Irreversible Port-Hamiltonian Formulation of some Non-isothermal Electrochemical Processes

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Abstract: Electrochemical processes have been developed for a wide range of applications such as, mineral refining, water purification, energy storage and generation. The development of models to describe these processes is very important for their analysis, optimization and operation. The framework of irreversible port-Hamiltonian systems has proven to be an important tool to analyze and integrate thermal models with models of different domains. This work discusses the modeling of non-isothermal electrochemical processes as irreversible port-Hamiltonian systems. An irreversible port-Hamiltonian model based on the internal energy function is derived for a simple but general example. The irreversible model is obtained from the molar and charge balance equations combined with the entropy balance equation. The resulting model can be interpreted as a thermodynamic system and aspects such as entropy production, thermodynamic driving forces and intensive/extensive variables are encoded in the representation. An electrochemical process with two simultaneous reactions is considered to illustrate the approach. The interconnection with a resistive load is also considered to illustrate the benefit of the port-based formulation of the model.

Keywords: Electrochemical reactions, port-Hamiltonian systems, irreversible thermodynamics, modeling.

1. INTRODUCTION

Electrochemical processes are ver important in many technological systems such as energy storage and water purification. These systems encompass many phenomena and their modeling for analysis and control requires the use of systematic approaches. The port-Hamiltonian framework (van der Schaft and Jeltsema, 2014; Macchelli, 2003) is modular approach based on port-based models and power-preserving interconnections. It emphasizes the geometry of the state space and the Hamiltonian function (total stored energy) as basic concepts for modeling multi-physics systems, (Duindam and Macchelli, 2009).

The modeling of chemical reactions using port-Hamiltoninan systems have been addressed and the basic ideas can be traced back to the seminal work of Oster, Perselson and Katchalsky (Oster et al., 1973). The problem remains however open specially when considering coupled electrical/mechanical/thermodynamic systems. In (van der Schaft and Maschke, 2011) the geometric formulation of the dynamics of chemical reaction networks within the port-Hamiltonian formalism is discussed. The formulation of a Dirac structure, based on the stoichiometric matrix, and the modeling of the interaction with the environment through the boundary metabolites and their boundary fluxes and affinities provide a framework to have a modular view of chemical reaction network dynamics. The work on expressing isothermal reaction networks as locally dissipative systems with respect to virtual energy and entropy functions has opened the path for addressing analysis and control design problems. Along this line, in (Maschke and van der Schaft, 1992) port-Hamiltonian systems (PHS) are proposed as control system representations for open reaction networks. In (van der Schaft et al., 2013) the geometric structure of the network is explored relating it with graph theory and some virtual energy and entropy function to study stability and model reduction.

In order to deal with non-isothermal reactions, Hoang et al. (2011) propose a thermodynamic pseudo Hamiltonian model for a Continuous Stirred Tank Reactor considering both the isothermal and non-isothermal cases. It is shown that the Gibbs free energy and the opposite of the entropy can be chosen as Hamiltonian function respectively. For the non-isothermal case, the stabilization of the system at a desired state is accomplished by designing a Passivity Based Control. Another work on this direction is presented in (Ramirez et al., 2013a), where the chemical reaction network is modeled as irreversible port-Hamiltonian control systems. These systems express, just like standard port-Hamiltonian systems, the conservation

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of energy as a structural property, but in addition they also express as a structural property the second law of Thermodynamics: the irreversible production of entropy.

The modeling of electrochemical processes has been addressed by several authors. Electrical equivalent representations for electrochemical system neglecting their inherent nonlinearities have been proposed in (Tofighi and Kalantar, 2011). Bond Graph models for modeling electrochemical energy storage systems has proposed by Karnopp (Karnopp, 1990). A a dissipative Lagrangian formalism is proposed in (Shiner et al., 1996) to derive of the state equations describing electrochemical systems. More recently in (Sbarbaro, 2018) port-Hamiltonian models of some isothermal electrochemical processes have been illustrated.

This work adopts an internal energy balance perspective to address the contribution of the non-isothermal characteristic of the electrochemical process. Similar to the energy balance approach used in (Bernardi et al., 1985) (see also (Rao and Newman, 1997; Gu and Wang, 2000) an energy balance equation is included in the dynamical model of the electrochemical process. Using the definition of the thermodynamic properties of the electrochemical systems (Kondepudi and Prigogine, 1998) and inspired by the IPHS formulation of chemical reaction networks (Ramirez et al., 2014) an IPHS model for a general electrochemical process is proposed. This model has a clear thermodynamic interpretation and since it is constructed in terms of energy conjugated ports it is straightforward to interconnect with other systems, such as electrical loads or sources.

The paper is organized as follows. Section 2 presents the basics on IPHS. Section 3 presents the class of electrochemical process to be studied. In Section 4 we give the IPHS formulation of this class of system and finally in Section 5 we present some final remarks and discussion of ongoing and future work.

2. IRREVERSIBLE PORT-HAMILTONIAN SYSTEMS

Irreversible port-Hamiltonian systems (IPHS) have been defined in Ramirez et al. (2013a) as an extension of port-Hamiltonian systems (PHS) for the purpose of representing not only the energy balance but also the entropy balance, essential in thermodynamic systems.

Definition 1. (Ramirez et al., 2013a) An input affine IPHS is defined by the dynamic equation and output relation

$$\begin{aligned} \dot{x} &= R\left(x, \tfrac{\partial U}{\partial x}\right) J \frac{\partial U}{\partial x}(x) + g\left(x, \tfrac{\partial U}{\partial x}\right) v, \\ y &= g^\top\left(x, \tfrac{\partial U}{\partial x}\right) \frac{\partial U}{\partial x}(x) \end{aligned} \tag{1}$$

where $x(t) \in \mathbb{R}^n$ is the state vector, the smooth functions $U(x) : \mathbb{R}^n \to \mathbb{R}$ and $S(x) : \mathbb{R}^n \to \mathbb{R}$ represent, respectively, the internal energy (the Hamiltonian) and the entropy functions, $J \in \mathbb{R}^{n\times n}$ is a constant skew-symmetric structure (interconnection) matrix of the Poisson bracket (Maschke et al., 1992) acting on any two smooth functions Z and G as:

$$\{Z, G\}_J = \frac{\partial Z}{\partial x}^\top(x) J \frac{\partial G}{\partial x}(x). \tag{2}$$

The real function $R = R\left(x, \frac{\partial U}{\partial x}\right)$ is composed by the product of a positive definite function γ and the Poisson bracket between the entropy and the energy functions:

$$R\left(x, \tfrac{\partial U}{\partial x}\right) = \gamma\left(x, \tfrac{\partial U}{\partial x}\right) \{S, U\}_J\,,$$

with $\gamma\left(x, \frac{\partial U}{\partial x}\right) : \mathbb{R}^n \to \mathbb{R}$, $\gamma \geq 0$, a non-linear positive function. The input map is defined by $g\left(x, \frac{\partial U}{\partial x}\right) \in \mathbb{R}^{n\times m}$ with the input $v(t) \in \mathbb{R}^m$ a time dependent function.

The drift dynamic in (1) is defined by a non-linear relation between the time derivative $\dot{x}$ of the state (extensive) variables and $\frac{\partial U}{\partial x}$, characterized by the modulating function $R\left(x, \frac{\partial U}{\partial x}\right)$, which explicitly depends on the co-energy (intensive) variables $\frac{\partial U}{\partial x}$. The balance equations of the total energy and entropy functions of IPHS express the first and second principles of irreversible Thermodynamics: the conservation of energy and the irreversible creation of entropy due to irreversible phenomena. By skew-symmetry of J, the balance equation of the internal energy, which is a convex function,

$$\frac{dU}{dt} = y^\top v, \tag{3}$$

expresses that the system (1) is a lossless dissipative systems with (energy) supply rate $y^\top v$ (Willems, 1972). The balance equation of the entropy function is given by

$$\begin{aligned} \frac{dS}{dt} &= R\left(x, \tfrac{\partial U}{\partial x}, \tfrac{\partial S}{\partial x}\right) \frac{\partial S}{\partial x}^\top J(x) \frac{\partial U}{\partial x} + \frac{\partial S}{\partial x}^\top g\left(x, \tfrac{\partial U}{\partial x}\right) v \\ &= \gamma\left(x, \tfrac{\partial U}{\partial x}\right) \{S, U\}_J^2 + \left(g^\top\left(x, \tfrac{\partial U}{\partial x}\right) \frac{\partial S}{\partial x}\right)^\top v. \\ &= \gamma\left(x, \tfrac{\partial U}{\partial x}\right) \{S, U\}_J^2 + y_s^\top v. \end{aligned} \tag{4}$$

where

$$\begin{aligned} y_s &= g^\top \left(\frac{\partial S}{\partial U}^\top \frac{\partial U}{\partial x} \right) \\ &= \frac{1}{T} g^\top \frac{\partial U}{\partial x} \\ &= \frac{1}{T} y, \end{aligned} \tag{5}$$

is an entropy conjugated output. Here $\frac{\partial S}{\partial x} = \frac{\partial S}{\partial U}^\top \frac{\partial U}{\partial x}$ has been written using the chain rule and $\frac{\partial S}{\partial U} = \frac{1}{T}$ has been used. By Definition 1 the first term is positive: $\gamma\left(x, \frac{\partial U}{\partial x}\right) \{S, U\}_J^2 = \sigma\left(x, \frac{\partial U}{\partial x}\right) \geq 0$. For irreversible thermodynamic systems, this term represents the *internal entropy production* and its positivity expresses the second principle of Thermodynamics. The second term in (4) corresponds to the definition of an entropy supply rate. For further details on IPHS and its thermodynamic interpretation we refer the reader to Ramirez et al. (2013a).

3. A CLASS OF NON-ISOTHERMAL ELECTROCHEMICAL PROCESSES

In this section we first give the basics of some general electrochemical process and then in the following section we present the IPHS representation of this class of system.

Electrochemical processes are characterized by chemical reactions that either produce or are produced by electrical energy. The electrochemical reactions take place at the electrodes, and since these are separated the electrons being transferred are forced to travel and produce an electrical current. The reaction rates taking place at the electrodes are assumed to be described by the Butler-Vollmer kinetics. Let's consider the following half-reaction taking place in one of the electrodes placed in a solution

$$X \overset{r}{\rightleftharpoons} Y + e^-$$

where e^- are the electrons produced on the electrode. The reaction rate is

$$r = \frac{d\xi}{dt} = k_1^+ n_X e^{f_1 Fq/RTC} - k_1^- n_Y e^{(f_1-1)Fq/RTC}$$

where n_X and n_Y are the number of moles of X and Y respectively, k_1^+ and k_1^- are rate constants, ξ is extent of reaction, F the Faraday's constant, R is the gas constant, C is the electrical capacitance of the electrode, T is the temperature, q is the charge on the electrode relative to that of the solution, f_1 is the symmetry constant. In this work the notation of Shiner et al. (1996) for the chemical potential is adopted; i.e. the chemical potential is the traditional electrochemical potential, and the traditional chemical potential is the chemical potential evaluated at the reference electrostatic potential. The relation between the current I; i.e. amount of charge transferred per second is

$$I = nF\frac{d\xi}{dt}$$

where n is the number of electrons transferred. The electrochemical affinity of the reaction considering the electrostatic energy at the electrodes is

$$\tilde{\mathcal{A}} = \mu_X - [\mu_Y + \mu_{e^{-o}}] + Fq/C \qquad (6)$$

where μ_X, μ_Y are the chemical potentials of X and Y, $\mu_{e^{-o}}$ is the chemical potential of the electrons at vanishing electrostatic potential. The bulk solution electrostatic potential is considered as the reference potential. The charge on the electrode is

$$q = Fn_{e^-}$$

where n_{e^-} is the number of electrons. The entropy balance of the reaction is (Kondepudi and Prigogine, 1998)

$$\frac{dS}{dt} = \frac{\tilde{\mathcal{A}}}{T}\frac{d\xi}{dt}. \qquad (7)$$

4. IPHS FORMULATION OF A CLASS OF NON-ISOTHERMAL ELECTROCHEMICAL PROCESSES

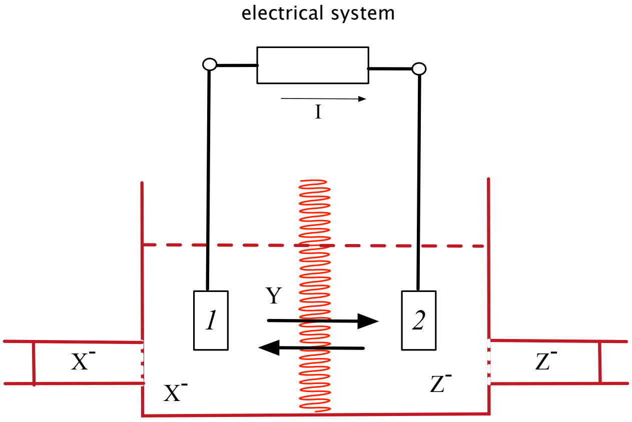

Fig. 1. Electrochemical cell (Hjelmfelt et al., 1991)

Consider a simple electrochemical cell (Hjelmfelt et al., 1991) consisting of two compartments separated by a semipermeable membrane only permeable to the uncharged species Y, as depicted in figure 1. The compartments are connected to reservoirs for X^- and Z^-. The following reactions take part on the electrodes
electrode 1:

$$X^- \overset{r_1}{\rightleftharpoons} Y + e_1^-$$

electrode 2:

$$Y + e_2^- \overset{r_2}{\rightleftharpoons} Z^-$$

The chemical potentials of X^- and Z^- are kept constant at the values of the external reservoirs; i.e. these reservoirs act as ideal sources. It is also assumed that the volume is constant. A normalized volume; i.e. $V = 1$ is considered. It is assumed that the cell is well stirred and the concentration of Y is considered to be uniform. The dynamic of the flow of Y across the membrane is considered to be much faster than the chemical reactions. Let C_1 and C_2 be the electrical capacitances of the electrodes. In this case, the reaction rates are defined as:

$$r_1 = k_1^+ n_X e^{f_1 Fq_1/RTC_1} - k_1^- n_Y e^{(f_1-1)Fq_1/RTC_1}$$
$$r_2 = k_2^+ n_X e^{-f_2 Fq_2/RTC_1} - k_2^- n_Z e^{-(f_2-1)Fq_2/RTC_2}$$

and; therefore, the kinetic equations for the reactions on the electrodes are

$$\frac{d\xi_1}{dt} = r_1$$
$$\frac{d\xi_2}{dt} = r_2$$

The molar balance equations for each species are:

$$\begin{aligned} \frac{dn_{X^-}}{dt} &= -\frac{d\xi_1}{dt} \\ \frac{dn_Y}{dt} &= \frac{d\xi_1}{dt} - \frac{d\xi_2}{dt} \\ \frac{dn_{Z^-}}{dt} &= \frac{d\xi_2}{dt} \end{aligned} \qquad (8)$$

where n_Y, n_{X^-} and n_{Z^-} are the mole number of especie Y, X^- and Z^- respectively. We shall assume that the temperature of the system is uniform throughout and changes due to the electrochemical reactions. Hence, we assume that there are no changes in the heat capacity of the system, no phase changes and no heat transfer with the surrondings.

4.1 IPHS formulation of the chemical reaction scheme

In a first instance we shall follow (Ramirez et al., 2013a, 2014) to propose a IPHS formulation of the chemical scheme, without considering the dynamic of the electrical part of the process. To this end we have that the IPHS model of the purely chemical reaction of the electrochemical process is formulated as

$$\dot{\bar{x}} = \frac{1}{T}\begin{bmatrix} 0 & 0 & 0 & -r_1 \\ 0 & 0 & 0 & (r_1 - r_2) \\ 0 & 0 & 0 & r_2 \\ r_1 & -(r_1 - r_2) & -r_2 & 0 \end{bmatrix} \frac{\partial \bar{U}}{\partial \bar{x}} \qquad (9)$$

with $\bar{U}$ the energy of the chemical process without considering the electrical energy of the charge, $\bar{x} = [n_{X^-}, n_Y, n_{Z^-}, S]^\top$ the vector of extensive variables and

$$\frac{\partial \bar{U}}{\partial \bar{x}} = \begin{bmatrix} \mu_{X^-} \\ \mu_Y \\ \mu_{Z^-} \\ T \end{bmatrix}$$

the vector of intensive variables. We observe in (9) that since we have two parallel reactions taking place the drift dynamic is the composition of two vector fields, each one related to one independent chemical reaction. Following (Ramirez et al., 2014) we split (9) in two vector fields, each one related to a skewsymmetric structure matrix,

$$\begin{aligned} \dot{\bar{x}} &= \frac{r_1}{T}\begin{bmatrix} 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \\ 1 & -1 & 0 & 0 \end{bmatrix}\frac{\partial \bar{U}}{\partial \bar{x}} + \frac{r_2}{T}\begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & -1 & 0 \end{bmatrix}\frac{\partial \bar{U}}{\partial \bar{x}} \\ &= \left(\frac{r_1}{T}\bar{J}_1 + \frac{r_2}{T}\bar{J}_2\right)\frac{\partial \bar{U}}{\partial \bar{x}}. \end{aligned} \tag{10}$$

From this model we identify R_1 and R_2, one for each chemical reaction,

$$\begin{aligned} R_1 &= \frac{r_1}{T}, \\ R_2 &= \frac{r_2}{T}. \end{aligned} \tag{11}$$

The thermodynamic driving forces of the chemical reactions are associated with the Poisson brackets defined by $\bar{J}_1$ and $\bar{J}_2$. Computing them we obtain

$$\begin{aligned} \frac{\partial S}{\partial \bar{x}}^{\top} \bar{J}_1 \frac{\partial \bar{U}}{\partial \bar{x}} &= \mathcal{A}_1, \\ \frac{\partial S}{\partial \bar{x}}^{\top} \bar{J}_2 \frac{\partial \bar{U}}{\partial \bar{x}} &= \mathcal{A}_2, \end{aligned} \tag{12}$$

which are indeed the affinities of reaction and which correspond to the driving force of the chemical reaction. From (11) and (12) we can identify γ_1 and γ_2 from Definition 1,

$$\begin{aligned} \gamma_1 &= \frac{r_1}{T\mathcal{A}_1}, \\ \gamma_2 &= \frac{r_2}{T\mathcal{A}_2}, \end{aligned}$$

which are indeed positive and well defined (Ramirez et al., 2013a).

4.2 IPHS formulation of the electrochemical process

To formulate the IPHS model of the electrochemical process we shall now take into account the electrical part of the process. The evolution of the charge on the electrodes is given by (Hjelmfelt et al., 1991)

$$\begin{aligned} \frac{dq_1}{dt} &= F\frac{d\xi_1}{dt} - I \\ \frac{dq_2}{dt} &= F\frac{d\xi_2}{dt} + I \end{aligned} \tag{13}$$

where I is the current through the electrical load. Define $x = [n_Y, n_{X^-}, n_{Z^-}, q_1, q_2, S]$, i.e., the vector containing the complete state space. The internal energy of the electrochemical process is given by the internal energy of the reaction and the electrical energy at the electrodes (Hjelmfelt et al., 1991; Shiner et al., 1996)

$$U = \bar{U} + \left(\frac{1}{2}\frac{q_1^2}{C_1} - \frac{q_1\mu_{e_1^{-o}}}{F}\right) + \left(\frac{1}{2}\frac{q_2^2}{C_2} - \frac{q_2\mu_{e_2^{-o}}}{F}\right). \tag{14}$$

The vector of intensive variables is obtained from (14),

$$\frac{\partial U}{\partial x} = \begin{bmatrix} \mu_Y, \\ \mu_{X^-}, \\ \mu_{Z^-}, \\ \dfrac{q_1}{C_1} - \dfrac{\mu_{e_1^{-o}}}{F}, \\ \dfrac{q_2}{C_2} - \dfrac{\mu_{e_2^{-o}}}{F} \end{bmatrix}.$$

It is composed by the chemical potentials and the electrical potentials of the electrochemical process. The IPHS representation is obtained similarly to (10) taken into account the electrical part. Hence we obtain

$$\dot{x} = \left(\frac{r_1}{T}J_1 + \frac{r_2}{T}J_2\right)\frac{\partial U}{\partial x} + gI \tag{15}$$

with

$$J_1 = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & F \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & -1 & 0 & -F & 0 & 0 \end{bmatrix},$$

$$J_2 = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & F \\ 0 & 1 & -1 & 0 & -F & 0 \end{bmatrix}.$$

We observe that in addition to the chemical reaction scheme, J_1 and J_2 maps the coupling between the electrical and chemical domain given by (13). The coupling is indeed modulated by the Faraday's constant F. The input map is given by

$$g = \begin{bmatrix} 0 \\ 0 \\ 0 \\ -1 \\ 1 \end{bmatrix}.$$

From (15) we identify the modulating functions $\bar{R}_1$ and $\bar{R}_2$, each for one electrochemical reaction.

$$\begin{aligned} \bar{R}_1 &= \frac{r_1}{T}, \\ \bar{R}_2 &= \frac{r_2}{T}. \end{aligned} \tag{16}$$

Notice that we have used the notation $\bar{R}$ to indicate that the modulating functions now depend on the electical charges. The thermodynamic driving forces of the process are now influenced by the electrical charge of the cell, which affects the reaction rates chemical balances. This is indeed expressed by the Poisson brackets defined by J_1 and J_2,

$$\begin{aligned} \frac{\partial S}{\partial x}^{\top} J_1 \frac{\partial U}{\partial x} &= \mu_{X^-} - \mu_Y - F\left(\frac{q_1}{C_1} - \frac{\mu_{e_1^{-o}}}{F}\right) = \tilde{\mathcal{A}}_1, \\ \frac{\partial S}{\partial x}^{\top} J_2 \frac{\partial U}{\partial x} &= \mu_Y - \mu_{Z^-} - F\left(\frac{q_2}{C_2} - \frac{\mu_{e_2^{-o}}}{F}\right) = \tilde{\mathcal{A}}_2, \end{aligned} \tag{17}$$

which correspond to the electrochemical affinities (Kondepudi and Prigogine, 1998), as expected. Analogous to the purely chemical reaction case, we can identify the positive definite functions $\tilde{\gamma}_1$ and $\tilde{\gamma}_2$,

$$\begin{aligned} \tilde{\gamma}_1 &= \frac{r_1}{T\tilde{\mathcal{A}}_1}, \\ \tilde{\gamma}_2 &= \frac{r_2}{T\tilde{\mathcal{A}}_2}. \end{aligned} \tag{18}$$

The functions $\tilde{\gamma}_1$ and $\tilde{\gamma}_1$ are indeed positive definite and well defined. This can be shown in the same manner as it has been shown in (Ramirez et al., 2013a) for chemical reactions. The IPHS of the process has as input the current of the load, and the energy conjugated output of the system is

$$\begin{aligned} y &= g^\top \frac{\partial U}{\partial x} \\ &= \left(\frac{q_2}{C_2} - \frac{\mu_{e_2^{-o}}}{F}\right) - \left(\frac{q_1}{C_1} - \frac{\mu_{e_1^{-o}}}{F}\right) \\ &= V_{12} \end{aligned}$$

which is the voltage drop over the electrodes, which we have denoted by V_{12}. At both electrodes, the chemical potential of the electrons at the vanishing potential is the same; i.e. $\mu_{e_1^{-o}} = \mu_{e_2^{-o}}$. The IPHS model (15) can be extended to more complex reaction schemes in a similar manner as it has been presented in Ramirez et al. (2014).

4.3 Energy and entropy balance

The energy balance of the process is given by (3),

$$\begin{aligned} \frac{dU}{dt} &= y^\top u \\ &= V_{12} I, \end{aligned} \tag{19}$$

i.e. the electrical power delivered or obtained by the electrochemical process. The entropy balance on the other-hand is given by (4), hence using (16), (17) and (18) we have

$$\begin{aligned} \frac{dS}{dt} &= \sum_{i=1,2} \bar{\gamma}_i \{S, U\}_{J_i}^2 + y_s v \\ &= \sum_{i=1,2} \frac{r_i}{T \tilde{\mathcal{A}}_i} (\tilde{\mathcal{A}}_i)^2 + \frac{V_{12} I}{T} \\ &= \sum_{i=1,2} \sigma_i + \frac{V_{12} I}{T}. \end{aligned} \tag{20}$$

Here $\sum_{i=1,2} \sigma_i = \sigma \geq 0$ is the total internal entropy production generated by the electrochemical reaction. The term $\frac{1}{T} V_{12} I$ represents the entropy flowing in our out of the process. Notice that (20) can be written as

$$\begin{aligned} \frac{dS}{dt} &= \sum_{i=1,2} \bar{R}_i \bar{\mathcal{A}}_i + \frac{V_{12} I}{T} \\ &= \sum_{i=1,2} \frac{\tilde{\mathcal{A}}_i}{T} \frac{d\xi}{dt} + \frac{V_{12} I}{T} \end{aligned}$$

which is the same as (7), but for an electrochemical process with two reactions and one port.

4.4 Interconnection with an electrical load

The interconnection with an electrical load can be done through the port variables. For instance if a resistor with conductance ρ_r is connected, then the current is characterized by the following feedback

$$\begin{aligned} I &= -\rho_r V_{12} \\ &= -\rho_r y \\ &= -\rho_r g^\top \frac{\partial U}{\partial x} \end{aligned} \tag{21}$$

The evolution of the internal energy of the whole system is then described by

$$\begin{aligned} \frac{dU}{dt} &= -\frac{\partial U}{\partial x}^T \left(\rho_r g g^\top\right) \frac{\partial U}{\partial x} \\ &= -\rho_r V_{12}^2 \end{aligned}$$

which corresponds to a dissipative IPHS. From a control perspective, this is indeed expected since the resisitive load can be formulated as a negative feedback and thus induce dissipation with respect to the open-loop Hamiltonian as it has been reported in (Ramirez et al., 2016). Furthemore, from a modelling perspecvtive the interconnection of a thermodynamic system with an electrical system can be formulated as the interconnection of a reversible and an irreversible PHS. This formulation can actually be seen as a generalization of IPHS to coupled mechanical-electrical-thermodynamic systems (Ramirez et al., 2013b, 2018). In this case the entropy balance is given by

$$\begin{aligned} \frac{dS}{dt} &= \sum_{i=1,2} \sigma_i - \frac{\rho_r}{T} V_{12}^2 \\ &= \sigma - \frac{\rho_r}{T} V_{12}^2. \end{aligned}$$

The interconnection with a simple resistive load shows that the IPHS model permits on one hand perform in a natural and simple manner the interconnection with other IPHS or PHS through the ports of the system, while preserving the passive properties of the system. On the other hand it is well suited for control design and stabilization since it provides two potential functions which can be used for passivity based control design (Ramirez et al., 2016).

5. FINAL REMARKS

An irreversible port-Hamiltonian system (IPHS) formulation for a class of non-isothermal electrochemical process has been proposed. An internal energy balance perspective has been adopted to address the contribution of the non-isothermal characteristic of the electrochemical process. An energy balance equation is included in the dynamical model of the process and by using the definition of the thermodynamic properties of the electrochemical systems and inspired by the IPHS formulation of chemical reaction networks, an IPHS model for a general electrochemical process is proposed. This model has a clear thermodynamic interpretation and since it is constructed in terms of internal energy and entropy conjugated ports it is straightforward to interconnect with other systems, such as electrical loads or sources. Futhermore, the passivity properties of the system make the proposed model well suited for control purposes. An example of a simple electrochemical process with two simultaneous reactions is used to derive and illustrate the model. Then a simple resistive load is considered to show the benefit of the port-based formulation of the model. The relation with controlled IPHS is done as well as the relation with reversible-IPHS. Future work will consider the interconnection of the proposed model with realistic loads, the study of more complex electrochemical reactions and the design of model based controllers.

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