. & Khonsari, M.M. (2011). An experimental approach to evaluate the critical damage, *International Journal of Damage Mechanics*, vol. 20 (89), doi: 10.1177/1056789509343082.
- Amiri, M. & Khonsari, M. M. (2012). On the role of entropy generation in processes involving fatigue, *Entropy*, vol. 14, pp. 24-31, doi:10.3390/e14010024.
- Archard, J.F. (1953). Contact and rubbing of flat surfaces, *Journal of Applied Physics*, vol. 24, pp. 981-988, doi:10.1063/1.1721448.
- Brown, F.T. (2006). *Engineering System Dynamics, a Unified Graph-Centered Approach*, 2nd Ed., NY: CRC Press.
- Broussely, M., Biensan, Ph., Bonhomme, F., Blanchard, Ph., Herreyre, S., Nechev, K. & Staniewicz, K. (2005). Main aging mechanisms in Li ion batteries, *Journal of Power Sources*, vol. 146, pp. 90-96, doi:10.1016/j.jpowsour.2005.03.172.
- Bryant, M.D. (2009). Unification of friction and wear, Chapter 4 of *Recent Developments in Wear Prevention, Friction, and Lubrication*, Research Signpost, Kerala, India, G. Nikas Ed., ISBN 978-81-308-0377-7, pp. 159-196.
- Bryant, M.D. & Khonsari, M.M. (2008). Application of degradation-entropy generation theorem to dry sliding friction and wear,” *Proceedings of STLE/ASME International Joint Tribology Conference*, Oct. 20-22, Miami, FL. IJTC2008-71079.
- Bryant, M.D., Khonsari, M.M. & Ling, F.F. (2008). On the thermodynamics of degradation, *Proceedings of Royal*

- Society of London Series A*, vol. 464 (2006), pp. 2001-2014, doi:10.1098/rspa.2007.0371.
- Doelling, K. L., Ling, F. F., Bryant, M. D. & Heilman B. P. (2000). An experimental study of the correlation between wear and entropy flow in machinery components, *Journal of Applied Physics*, vol. 88, pp. 2999-3003.
- Erdinc, O., Vural, B. & Uzunoglu, M. (2009). A dynamic lithium-ion battery model considering the effects of temperature and capacity fading, *2009 International Conference on Clean Electrical Power*, pp. 383-386, June 9-11, doi: 10.1109/ICCEP.2009.5212025.
- Karnopp, D.C., Margolis, D.L. & Rosenberg, R.C. (2000). *System Dynamics, a Unified Approach*, 3rd ed., New York: Wiley.
- Kondepudi, D. & Prigogine, I. (1998). *Modern thermodynamics from heat engines to dissipative structures*, New York, NY: John Wiley & Sons, Inc.
- Lemaitre, J. & Chaboche, J.L. (1990) *Mechanics of solid materials 1st ed.*, Cambridge, UK: University Press.
- Ménard, L., Fontès, G. & Astier, S. (2010). Dynamic energy model of a lithium-ion battery, *Mathematics and Computers in Simulation*, vol. 81, pp. 327-339, doi:10.1016/j.matcom.2010.07.026.
- Naderi, M., Amiri, M. & Khonsari, M.M. (2010). On the thermodynamic entropy of fatigue fracture, *Proceedings of Royal Society of London Series A*, vol. 466, pp. 423-438, 10.1098/rspa.2009.0348.
- Naderi, M. & Khonsari, M.M. (2010). A thermodynamic approach to fatigue damage accumulation under variable loading, *Materials Science & Engineering A*, vol. 527, pp. 6133-6139, doi:10.1016/j.msea.2010.05.018.
- Naderi, M. & Khonsari, M.M. (2012). A comprehensive fatigue failure criterion based on thermodynamic approach, *Journal of Composite Materials*, vol. 46 (437) doi: 10.1177/0021998311419540.
- Rabinowicz, E. (1980). *Wear control handbook*, New York, NY: ASME press, pp. 486.
- Vetter, J., Novak, P., Wagner, M.R., Veit, C., Moller, K.C., Besenhard, J.O., Winter, M., Wohlfahrt-Mehrens, M., Vogler, C. & Hammouche, A. (2005). Ageing mechanisms in lithium-ion batteries, *Journal of Power Sources*, vol. 147, pp. 269-281, doi:10.1016/j.jpowsour.2005.01.006.

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