

A Simple Method for Identifying the Thermodynamic Limits to the Specific Energy of Electrochemical Energy Storage Systems

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This article outlines a simple method for identifying the thermodynamic limits to electrochemical reversible energy storage systems based on the Nernst equation and previous results obtained from work on reversible chemical hydrogen sorption. The model is successfully validated for five reversible battery chemistries capable of providing specific energies of more than 100 Wh kg⁻¹ at cell level. The findings of this work substantiate the idea of a general thermodynamic principle limiting reversible chemical energy storage and suggest a change of paradigm towards a global understanding of the matter.

1. Introduction

The successful unveiling of the invisible yet manifest empirical boundaries to reversible chemical hydrogen sorption by means of fundamental thermodynamics entails the conclusion that not only reversible hydrogen but all reversible mass transfer is limited by the same thermodynamic principle.¹

The initial concept bases on ideal hydrogen transfer in a two-phase gas-sorbent system which is a sound theoretical base for tackling the issue because of two reasons: *first reason*, the ideal gas law approximates hydrogen behaviour well at typical metal hydride sorption reaction conditions. *Second reason*, the ideal gas law makes for a suitable theoretical base describing the ultimate thermodynamic limits because there cannot be a less hindered mass transfer across phase boundaries.

The nature of the sorbent phase is secondary to the formalism as long as it is separate from the gas phase and since the standard hydrogen electrode (SHE) is a reference of central importance to electrochemistry, the existence of a relationship in applicability is a proximate conclusion. This work outlines how that relation may be unveiled in a fundamental manner.

2. Methodical Approach

The Nernst equation is an apt starting point towards a static theoretical model assessing the maximum reversible specific energy of electrochemical systems; it is shown in equation 1.²

$$E = E^\circ + \frac{R T}{z F} \ln \left(\frac{a_{\text{Ox}}}{a_{\text{Red}}} \right) = E^\circ + \frac{R T}{z F} \ln Q \quad (1)$$

The Nernst potential E refers to a static equilibrium state and measures relative to the SHE chemical potential E° of the cell reaction. In equation 1, R is the universal gas constant, T the thermodynamic temperature, z the number of electrons transferred in the redox reaction and F is Faraday's constant. The \ln -term contains the activities of the reactants at the respective system condition; the fraction is also referred to as reaction quotient Q .

The Nernst equation bases on the transfer of charge, not mass; yet since it measures by SHE potential excursions, it can be by principle calibrated for the maximum reversible mass transfer on the basis of previous work.¹ Starting from equation 1, that objective is achievable in five-steps.

2.1 The fundament

Equation 1 refers to a single static state but the description of a reversible electrochemical system requires at least one initial and one end state. This can be accounted for by a sum of two Nernst potentials E_1 and E_2 as given by equations 2a and 2b.

$$E_1 = E^\circ + \frac{R T}{z F} \ln Q_1 \quad (2a)$$

$$E_2 = E^\circ + \frac{R T}{z F} \ln Q_2 \quad (2b)$$

Since the featured excursion of the SHE potential E° is vital to the approach, it is sensible to move E° from the right to the left side and subsequently multiply with (-1) , followed by squaring of the whole equation what leads to equations 3a and 3b.

$$(E^\circ - E_1)^2 = \left(\frac{-R T}{z F} \right)^2 \ln^2 Q_1 \quad (3a)$$

$$(E^\circ - E_2)^2 = \left(\frac{-R T}{z F} \right)^2 \ln^2 Q_2 \quad (3b)$$

Equations 3a and 3b are added up to equation 4 and the \ln -term is transformed according to logarithmic laws. For the sake of simplicity, there is only one operational temperature T .

$$\begin{aligned} (E^\circ - E_1)^2 + (E^\circ - E_2)^2 &= \left(\frac{-R T}{z F} \right)^2 (\ln^2 Q_1 + \ln^2 Q_2) \\ &= \left(\frac{-R T}{z F} \right)^2 \ln^2 (Q_1 Q_2) \end{aligned} \quad (4)$$

It is expedient to substitute $Q_1 Q_2$ by the square of the geometric mean $\bar{Q} = \sqrt{Q_1 Q_2}$ as shown in equation 5.

$$(E^\circ - E_1)^2 + (E^\circ - E_2)^2 = \left(\frac{-R T}{z F} \right)^2 \ln^2 \bar{Q}^2 \quad (5)$$

Taking the square root of equation 5 provides an expression of a vector quantity as shown in equation 6.

$$\sqrt{(E^\circ - E_1)^2 + (E^\circ - E_2)^2} = \left(\frac{-R T}{z F} \right) \ln \bar{Q}^2 = \left(\frac{R T}{z F} \right) \ln \bar{Q}^{-2} \quad (6)$$

Figure 1 illustrates that vector quantity on the left of equation 6 as the dotted line within the grey shaded box.

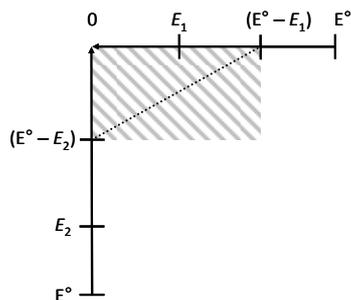


Figure 1 Schematic illustration of the vector quantity described in equation 6 as the dotted diagonal in the grey shaded box, representing the gradient between the two Nernst cell potentials E_1 and E_2 .

Equation 6 can be further simplified by extracting the square root exponent from \bar{Q}^{-2} in front of the ln-term and move it to the left side which is shown in equation 7.

$$-\frac{1}{2}\sqrt{(E^\circ - E_1)^2 + (E^\circ - E_2)^2} = \frac{RT}{zF} \ln \bar{Q} \quad (7)$$

The information conveyed in the voltage gradient respective equation 7 can be now calibrated for the ideal maximum reversible mass transfer. Since the Nernst equation bases on the transfer of charge, not particles, this objective requires the transformation of the mass-based reference hydrogen gas phase chemical potential $\mu_{1\%}^{\circ\circ}$ to the according potential $E_{1\%}^{\circ\circ}$.

2.2 Transformation of $\mu_{1\%}^{\circ\circ}$ to $E_{1\%}^{\circ\circ}$

The detailed line of argument towards $\mu_{1\%}^{\circ\circ}$ can be found here;¹ it is just mentioned that it moves along three questions: *First question*, what is the irreducible setup of an ideal two-phase gas-sorbent hydrogen storage system based on the periodic table respective molarity?

Second question, how far this system can be moved away from equilibrium at IUPAC standard pressure and temperature (STP) conditions? The answer to the first question is a confined volume of the ideal gas V_m° at STP (22.71 L) containing 1 gram equal to 1 mole of matter respective hydrogen atoms (by definition, a mole of matter cannot weigh less than 1 gram).

The answer to the second question: all hydrogen is in the solid state, none in the gas phase; that is the definite maximum off-equilibrium state of the system.

The *third question* is crucial: How does now the reversible transfer of 1 % w/w from the solid into the gas phase as ideal hydrogen at STP affect the chemical potential of the gas phase? The answer leads eventually to the irreducible ideal mass transfer constant designated as $\mu_{1\%}^{\circ\circ}$ of $-12033 \text{ kJ} (\text{mol H}_2)^{-1} [1 \% \text{ w/w H}]_{\text{max, rev}}^{-1}$. The somewhat unusual designation $\mu_{1\%}^{\circ\circ}$ is to underscore the fact that the irreducible character qualifies it a standard for ideal reversible mass transfer at STP conditions. The detailed line of argument further shows that the division of a negative metal hydride desorption reaction enthalpy $-\Delta H$ ($\Delta H > 0$) by $\mu_{1\%}^{\circ\circ}$ leads to an ideal gas pV_m -energy proportionality term which is multiplied with the quotient of the logarithms to the base of 1.618, the golden section Φ and $[1 \% \text{ w/w H}]_{\text{max, rev}}$.

Communicating chemical potentials, which are logarithmic by nature, are the essence of reversible energy storage chemistry: a linear order is only possible if the logarithm base changes from e to Φ and the unique properties of the golden section are exploited. The ensuing direct proportionality is rooted in the golden number sequence. Since the mass of a hydrogen atom virtually equals those of a nuclear particle mass unit, the formalism actually refers to nuclear particle mass transfer as ideal hydrogen gas and for that reason the statements are of general validity. The chemical potential $\mu_{1\%}^{\circ\circ}$ equals a ΔG_m° of $-12033 \text{ J} (\text{mol H}_2)^{-1} [1 \% \text{ w/w H}]_{\text{max, rev}}^{-1}$ which by Faraday's law corresponds to the equilibrium voltage $E_{1\%}^{\circ\circ}$ (equation 8).

$$\Delta G_m^\circ = z F E^\circ \quad \Rightarrow \quad \mu_{1\%}^{\circ\circ} = z F E_{1\%}^{\circ\circ} \quad (8)$$

Since 1 mole of hydrogen provides 2 moles of electrons, the irreducible voltage change $E_{1\%}^{\circ\circ}$ associated with the ideal reversible transfer of 1 % w/w nuclear particle mass figures to $-0.06235(7) \text{ V}$ as shown on equation 9 (taking up the original figures from the reasoning towards $\mu_{1\%}^{\circ\circ}$ at $T^\circ = 273.15 \text{ K}$)¹.

$$\begin{aligned} \mu_{1\%}^{\circ\circ} &= R T^\circ \ln \left(\frac{0.005 \text{ bar}}{p^\circ} \right) = R T^\circ (-11) \ln (1.618) \quad (9) \\ &= -12033 \text{ J} (\text{mol H}_2)^{-1} [1 \% \text{ w/w H}]_{\text{max, rev}}^{-1} \\ &= 2 \cdot 96485 \text{ C} (\text{mol H}_2)^{-1} E_{1\%}^{\circ\circ} \\ \Rightarrow E_{1\%}^{\circ\circ} &= -0.06235(7) \text{ V} [1 \% \text{ w/w H}]_{\text{max, rev}}^{-1} \end{aligned}$$

2.3 Bringing the parts together

Division of Equation 7 by equation 9 calibrates the potential gradient of an electrochemical energy storage system for ideal reversible mass transfer which is shown in equation 10.

$$\begin{aligned} -\frac{1}{2 E_{1\%}^{\circ\circ}} \sqrt{(E^\circ - E_1)^2 + (E^\circ - E_2)^2} &= \quad (10) \\ \frac{2 T}{z T^\circ (-11) \ln (1.618)} \ln \bar{Q} & [1 \% \text{ w/w H}]_{\text{max, rev}}^{-1} \end{aligned}$$

Equation 10 is rearranged by moving the factor $2/z$ from the right to the left side and changing the base of ln-term from e to the golden section $\Phi = 1.618$: Equation 11 accounts for these transformations.

$$\begin{aligned} -\frac{z}{2} \frac{1}{E_{1\%}^{\circ\circ}} \sqrt{(E^\circ - E_1)^2 + (E^\circ - E_2)^2} &= \quad (11) \\ \frac{T}{T^\circ} \frac{\log_{1.618} \bar{Q}}{(-11)} & [1 \% \text{ w/w H}]_{\text{max, rev}}^{-1} \end{aligned}$$

The temperature quotient T/T° is synonymous to a quotient of ideal gas pV_m -terms. Thus, equation 11 represents exactly the electrochemical pendant to the result previously obtained for the reversible hydrogen storage problem based on the van't Hoff equation:¹ a pV_m -energy proportionality term that is multiplied with a quotient of the logarithms to the base of Φ . This is shown in equation 12; the negative arithmetic sign on the left side cancels out with those organic to $E_{1\%}^{\circ\circ}$.

$$-\frac{z}{2} \frac{1}{E_{1\%}^{\circ\circ}} \sqrt{(E^{\circ} - E_1)^2 + (E^{\circ} - E_2)^2} = \quad (12)$$

$$\frac{\rho V_m}{\rho^{\circ} V_m^{\circ}} \frac{Y}{X} [1 \% \text{ w/w H}]^{-1}_{\text{max., rev}}$$

$$\begin{aligned} p^{\circ} &= 1 \text{ bar} & E_{1\%}^{\circ\circ} &= -0.06235(7) \text{ V } [1 \% \text{ w/w H}]^{-1}_{\text{max., rev}} \\ V_m^{\circ} &= 22.71 \text{ L} & Y &= \log_{1.618} \bar{Q} & X &= (-11) \end{aligned}$$

The next step is adjusting the outer frame provided by E° in such a manner that the information about maximum reversible mass transfer becomes accessible.

2.4 Adjustment of E° boundaries

In equation 12, E° refers to the SHE reduction potential of the overall battery cell reaction which cannot provide the sought information about the ultimate boundary to reversible specific energy. However, if E° is substituted by the SHE potential of the migrating species E_{M/M^+}° such as Li/Li^+ or Na/Na^+ renders that information available.³ The shift of base is by principle in line with the Nernst equation (see figure 1) and reference to E° is not lost since organic to E_1 and E_2 . Yet a novel quality is created in the event since the reduction potential of the pure metal represents the ultimate reductive power threshold of the electrochemical system. Changing the reference to E_{M/M^+}° is in equation 13 taken into account by an adjusted reaction quotient \bar{Q} of which no detailed knowledge is required as all vital information is subsumed in the voltages on its left side.

$$-\frac{z}{2} \frac{1}{E_{1\%}^{\circ\circ}} \sqrt{(E_{M/M^+}^{\circ} - E_1)^2 + (E_{M/M^+}^{\circ} - E_2)^2} = \quad (13)$$

$$\frac{\rho V_m}{\rho^{\circ} V_m^{\circ}} \frac{Y}{X} [1 \% \text{ w/w H}]^{-1}_{\text{max., rev}}$$

$$\begin{aligned} p^{\circ} &= 1 \text{ bar} & E_{1\%}^{\circ\circ} &= -0.06235(7) \text{ V } [1 \% \text{ w/w H}]^{-1}_{\text{max., rev}} \\ V_m^{\circ} &= 22.71 \text{ L} & Y &= \log_{1.618} \bar{Q} & X &= (-11) \end{aligned}$$

Abbreviating equation 13 to equation 14 gives the maximum ideal mass transfer in $[\Delta \% \text{ w/w H}]$ with the mass of the hydrogen atom virtually equal to a nuclear particle mass unit.

$$-\frac{z}{2} \frac{1}{E_{1\%}^{\circ\circ}} \sqrt{(E_{M/M^+}^{\circ} - E_1)^2 + (E_{M/M^+}^{\circ} - E_2)^2} = [\Delta \% \text{ w/w H}]^{-1}_{\text{max., rev}} \quad (14)$$

2.5 Final adjustments and accomplishing the objective

$[\Delta \% \text{ w/w H}]^{-1}_{\text{max., rev}}$ refers to the reversible transfer of 0.01 g out of 1 g hydrogen respective nuclear particle mass and is thus synonymous to 1 gram out of 100 grams. Therefore, equation 14 needs scaling to grams per kilogram by multiplying with the factor of 10 which is displayed in equation 15.

$$-\frac{z}{2} \frac{10}{E_{1\%}^{\circ\circ}} \sqrt{(E_{M/M^+}^{\circ} - E_1)^2 + (E_{M/M^+}^{\circ} - E_2)^2} = [\Delta \text{ g} / \text{kg}^{-1}]_{\text{max., rev}} \quad (15)$$

Division of the reversibly transferable mass obtained from equation 15 by the molar mass of the migrating species yields the according number of moles.

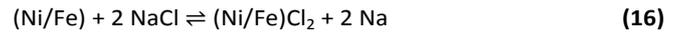
These allow the calculation the maximum reversible specific energy via Faraday's law with the geometric mean cell voltage.

3. Results

It is just consequential to see how equation 15 figures fare in comparison to the practical limits to specific energy of battery cells; emphasis is placed on cell reactions which allow for more than 100 Wh kg^{-1} . High temperature systems like the $(\text{Fe}/\text{Ni})\text{Cl}_2$ (ZEBRA) and the sodium-sulphur (NAS) cell provide well-suited study cases for they are near-perfect thermodynamic systems; LiCoO_2 and LiFePO_4 cells are considered as representative examples of lithium intercalation battery chemistry. Finally, a predictive case study for the lithium-sulphur (LIS) cell seems well suited for closing the circle. The prime objective of this effort is not a detailed review but a brief assessment whether generic yet representative input data to equation 15 yield the known practical specific energy thresholds of these well-investigated systems. A secondary objective is to get an idea of the spread between theory predictions and empiric results.

3.1 The $(\text{Ni}/\text{Fe})\text{Cl}_2$ ZEBRA cell

The cell reaction of the ZEBRA-battery in the advanced $(\text{Ni}/\text{Fe})\text{Cl}_2$ setup is shown in equation 16.



The reaction requires the transfer of two sodium ions, thus is $z = 2$ and there are two approximate open circuit potential (OCP) plateaus:⁴ one at 2.58 V for a state of charge (SOC) between 98 % and 30 % belonging to the NiCl_2 reaction; below a SOC of 30% there is the plateau at 2.35 V of the likewise FeCl_2 reaction. The lower FeCl_2 reaction plateau ends at about 2.2 V.⁴ Above a SOC of 98 %, there is an overcharge reaction which raises the OCP up to 3.05 V. By design, this approach is anchored to the reduction capability of the system relative to a SHE reduction potential reference: for this formal reason, the voltages E_1 and E_2 need to feature a negative arithmetic sign in the calculation. With the E_1 and E_2 boundaries set at -2.58 V and -2.2 V , the maximum reversible specific mass transfer figures by equation 17 to 42.49 g kg^{-1} .

$$-\frac{z}{2} \frac{10}{E_{1\%}^{\circ\circ}} \sqrt{(E_{M/M^+}^{\circ} - E_1)^2 + (E_{M/M^+}^{\circ} - E_2)^2} = 42.49 \text{ g kg}^{-1} \quad (17)$$

$$\begin{aligned} E_{M/M^+}^{\circ} \text{ for Na/Na}^+ &= -2.713 \text{ V} & E_{1\%}^{\circ\circ} &= -0.06235(7) \text{ V g kg}^{-1} \\ E_1 &= -2.58 \text{ V} & E_2 &= -2.2 \text{ V} \end{aligned}$$

Reversible 42.49 g kg^{-1} correspond to $1.85 \text{ (mol Na) kg}^{-1}$; employing this quantity in Faraday's law with the geometric mean voltage $\bar{E} = 2.38 \text{ V}$ as by equation 18 yields a maximum reversible specific energy of 118 Wh kg^{-1} .

$$\bar{E} = \sqrt{(2.58 \cdot 2.2)} \text{ V} = 2.38 \text{ V} \quad \text{MW}_{\text{Na}} = 22.99 \text{ g mol}^{-1} \quad (18)$$

$$\frac{1.85 \text{ (mol Na)} \cdot 96485 \text{ C} \cdot 2.513 \text{ V} \cdot \text{Wh}}{\text{kg} \cdot \text{(mol Na)} \cdot 3600 \text{ J}} = 118 \text{ Wh kg}^{-1}$$

The figure of 118 Wh kg⁻¹ matches well the upper threshold of 117 Wh kg⁻¹ according to DUSTMANN and BITO which is realized in the Z5 standard battery type by MES DEA S.A. company.⁴

3.2 The sodium-sulphur cell

The cell reaction of a sodium-sulfur (NAS) battery is complex due to the formation of various polysulphide intermediates,^{4,5} equation 19 provides a general description of the reaction.



However, 100 % depth-of-discharge (DOD) are not marked by reduction of the sulphur electrolyte to Na₂S but Na₂S₃.⁶ Yet the NAS battery cell is in practice often designed to stop discharging at 85 to 90 % of that theoretical capacity due to the corrosive nature of Na₂S₃.⁷ The NAS battery shows a stable OCP of 2.075 V up to 59 % DOD just short of the stoichiometry Na₂S₅ (60% DOD). Then the OCP drops rather linearly to 1.78 V at the stoichiometry Na₂S₃ respective 100 % DOD,^{4,8} in any case applies z = 2, though at a varying sodium-sulfur ratio.

Since the system stoichiometry with respect to DOD and cell potential is well investigated, it is sensible to approach the comparison by means of the plateau at 2.075 V corresponding to 59 % DOD: equation 20a predicts 72.23 g kg⁻¹ for maximum reversible mass transfer, which correspond by equation 20b to a maximum reversible specific energy of 175 Wh kg⁻¹. Thus, at theoretical 100 % DOD a maximum of 297 Wh kg⁻¹ may be stored by the system.

$$-\frac{z}{2} \frac{10}{E_{1\%}^{\circ\circ}} \sqrt{(E_{M/M^+}^{\circ} - E_1)^2 + (E_{M/M^+}^{\circ} - E_2)^2} = 72.35 \text{ g kg}^{-1} \quad (20a)$$

$$E_{M/M^+}^{\circ} \text{ for Na/Na}^+ = -2.713 \text{ V} \quad E_{1\%}^{\circ\circ} = -0.062357 \text{ V g kg}^{-1}$$

$$E_1 = -2.075 \text{ V} \quad E_2 = -2.075 \text{ V}$$

$$\bar{E} = 2.075 \text{ V (59 \% DOD)} \quad MW_{Na} = 22.99 \text{ g mol}^{-1} \quad (20b)$$

$$\frac{3.15 \text{ (mol Na)} \cdot 96485 \text{ C} \cdot 2.075 \text{ V} \cdot \text{Wh}}{\text{kg} \cdot (\text{mol Na}) \cdot 3600 \text{ J}} = 175 \text{ Wh kg}^{-1}$$

$$\Rightarrow 297 \text{ Wh kg}^{-1} \text{ (100 \% DOD)}$$

The NGK insulators T5 NAS-cell model represent the current pinnacle of the technology; it features a rated voltage of 2.075 V and a rated capacity of 632 Ah at a mass of 5.5 kg.^{4,9} These figures combine to a nominal specific energy of 238 Wh kg⁻¹. However, the T5 cells are designed to yield that value in practice after 2500 cycles and at 81 % DC efficiency.¹⁰ Thus, the specific energy at theoretical 100 % DC efficiency is 294 Wh kg⁻¹ what virtually closes the gap to the predicted value.

3.3 The LiCoO₂ cell

Lithium cobalt oxide cell bases on Li-intercalation chemistry and shows no potential plateau but a rather steady decrease in potential from 4.2 V up to 2.5 V upon discharge. Up to 50 % of the lithium (hence z = 0.5) can be excalated from the LiCoO₂

cathode until the host lattice becomes instable. The overall cell reaction is shown in equation 21 for a graphite anode.



Since there is a virtual continuum of possible cut-off settings and thus, average voltages, it is sensible to anchor this case to a commercial cell that makes a fair example of the practical benchmark: the Panasonic NCR18650GA cell features a rated capacity of 3300 mAh and a nominal voltage of 3.6 V at a mass of 0.048 kg; the nominal specific energy density is 224 Wh kg⁻¹. Equation 22a predicts on the basis of these figures a maximum mass transfer of 15.88 g kg⁻¹ that by equation 22b correspond to a specific energy of 221 Wh kg⁻¹.

$$-\frac{0.5}{2} \frac{10}{E_{1\%}^{\circ\circ}} \sqrt{(E_{M/M^+}^{\circ} - E_1)^2 + (E_{M/M^+}^{\circ} - E_2)^2} = 15.88 \text{ g kg}^{-1} \quad (22a)$$

$$E_{M/M^+}^{\circ} \text{ for Li/Li}^+ = -3.04 \text{ V} \quad E_{1\%}^{\circ\circ} = -0.062357 \text{ V g kg}^{-1}$$

$$E_1 = -3.6 \text{ V} \quad E_2 = -3.6 \text{ V}$$

$$\bar{E} = 3.6 \text{ V} \quad MW_{Li} = 6.94 \text{ g mol}^{-1} \quad (22b)$$

$$\frac{2.29 \text{ (mol Li)} \cdot 96485 \text{ C} \cdot 3.6 \text{ V} \cdot \text{Wh}}{\text{kg} \cdot (\text{mol Li}) \cdot 3600 \text{ J}} = 221 \text{ Wh kg}^{-1}$$

3.4 The LiFePO₄ cell

The LiFePO₄ battery cell reaction is shown in equation 23 (for a graphite anode) and bases likewise those of the LiCoO₂ cell on intercalation at the difference that by principle all lithium may be excalated, thus is z = 1.¹¹



The cell potential-capacity diagram shows a plateau at 3.2 V, equation 24a predicts on the basis of this average voltage a maximum mass transfer of 9.07 g kg⁻¹ that by equation 24b correspond to a maximum reversible specific energy of 112 Wh kg⁻¹, in fine agreement with the literature threshold of 110 Wh kg⁻¹ achievable in a LiFePO₄ cell.

$$-\frac{1}{2} \frac{10}{E_{1\%}^{\circ\circ}} \sqrt{(E_{M/M^+}^{\circ} - E_1)^2 + (E_{M/M^+}^{\circ} - E_2)^2} = 9.07 \text{ g kg}^{-1} \quad (24a)$$

$$E_{M/M^+}^{\circ} \text{ for Li/Li}^+ = -3.04 \text{ V} \quad E_{1\%}^{\circ\circ} = -0.062357 \text{ V g kg}^{-1}$$

$$E_1 = -3.2 \text{ V} \quad E_2 = -3.2 \text{ V}$$

$$\bar{E} = 3.2 \text{ V} \quad MW_{Li} = 6.94 \quad (24b)$$

$$\frac{1.31 \text{ (mol Li)} \cdot 96485 \text{ C} \cdot 3.2 \text{ V} \cdot \text{Wh}}{\text{kg} \cdot (\text{mol Li}) \cdot 3600 \text{ J}} = 112 \text{ Wh kg}^{-1}$$

3.5 The lithium-sulphur cell

The lithium-sulphur (LIS) cell is chemically related to the NAS-cell but promises a substantially higher specific energy due to the comparatively lower mass of lithium.¹²

The alleged theoretical maximum is 2600 Wh kg⁻¹.¹³ For a traditional liquid LIS-battery cell the potential follows upon discharge about the course outlined in Table 1.¹⁴

Table 1 Schematic potential-capacity course of a liquid LIS-battery cell during discharge

Curve behaviour	Potential [V]	Capacity [mAh g ⁻¹]	Capacity %
Potential drop	3.2 – 2.4	0 - 100	0.077
Plateau	2.4	100 - 300	0.154
Potential drop	2.4 – 2.0	300 - 600	0.231
Plateau	2.0	600 - 1100	0.385
Potential drop	2.0 – 1.74	1100 - 1300	0.154

For E_1 and E_2 boundaries set at $-\bar{E} = -2.13$ V, equation 25a yields a maximum reversible mass transfer of 103.12 g kg⁻¹ which by equation 25b correspond to 849 Wh kg⁻¹.

$$\bar{E} = (\nu(3.2 \cdot 2.4))^{0.077} \cdot 2.4^{0.154} \cdot (\nu(2.4 \cdot 2.0))^{0.231} \cdot 2.0^{0.385} \cdot (\nu(2.0 \cdot 1.74))^{0.154} \text{ V} = 2.13 \text{ V} \quad (25a)$$

$$-\frac{2}{2} \frac{10}{E_{1\%}^{\circ\circ}} \sqrt{(E_{M/M^+}^{\circ} - E_1)^2 + (E_{M/M^+}^{\circ} - E_2)^2} = 103.19 \text{ g kg}^{-1}$$

$$E_{M/M^+}^{\circ} \text{ for Li/Li}^+ = -3.04 \text{ V} \quad E_{1\%}^{\circ\circ} = -0.062357 \text{ V g kg}^{-1}$$

$$E_1 = -2.13 \text{ V} \quad E_2 = -2.13 \text{ V}$$

$$\bar{E} = 2.13 \text{ V} \quad MW_{\text{Li}} = 6.94 \quad (25b)$$

$$\frac{14.87 \text{ (mol Li)} \cdot 96485 \text{ C} \cdot 2.13 \text{ V} \cdot \text{Wh}}{\text{kg} \cdot (\text{mol Li}) \cdot 3600 \text{ J}} = 849 \text{ Wh kg}^{-1}$$

2.15 V and 2.2 V are also common average voltage values in literature, placing these figures in lieu of 2.13 V yields specific energies of 838 Wh kg⁻¹ and 809 Wh kg⁻¹, respectively. In sum, the predicted maximum reversible specific energies from these generic average voltages range between 800 and 850 Wh kg⁻¹. These figures refer to 100 % DOD and since the stoichiometric LIS-cell sulphur electrolyte solubility pattern is identical to those of the NAS-cell, it may be expected that Li₂S₃ respective 36 % DOD (= 5.33 mol Li / 14.87 mol Li) according to equations 19 and 25b mark a barrier to easy improvements in specific energy. By the above figures this corresponds to a specific energy between 291 – 306 Wh kg⁻¹; specific energies >306 Wh kg⁻¹ may be attainable only at disproportionate difficulty. The current cue target in LIS-cell R&D is a specific energy of 500 Wh kg⁻¹ with manufacturer OXIS Energy Ltd announcing leading-edge 400 ±10 Wh kg⁻¹. However, cycle life is rather limited (60 – 100 cycles) and interestingly enough, the also experimental high power cell model features a substantially lower specific energy of 300 ±5 Wh kg⁻¹.

4. Discussion

Is it possible to theoretically reproduce the empiric maximum reversible specific energies of electrochemical systems by a single unified approach? There is much reason for answering that question with yes. The present solution approaches the issue from the reductive end of the reversible electrochemical system and yields reasonable figures for the maximum specific energy. However, the quality of the result evidently depends much on the proper determination of the mean voltage.

This may be complicated by the fact that in electrochemical systems thermodynamics and kinetics are intertwined and the concept of reversibility is bound to infinitesimally slow progress. It is noteworthy that by this formalism a higher mean cell voltage corresponds to a lower specific energy if it is smaller than the SHE potential of the pristine metal redox pair. Proper determination of mean cell voltage is one of two factors affecting the quality of the theoretical assessments; the other is the amount of atomic mass transferred in the redox reaction. The overall relation is the following: the smaller the molecular mass transferred, the larger the entailing deviation from misplaced mean voltage.

Consequently, it is the mass of the migrating species and not those of the chemical reaction that is of primary importance to the system's specific energy; the latter merely sets the frame.

The model developed in this work may be simple but if fed with representative data, it yields representative results: this works irrespective of the actual cell reaction (as it should for a thermodynamic model). The spread to typical blanket specific energy threshold values is in the order of just a few Wh kg⁻¹. Even if the deviation was more substantial, say in the order of several tens of Wh kg⁻¹, this still would represent a noteworthy improvement compared to the plain sum formula-based ΔG calculations leading to figures such as the 2600 Wh kg⁻¹ for the LIS-cell. Practical specific energies make only for a very minor fraction of such figures and relating that fact to the undeniably correct yet non-expedient explanations that further stuff is needed for building the cell and more stuff happens while operating the cell does not make the best possible basis for describing empiric reality and thus, decision making. Yet no one seemed to have cared much about that blatant divergence so far and hence the need for a better explanation, at least from a science theory point of view.

This simple thermodynamic formalism provides just that and gives a much better idea than anything previous what practical specific energy may be expected at best from a reversible electrochemical energy storage system. Figuratively speaking in analogy to a tree trunk, an energy storage system may be envisaged as composing of ideal core wood covered by sapwood and all engineering and science can do is proceeding towards that solid core by optimization.

5. Conclusions

Fathoming the thermodynamic limitations of reversible energy storage systems was initially motivated by ameliorating the evidently inadequate theoretical understanding of reversible chemical hydrogen storage; there the concept works with great effect as a connecting principle to (allegedly isolated) empiric results. But if reversible mass transfer limitation was truly rooted in thermodynamics, the principle must be organic to reversible chemical energy storage systems of any kind.

While such an exhaustive treatise is beyond the means of a research paper, the foundations and the line of argument of the present demonstration for reversible electrochemical energy storage are clearly outlined from start to finish.

The result suggests the conclusion that nature offers much less freedom for the engineering of reversible chemical energy storage systems as authoritative positivist opinion on the matter likes to suggest to this day.

This is where this work makes a real difference; there is now a theorem existent that reveals a still sketchy yet sound global thermodynamic order to reversible chemical energy storage; on the specific level it provides theoretical assessments that meet long-standing empiric thresholds more closely than any previous method.

That may be all what a sound theory can deliver.

It is hoped that the reader profited from reading this and the other paper and that this comprehensive effort will contribute towards a better global understanding of reversible chemical energy storage.

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7. Conflicts of interest

There are no conflicts to declare.

8. Notes and references

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