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Optimal performance of a generalized irreversible four-reservoir isothermal chemical potential transformer

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A new cyclic model of a four-reservoir isothermal chemical potential transformer with irreversible mass transfer, mass leakage and internal dissipation is put forward in this paper. The optimal relation between the coefficient of performance (COP) and the rate of energy pumping of the generalized irreversible four-reservoir isothermal chemical potential transformer has been derived by using finite-time thermodynamics or thermodynamic optimization. The maximum COP and the corresponding rate of energy pumping, as well as the maximum rate of energy pumping and the corresponding COP, have been obtained. Moreover, the influences of the irreversibility on the optimal performance of the isothermal chemical potential transformer have been revealed. It was found that the mass leakage affects the optimal performance both qualitatively and quantitatively, while the internal dissipation affects the optimal performance quantitatively. The results obtained herein can provide some new theoretical guidelines for the optimal design and development of a class of isothermal chemical potential transformers, such as mass exchangers, electrochemical, photochemical and solid state devices, fuel pumps, etc.

isothermal four-reservoir chemical potential transformer, coefficient of performance, rate of energy pumping, finite time thermodynamics

1 Introduction

In recent years, finite-time thermodynamics[1−9] has been applied to the performance study of various thermodynamic cycles and devices. It has also been extended to the cyclic devices driven by mass flow, such as chemical reactions and chemical engines, by many researchers. Heat engines generate work from differences in temperature. Similarly, chemical engines generate work from differences in chemical potentials. Chemical potential and mass transfer in chemical engines play the analogous roles of temperature and heat current in heat engines[10−19]. The inverse cycle of a heat engine is a refrigerator cycle, a heat pump cycle or a heat transformer cycle. Similarly, the inverse cycle of a chemical engine is a chemical pump cycle or a chemical potential transformer cycle. There are three- and four-heat-reservoir heat transformers. Similarly, there are also three- and four-reservoir chemical potential transformers. The performance of two- and three-reservoir isothermal chemical pumps has been studied[20−23]. Lin et al.[24] analyzed the optimal performance of an endoreversible three-reservoir isothermal chemical potential transformer. They have proved that an endoreversible isothermal chemical potential transformer can be considered as an equivalent combined cycle system having an endoreversible two-reservoir isothermal chemical pump driven by an endoreversible isothermal chemical engine. Wu et al.[25] also studied the performance of an irre-

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versible three-reservoir isothermal chemical potential transformer with the irreversibility of mass transfer and the mass leakage.

An extension of the study of isothermal chemical engines, isothermal chemical pumps and isothermal chemical potential transformers is to analyze the performance characteristics of isothermal chemical cyclic system operating among four reservoirs at different chemical potentials. Xia et al.[26] studied the performance of a four-reservoir isothermal chemical potential transformer with the irreversibility of mass transfer and the mass leakage. A four-reservoir isothermal chemical potential transformer is a new type of these isothermal chemical systems[26]. Just as a four-heat-reservoir heat transformer[27−30] operating among four heat reservoirs is a direct generalization of heat engines, a four-reservoir isothermal chemical potential transformer is a direct generalization of isothermal chemical engines. A four-reservoir isothermal chemical potential transformer is composed of a two-reservoir isothermal chemical pump[20] and an isothermal chemical engine while the former is driven by the latter[13－19]. The isothermal chemical cyclic system is an analogue to the photosynthetic engine discussed by De Vos[31,32], which consists of a fuel pump (i.e. chemical pump) driven by a photovoltaic engine. This new type of isothermal chemical potential transformer is characterized by the capability of improving chemical potentials while simultaneously decreasing environmental pollution. The advantage of this new type model of isothermal chemical potential transformer is that it resembles more the true model of a two-reservoir isothermal chemical pump driven by a isothermal chemical engine than the model of three-reservoir isothermal chemical potential transformer model[24,25], which is analogous to that the model of a four-heat-reservoir heat transformer[27−30] resembles more the true model of an absorption heat transformer[33,34] than the model of a three-heat-reservoir heat transformer[35−38].

In this research, a further step beyond refs. [24－26] has been taken to establish a four-reservoir isothermal chemical potential transformer cycle model with multi-irreversibilities. Besides finite-time mass transfer between the mass reservoirs and the working substance, the mass leakage between the mass reservoirs and the internal dissipation of the cyclic working substance are usually two of the most important irreversible factors for the performance of isothermal chemical potential transformers. Based on the cyclic model, the optimal relation between coefficient of performance (COP) and the rate of energy pumping of a generalized irreversible four-reservoir isothermal chemical potential transformer has been derived by using finite-time thermodynamics or thermodynamic optimization. The maximum COP and the corresponding rate of energy pumping, as well as the maximum rate of energy pumping and the corresponding COP have been also obtained analytically. Moreover, the influences of these irreversibilities on the optimal performance of the isothermal chemical potential transformer have been revealed. The method used herein is analogous to that used in ref. [29] for four-heat-reservoir heat-transformers with irreversibility of heat transfer, heat leakage and internal dissipation of the cyclic working substance.

The problem mentioned above is of practical value to many devices, such as chemical reactive devices, mass exchangers, photochemical cells and solid-state devices[39,40]. As explored by de Vos[31,32], a generalized model of photochemical engine is with four reservoirs at different temperatures and different chemical potentials (see Figure 1). The generalized model of photochemical engine can be simplified as a model of true photochemical engine (Figure 2), or a model of photosynthetic engine (Figure 3), depending on the simplified conditions. The four-reservoir isothermal chemical potential transformer cycle was studied in this work. In fact, the

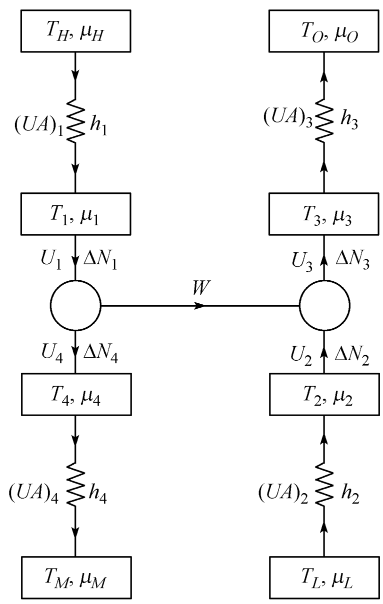

Figure 1 The generalized model of photochemical engines.

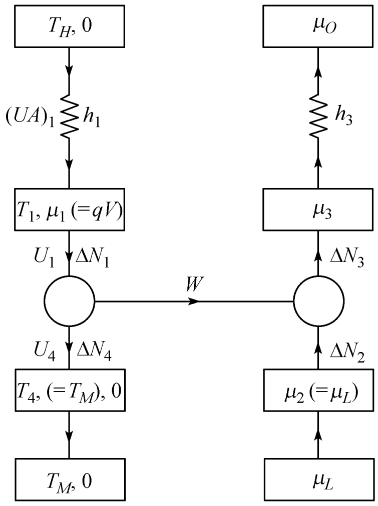

Figure 2 A true photochemical engine.

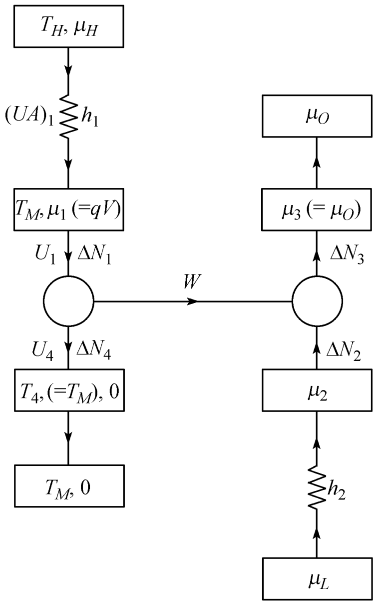

Figure 3 The model of photosynthetic engines.

performance of a three-reservoir isothermal chemical potential transformer is better than that of a four-reservoir isothermal chemical potential transformer. A three-reservoir isothermal chemical potential transformer cycle is a simplified model that has the same chemical potential for two mass-reservoirs, which is different from the situation for a real chemical potential transformer. Therefore, a four-reservoir isothermal chemical potential transformer cycle model is closer to a real chemical potential transformer.

2 A generalized irreversible cycle model

The schematic diagram of a generalized irreversible isothermal chemical potential transformer operated among four-mass-reservoirs is shown in Figure 4. In the Figure, parameters μ_H, μ_L, μ_O and μ_M are, respectively, the chemical potentials of the four reservoirs and they are supposed to be constants and have a relation: $\mu_O > \mu_H > \mu_L > \mu_M$; parameters μ_1, μ_2, μ_3 and μ_4 are, respectively, the chemical potentials of the chemicals involved in the processes in the cyclic working fluid. Because of the existence of finite-rate mass transfer, parameters μ_1, μ_2, μ_3 and μ_4 are, respectively, different from those of the four mass-reservoirs. Parameters ΔN_1, ΔN_2, ΔN_3 and ΔN_4 are, respectively, the amounts of mass exchange between the cyclic working fluid and the four mass reservoirs at chemical potentials μ_H, μ_L, μ_O and μ_M per cycle. Parameters h_1, h_2, h_3 and h_4 are, respectively, the mass-transfer coefficients between the cyclic working fluid and the mass reservoirs at chemical potentials μ_H, μ_L, μ_O and μ_M. According to refs. [33, 34], a four-reservoir chemical potential transformer has similar flow charts as an absorption heat transformer, as shown in Figure 5. The imagined chemical engine transfers mass from one or both of the chemical potential levels μ_1 and μ_2 to the chemical potential level μ_4. On the other hand, the imagined chemical pump transfers mass from one or both of the chemical potential levels μ_1 and μ_2 to the chemical potential level μ_3. The different mass transport paths are entirely chemical potential dependent.

Finally, parameters t_1, t_2, t_3 and t_4 are the corresponding times spent on the four mass transfer processes. Besides the four mass transfer processes between the cyclic

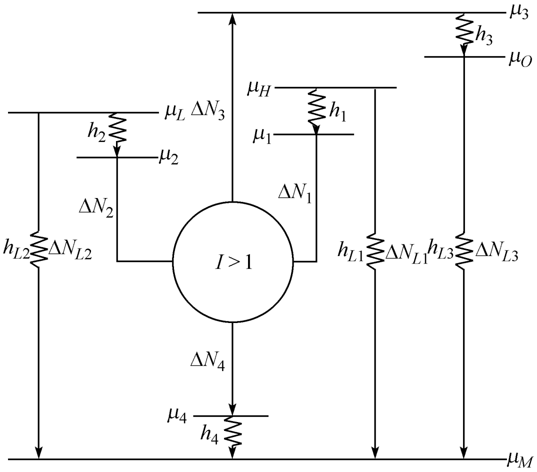

Figure 4 A generalized irreversible four-reservoir isothermal chemical potential transformer model.

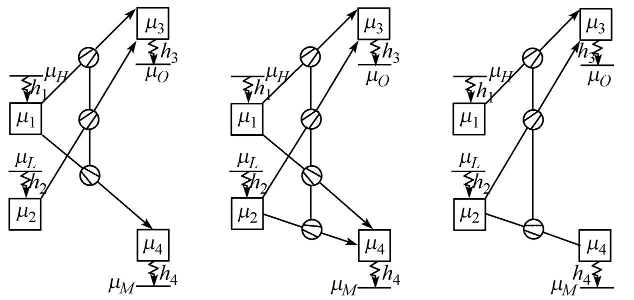

Figure 5 The possible flow charts of four-reservoir chemical potential transformer models.

working substance and the mass reservoirs, there also exist other additional branches of the cycle that connect the four mass-transfer processes. The additional branches do not have mass transfer so that the times spent on the connecting branches without mass transfer are neglected. Therefore, the cyclic period τ of the chemical potential transformer equals, approximately, the sum of t_1, t_2, t_3 and t_4, i.e.

$$\tau = t_1 + t_2 + t_3 + t_4. \tag{1}$$

On the other hand, the mass leakage between the mass reservoirs is often unavoidable for an irreversible four-reservoir isothermal chemical potential transformer. It is supposed that there exists the mass leakage between the mass reservoirs[26]: The quantity of mass leakage between the two mass reservoirs at chemical potentials μ_H and μ_M is ΔN_{L1}; the quantity of mass leakage between the two mass reservoirs at chemical potentials μ_L and μ_M is ΔN_{L2}; the quantity of mass leakage between the two mass reservoirs at chemical potentials μ_O and μ_M is ΔN_{L3}. Finally, parameters h_{L1}, h_{L2} and h_{L3} are the coefficients of mass leakage. It is assumed that the chemical potential capacities of the mass reservoirs (similar to the thermal capacity of a heat reservoir, see ref. [11]) are infinite, and the mass exchange obeys the mass transfer law of linear irreversible thermodynamics[10−23]. Under this circumstance, there exist the following relationships:

$$\Delta N_1 = h_1(\mu_H - \mu_1)t_1,\quad \Delta N_2 = h_2(\mu_L - \mu_2)t_2,$$
$$\Delta N_3 = h_3(\mu_3 - \mu_O)t_3,\quad \Delta N_4 = h_4(\mu_4 - \mu_M)t_4, \tag{2}$$
$$\Delta N_{L1} = h_{L1}(\mu_H - \mu_M)\tau,\quad \Delta N_{L2} = h_{L2}(\mu_L - \mu_M)\tau,$$
$$\Delta N_{L3} = h_{L3}(\mu_O - \mu_M)\tau. \tag{3}$$

Besides the irreversibility of mass transfer and mass leakage, the internal dissipation resulting from friction, eddies and other irreversible effects inside the cyclic working substance should be taken into account. Owing to the existence of the internal irreversibility, the entropy flowing out of the working substance per cycle is larger than that flowing into the working substance per cycle. According to the definition of entropy without volume change and the second law for the system including the working substance and the mass reservoirs, considering the features of isothermal cycle, one has

$$[(\Delta U_3 - \mu_3\Delta N_3) + (\Delta U_4 - \mu_4\Delta N_4)] - [(\Delta U_1 - \mu_1\Delta N_1) + (\Delta U_2 - \mu_2\Delta N_2)] \geqslant 0, \tag{4}$$

where ΔU_1 and ΔU_2 are , respectively, the internal energy flowing into the iso-chemical potential processes at chemical potentials μ_1 and μ_2; ΔU_3 and ΔU_4 are, respectively, the internal energy flowing out of the iso-chemical potential processes at chemical potentials μ_3 and μ_4. They satisfy the following relation according to the law of energy conservation

$$\Delta U_1 + \Delta U_2 = \Delta U_3 + \Delta U_4. \tag{5}$$

Substituting eq. (5) into eq. (4), one obtains

$$\mu_1\Delta N_1 + \mu_2\Delta N_2 - \mu_3\Delta N_3 - \mu_4\Delta N_4 \geqslant 0. \tag{6}$$

Now, one may introduce a parameter

$$I = \frac{\mu_1\Delta N_1 + \mu_2\Delta N_2}{\mu_3\Delta N_3 + \mu_4\Delta N_4}, \tag{7}$$

to describe the internal irreversibility of the working substance. It is clear that the internal irreversible parameter I is always lager than 1. When the internal irreversibility is small enough, it may be negligible, i.e. I = 1. The definition of parameter I comes from the first and second laws of thermodynamics, and the similar definitions were adopted for irreversible three- and four-heat-reservoir heat transformer cycles[29,36], two-reservoir isothermal chemical engine cycles[18] and three-reservoir isothermal chemical potential transformer cycle[24,25]. In practical use, parameter I can be calculated from the collected data by using eq. (7), and the averaged value for a class of devices can be used to predict performance of new devices. Of course, one can use other parameters to characterize internal irreversibility of the working substance, such as entropy production.

According to the law of mass conservations, one has

$$\Delta N_3 + \Delta N_4 - \Delta N_1 - \Delta N_2 = 0. \tag{8}$$

3 Optimal characteristic

Parameter b denotes the ratio of the transferred energy quantity of the second mass reservoir to the total transferred energy quantity of the first and the second mass reservoirs

$$b = \frac{\mu_L \Delta N_2}{\mu_H \Delta N_1 + \mu_L \Delta N_2}. \tag{9}$$

According to the definitions of COP χ and the rate of energy pumping Σ of the isothermal chemical potential transformer, one has

$$\chi = \frac{\mu_O(\Delta N_3 - \Delta N_{L3})}{\mu_H(\Delta N_1 + \Delta N_{L1}) + \mu_L(\Delta N_2 + \Delta N_{L2})}, \tag{10}$$

$$\Sigma = \frac{\mu_O(\Delta N_3 - \Delta N_{L3})}{\tau}. \tag{11}$$

Combining equations (1)—(11) gives

$$\begin{aligned}\chi = \mu_O\{&[(1-b)\mu_H{}^{-1}(\mu_1 - I\mu_4) + b\mu_L{}^{-1}(\mu_2 - I\mu_4)]\\ &\times[I(\mu_3-\mu_4)]^{-1} - h_{L3}(\mu_O - \mu_M)A\}\\ &\times\{1+[h_{L1}\mu_H(\mu_H-\mu_M)+h_{L2}\mu_L(\mu_L-\mu_M)]A\}^{-1},\end{aligned} \tag{12}$$

$$\begin{aligned}\Sigma = \mu_O&[(1-b)\mu_H{}^{-1}(\mu_1 - I\mu_4) + b\mu_L{}^{-1}(\mu_2 - I\mu_4)]\\ &\times[AI(\mu_3-\mu_4)]^{-1} - h_{L3}\mu_O(\mu_O - \mu_M),\end{aligned} \tag{13}$$

where

$$\begin{aligned}A = &\frac{(1-b)\mu_H{}^{-1}}{h_1(\mu_H-\mu_1)} + \frac{b\mu_L{}^{-1}}{h_2(\mu_L-\mu_2)}\\ &+\frac{(1-b)\mu_H{}^{-1}(\mu_1 - I\mu_4) + b\mu_L{}^{-1}(\mu_2 - I\mu_4)}{h_3 I(\mu_3-\mu_4)(\mu_3-\mu_O)}\\ &+\frac{(1-b)\mu_H{}^{-1}(I\mu_3 - \mu_1) + b\mu_L{}^{-1}(I\mu_3 - \mu_2)}{h_4 I(\mu_3-\mu_4)(\mu_4-\mu_M)}.\end{aligned}$$

3.1 Fundamental optimal relation

Now, the problem is to determine the optimal rate of energy pumping of the four-reservoir isothermal chemical potential transformer for a given COP. Therefore, a Lagrangian function $L = \Sigma + \lambda\chi$ can be introduced, where λ is the Lagrangian multiplier. There exists the following relationship:

$$\begin{aligned}L = \mu_O&[(1-b)\mu_H{}^{-1}(\mu_1 - I\mu_4) + b\mu_L{}^{-1}(\mu_2 - I\mu_4)]\\ &\times[AI(\mu_3-\mu_4)]^{-1} - h_{L3}\mu_O(\mu_O-\mu_M)\\ &+\lambda\mu_O\{[(1-b)\mu_H{}^{-1}(\mu_1 - I\mu_4) + b\mu_L{}^{-1}(\mu_2 - I\mu_4)]\\ &\times[I(\mu_3-\mu_4)]^{-1} - h_{L3}(\mu_O-\mu_M)A\}\\ &\times\{1+[h_{L1}\mu_H(\mu_H-\mu_M)+h_{L2}\mu_L(\mu_L-\mu_M)]A\}^{-1}.\end{aligned} \tag{14}$$

From the Euler-Lagrange equations $\partial L/\partial\mu_1 = 0$, $\partial L/\partial\mu_2 = 0$, $\partial L/\partial\mu_3 = 0$ and $\partial L/\partial\mu_4 = 0$, one can find that the following equations must be satisfied:

$$\begin{aligned}\mu_L - \mu_2 &= \sqrt{h_1/h_2}(\mu_H - \mu_1),\\ \mu_3 - \mu_O &= \sqrt{h_1/Ih_3}(\mu_H - \mu_1),\\ \mu_4 - \mu_M &= \sqrt{h_1/Ih_4}(\mu_H - \mu_1).\end{aligned} \tag{15}$$

Substituting eq. (15) into eqs. (12) and (13) yields the optimal COP and the optimal dimensionless rate of energy pumping $\Sigma^* = \Sigma/(h_1\mu_H\mu_O)$ as follows:

$$\chi = \frac{\begin{aligned}&\mu_O/\mu_H\{1 - I\mu_M[(1-b)\mu_H^{-1} + b\mu_L^{-1}]\\ &-[(1-b)(1+\sqrt{Ib_3}) + b\mu_H\mu_L^{-1}(\sqrt{b_1}+\sqrt{Ib_3})]k\\ &-b_{L3}(\mu_O-\mu_M)\mu_H^{-1}A_1/k\}\end{aligned}}{\begin{aligned}&I(\mu_O-\mu_M)\mu_H^{-1} + (\sqrt{Ib_2}-\sqrt{Ib_3})k\\ &+A_1[b_{L1}\mu_H(\mu_H-\mu_M)+b_{L2}\mu_L(\mu_L-\mu_M)]/\mu_H^2/k\end{aligned}}, \tag{16}$$

$$\begin{aligned}\Sigma^* = kA_1^{-1}&\{1 - I\mu_M[(1-b)\mu_H^{-1} + b\mu_L^{-1}]\\ &-[(1-b)(1+\sqrt{Ib_3}) + b\mu_H\mu_L^{-1}(\sqrt{b_1}+\sqrt{Ib_3})]k\}\\ &-b_{L3}(\mu_O-\mu_M)/\mu_H,\end{aligned} \tag{17}$$

where

$$\begin{aligned}A_1 = &\sqrt{Ib_2} - \sqrt{Ib_3} + (1-b)\mu_H^{-1}I[(1+\sqrt{Ib_3})\mu_O\\ &-(1+\sqrt{Ib_2})\mu_M] + b\mu_L^{-1}I[(\sqrt{b_1}+\sqrt{Ib_3})\mu_O\\ &-(\sqrt{b_1}+\sqrt{Ib_2})\mu_M],\end{aligned}$$

$k = 1 - \mu_1/\mu_H$, $b_1 = h_1/h_2$, $b_2 = h_1/h_3$, $b_3 = h_1/h_4$, $b_{L1} = h_{L1}/h_1$, $b_{L2} = h_{L2}/h_1$, and $b_{L3} = h_{L3}/h_1$. Eliminating $k = 1 - \mu_1/\mu_H$ from eqs. (16) and (17) yields the fundamental optimal relation for the four-reservoir isothermal chemical potential transformer with irreversible mass transfer, mass leakage and internal dissipation, which may be used directly to analyze the influences of major irreversibilities on the performance of an irreversible four-reservoir isothermal chemical potential transformer.

3.2 The maximum COP $\chi_{\max}$ and the corresponding dimensionless rate of energy pumping Σ_χ^*

Using eq. (16) and the extreme condition $\partial\chi/\partial k = 0$, one can find that when

$$k_\chi = A_1[B_1 + (B_1^2 + B_2B_3/A_1)^{1/2}]/B_2, \tag{18}$$

the COP attains its extremum, i.e.

$$\chi_{\max}=\frac{\mu_O}{\mu_H}$$

$$\times\frac{\begin{array}{l}1-I\mu_M[(1-b)\mu_H^{-1}+b\mu_L^{-1}]-[(1-b)(1+\sqrt{Ib_3})\\+b\mu_H\mu_L^{-1}(\sqrt{b_1}+\sqrt{Ib_3})]A_1[B_1+(B_1^2+B_2B_3/A_1)^{1/2}]/\\B_2-b_{L3}(\mu_O-\mu_M)\mu_H^{-1}B_2[B_1+(B_1^2+B_2B_3/A_1)^{1/2}]^{-1}\end{array}}{\begin{array}{l}(\sqrt{Ib_2}-\sqrt{Ib_3})A_1[B_1+(B_1^2+B_2B_3/A_1)^{1/2}]/B_2\\+I(\mu_O-\mu_M)\mu_H^{-1}+[b_{L1}\mu_H(\mu_H-\mu_M)\\+b_{L2}\mu_L(\mu_L-\mu_M)]/\mu_H^2B_2[B_1+(B_1^2+B_2B_3/A_1)^{1/2}]^{-1}\end{array}}. \quad (19)$$

and the corresponding dimensionless rate of energy pumping is given by

$$\begin{aligned}\Sigma_\chi^*=&\{1-I\mu_M[(1-b)\mu_H^{-1}+b\mu_L^{-1}]-A_1[(1-b)(1+\sqrt{Ib_3})\\&+b\mu_H\mu_L^{-1}(\sqrt{b_1}+\sqrt{Ib_3})][B_1+(B_1^2+B_2B_3/A_1)^{1/2}]/B_2^2\}\\&\times[B_1+(B_1^2+B_2B_3/A_1)^{1/2}]/B_2-b_{L3}(\mu_O-\mu_M)/\mu_H,\end{aligned} \quad (20)$$

where

$$\begin{aligned}B_1=&(\sqrt{Ib_2}-\sqrt{Ib_3})b_{L3}(\mu_O-\mu_M)\mu_H^{-1}\\&-[(1-b)(1+\sqrt{Ib_3})+b\mu_H\mu_L^{-1}(\sqrt{b_1}+\sqrt{Ib_3})]\\&\times[b_{L1}\mu_H(\mu_H-\mu_M)+b_{L2}\mu_L(\mu_L-\mu_M)]/\mu_H^2,\end{aligned}$$

$$\begin{aligned}B_2=&\{1-I\mu_M[(1-b)\mu_H^{-1}+b\mu_L^{-1}]\}(\sqrt{Ib_2}-\sqrt{Ib_3})\\&+I(\mu_O-\mu_M)[(1-b)\mu_H^{-1}(1+\sqrt{Ib_3})\\&+b\mu_L^{-1}(\sqrt{b_1}+\sqrt{Ib_3})],\end{aligned}$$

and

$$\begin{aligned}B_3=&(\{1-I\mu_M[(1-b)\mu_H^{-1}+b\mu_L^{-1}]\}[b_{L1}\mu_H(\mu_H-\mu_M)\\&+b_{L2}\mu_L(\mu_L-\mu_M)]-Ib_{L3}(\mu_O-\mu_M)^2)/\mu_H^2.\end{aligned}$$

$\chi_{\max}$ and Σ_χ^* are two important parameters for the irreversible four-reservoir isothermal chemical potential transformer, which determine the upper bound of the coefficient of performance and the lower bound of the rate of energy pumping of the irreversible four-reservoir isothermal chemical potential transformer.

3.3 The maximum dimensionless rate of energy pumping $\Sigma_{\max}^*$ and the corresponding COP Σ_{χ^*}

Using eq. (17) and the extreme condition $\partial\Sigma^*/\partial k=0$, one can find that when

$$k_{\Sigma^*}=\frac{1-I\mu_M[(1-b)\mu_H^{-1}+b\mu_L^{-1}]}{2[(1-b)(1+\sqrt{Ib_3})+b\mu_H\mu_L^{-1}(\sqrt{b_1}+\sqrt{Ib_3})]}. \quad (21)$$

The dimensionless rate of energy pumping attains its extremum, i.e.

$$\begin{aligned}\Sigma_{\max}^*=&\frac{1}{4}\{1-I\mu_M[(1-b)\mu_H^{-1}+b\mu_L^{-1}]\}^2[(1-b)(1+\sqrt{Ib_3})\\&+b\mu_H\mu_L^{-1}(\sqrt{b_1}+\sqrt{Ib_3})]^{-1}A_1^{-1}-b_{L3}(\mu_O-\mu_M)/\mu_H,\end{aligned} \quad (22)$$

and the corresponding COP is given by

$$\chi_{\Sigma^*}=\frac{\begin{array}{l}\{1-I\mu_M[(1-b)\mu_H^{-1}+b\mu_L^{-1}]\}/2\\-2A_1b_{L3}(\mu_O-\mu_M)[(1-b)\mu_H^{-1}(1+\sqrt{Ib_3})+b\mu_L^{-1}\\(\sqrt{b_1}+\sqrt{Ib_3})]\{1-I\mu_M[(1-b)\mu_H^{-1}+b\mu_L^{-1}]\}^{-1}\end{array}}{\begin{array}{l}I(\mu_O-\mu_M)/\mu_O+\{1-I\mu_M[(1-b)\mu_H^{-1}+b\mu_L^{-1}]\}\\(\sqrt{Ib_2}-\sqrt{Ib_3})\{[(1-b)(1+\sqrt{Ib_3})\\+b\mu_H\mu_L^{-1}(\sqrt{b_1}+\sqrt{Ib_3})]\}^{-1}+2A_1[b_{L1}\mu_H(\mu_H-\mu_M)\\+b_{L2}\mu_L(\mu_L-\mu_M)]/\mu_H[(1-b)\mu_H^{-1}(1+\sqrt{Ib_3})\\+b\mu_L^{-1}(\sqrt{b_1}+\sqrt{Ib_3})]\{1-I\mu_M[(1-b)\mu_H^{-1}+b\mu_L^{-1}]\}^{-1}\end{array}}. \quad (23)$$

$\Sigma_{\max}^*$ and χ_{Σ^*} are other two important parameters for the irreversible four-reservoir isothermal chemical potential transformer, which determine the upper bound of the rate of energy pumping and the lower bound of the COP of the irreversible four-reservoir isothermal chemical potential transformer.

4 Numerical examples

In order to study the characteristics of a four-reservoir irreversible isothermal chemical potential transformer, one numerical example is provided. The characteristic curve of a four-reservoir isothermal chemical potential transformer with irreversible mass transfer, mass leakage and internal dissipation was plotted, as shown in Figure 6. Figure 6 shows that there exist a maximum COP $\chi_{\max}$ and the corresponding dimensionless rate of energy pumping Σ_χ^*, as well as a maximum dimensionless rate of energy pumping $\Sigma_{\max}^*$ and the corresponding COP χ_{Σ^*}. In the calculations, $I=1.05$, $b_{L1}=0.001$, $b_{L2}=0.001$, $b_{L3}=0.001$, $\mu_M/\mu_O=0.5$, $\mu_O/\mu_L=1.25$, $\mu_H/\mu_M=1.45$, $b=0.5$, $\sqrt{b_1}=1.1$, $\sqrt{b_2}=1.3$ and $\sqrt{b_3}=1.2$ are set.

The influence of b_{Li} ($i=1,\ 2,\ 3$) on the performance of the four-reservoir chemical potential transformer cycle without internal dissipation ($I=1$) and with μ_O/μ_L

$=1.25$, $\mu_H / \mu_M = 1.45$, and $b = 0.5$ is shown in Figure 7. The influence of b_{Li} ($i = 1, 2, 3$) on the performance of irreversible cycle the four-reservoir chemical potential transformer cycle with $I = 1.05$, $\mu_O / \mu_L = 1.25$, $\mu_H / \mu_M = 1.45$, and $b = 0.5$ is shown in Figure 8. It can be seen from Figures 7 and 8 that the fundamental optimal relation between the dimensionless rate of energy pumping and the COP is similar to a parabolic curve when mass leakage can be ignored ($b_{Li} = 0$), and the fundamental optimal relation between the dimensionless rate of energy pumping and the COP shows a loop-shape when mass leakage cannot be ignored ($b_{Li} > 0$). It shows that the optimal performance is influenced by mass leakage qualitatively. When the mass leakage is considered, the optimal COP for a given

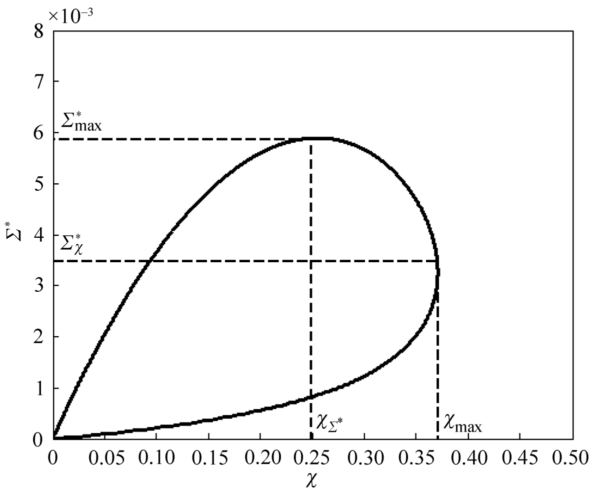

Figure 6 The optimal dimensionless rate of energy pumping Σ^* versus COP χ.

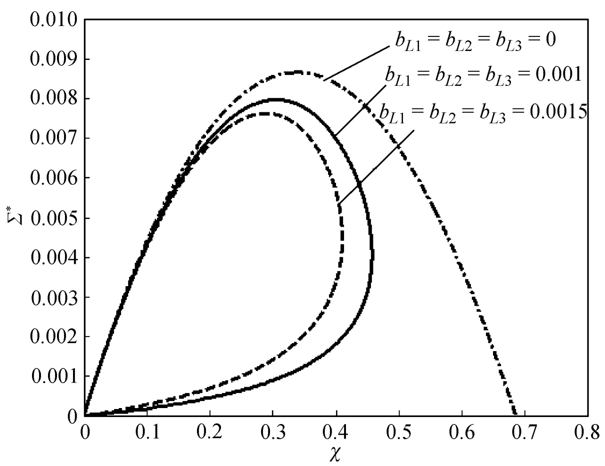

Figure 7 Influence of b_{Li} on the performance of the chemical potential transformer with $I = 1$.

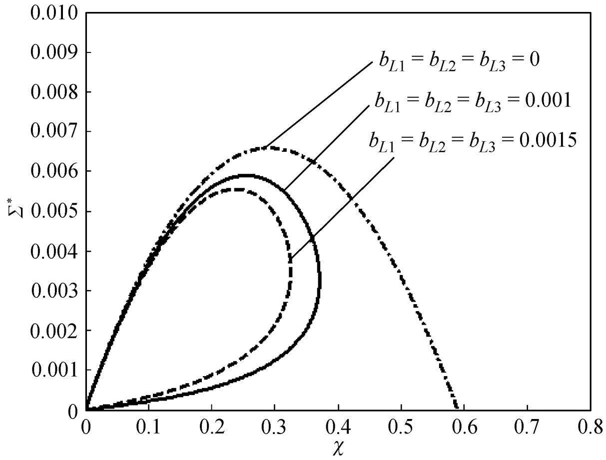

Figure 8 Influence of b_{Li} on the performance of the chemical potential transformer with $I = 1.05$.

dimensionless rate of energy pumping and the optimal dimensionless rate of energy pumping for a given COP decrease as the mass leakage coefficient b_{Li} increases.

The influence of I on the performance of the four-reservoir chemical potential transformer cycle without mass leakage ($b_{Li} = 0$, $i = 1, 2, 3$) and with $\mu_O / \mu_L = 1.25$, $\mu_H / \mu_M = 1.45$, and $b = 0.5$ is shown in Figure 9. It can be seen from Figure 9 that the fundamental optimal relation shows a parabolic curve whether the internal irreversibility is ignored ($I = 1$) or not ($I > 1$). The influence of I on the performance of the four-reservoir chemical potential transformer cycle with mass leakage ($b_{Li} = 0.001, i = 1, 2, 3$) and with $\mu_O / \mu_L = 1.25$, $\mu_H / \mu_M = 1.45$, and $b = 0.5$ is shown in Figure 10. It can be seen from Figure 10 that the fundamental optimal

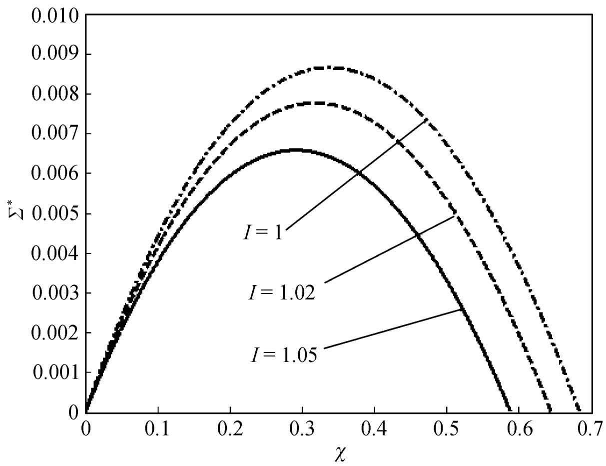

Figure 9 Influence of I on the performance of the chemical potential transformer with $b_{Li} = 0$.

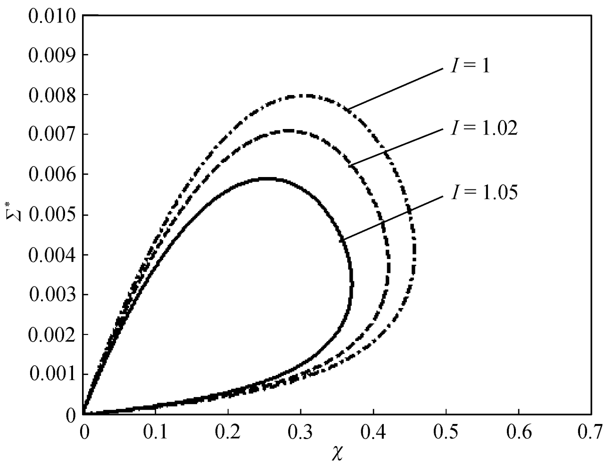

Figure 10 Influence of I on the performance of the chemical potential transformer with $b_{Li} = 0.001$.

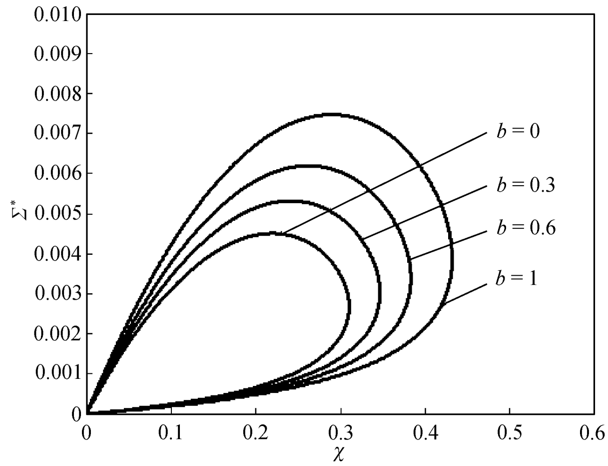

Figure 11 The influence of b on Σ^* versus χ with $b_{Li} = 0.001$ (i = 1, 2, 3) and I = 1.05.

relation exhibits a loop-shape whether the internal irreversibility is ignored ($I = 1$) or not ($I > 1$). The optimal performance is influenced by the internal irreversibility quantitatively, and the optimal COP for a given dimensionless rate of energy pumping and the optimal dimensionless rate of energy pumping for a given COP decrease as the internal irreversibility factor I increases.

The influence of b on the dimensionless rate of energy pumping Σ^* versus the COP χ with $b_{Li} = 0.001$ ($i = 1, 2, 3$), I = 1.05, $\mu_O / \mu_L = 1.25$ and $\mu_H / \mu_M = 1.45$ is shown in Figure 11. The influence of μ_O / μ_L on Σ^* versus χ with $b_{Li} = 0.001$ ($i = 1, 2, 3$), $I = 1.05$, $b = 0.5$ and $\mu_H / \mu_M = 1.45$ is shown in Figure 12. The influence of μ_H / μ_M on Σ^* versus χ with b_{Li} = 0.001 ($i = 1, 2, 3$), I = 1.05, b = 0.5 and $\mu_O / \mu_L = 1.25$ is shown in Figure 13. It can be seen that the relationship between the dimensionless rate of energy pumping Σ^* and the COP χ for the generalized irreversible four-reservoir chemical potential transformer cycle with multi-irreversibility always exhibits a loop-shape.

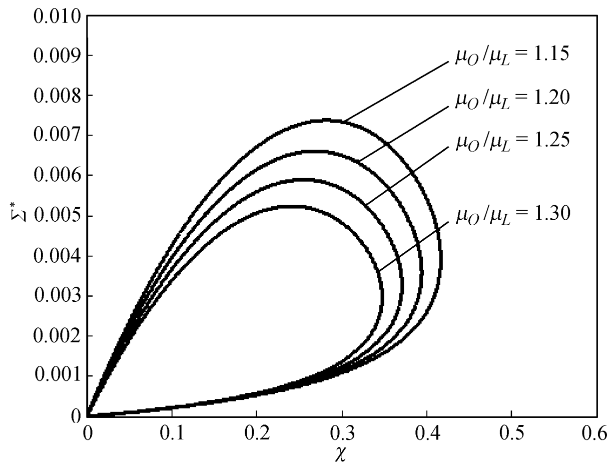

Figure 12 The influence of μ_O/μ_L on Σ^* versus χ with $b_{Li} = 0.001$ (i = 1, 2, 3) and I = 1.05.

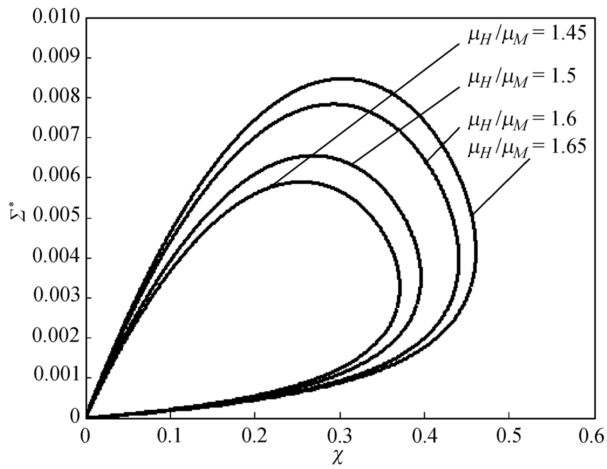

Figure 13 The influence of μ_H/μ_M on Σ^* versus χ with $b_{Li} = 0.001$ (i = 1, 2, 3) and I = 1.05.

5 Results and discussion

(1) It can be seen clearly from Figure 6 that the Σ^*-χ characteristic curve of a four-reservoir isothermal chemical potential transformer with mass transfer resistance, mass leakage and internal irreversibility is divided into three parts by the three operating states of $\chi = 0$, $\chi = \chi_{\Sigma^*}$ and $\chi = \chi_{\max}$. When the four-reservoir isother-

mal chemical potential transformer is designed in those parts of the Σ^*-χ curve that have a positive slope, the COP decreases as the dimensionless rate of energy pumping decreases. Those regions are not the optimal designing regions. The optimal operating regions of a four-reservoir isothermal chemical potential transformer with irreversible mass transfer and mass leakage should be situated in that part of the Σ^*-χ curve that has a negative slope. In such a case, the COP will increases as the dimensionless rate of energy pumping decreases, and vice versa. Thus, the COP and the dimensionless rate of energy pumping should be, respectively, constrained by:

$$\chi_{\Sigma^*} \leqslant \chi \leqslant \chi_{\max}, \quad \Sigma^*_{\max} \geqslant \Sigma^* \geqslant \Sigma^*_{\chi}. \tag{24}$$

(2) In order to make the chemical potential transformer operates in the optimal state, the times spent on the mass transfer processes between the working substance and the four reservoirs must satisfy certain conditions. Using eqs. (2) and (15), one can obtain the optimal times of the four mass transfer processes as follows:

$$\begin{aligned} t_1 = {} & \tau(1-b)\mu_H^{-1} \\ & \times[\Sigma\chi^{-1} - \mu_H h_{L1}(\mu_H - \mu_M) - \mu_L h_{L2}(\mu_L - \mu_M)] \\ & \times\{[\Sigma\mu_O^{-1} + h_{L3}(\mu_O - \mu_M)](\sqrt{Ih_1/h_3} - \sqrt{Ih_1/h_4}) \\ & +[(1-b)\mu_H^{-1}(1+\sqrt{Ih_1/h_4}) + b\mu_L^{-1}(\sqrt{h_1/h_2} + \sqrt{Ih_1/h_4})] \\ & \times[\Sigma\chi^{-1} - \mu_H h_{L1}(\mu_H - \mu_M) - \mu_L h_{L2}(\mu_L - \mu_M)]\}^{-1}, \end{aligned} \tag{25}$$

$$\begin{aligned} t_2 = {} & \tau\sqrt{h_1 h_2^{-1}}\, b\mu_L^{-1}[\Sigma\chi^{-1} - \mu_H h_{L1}(\mu_H - \mu_M) \\ & - \mu_L h_{L2}(\mu_L - \mu_M)]\{[\Sigma\mu_O^{-1} + h_{L3}(\mu_O - \mu_M)] \\ & \times(\sqrt{Ih_1/h_3} - \sqrt{Ih_1/h_4}) + [(1-b)\mu_H^{-1}(1+\sqrt{Ih_1/h_4}) \\ & + b\mu_L^{-1}(\sqrt{h_1/h_2} + \sqrt{Ih_1/h_4})] \\ & \times[\Sigma\chi^{-1} - \mu_H h_{L1}(\mu_H - \mu_M) - \mu_L h_{L2}(\mu_L - \mu_M)]\}^{-1}, \end{aligned} \tag{26}$$

$$\begin{aligned} t_3 = {} & \tau\sqrt{h_1/(Ih_3)}[\Sigma\mu_O^{-1} + h_{L3}(\mu_O - \mu_M)] \\ & \times\{[\Sigma\mu_O^{-1} + h_{L3}(\mu_O - \mu_M)](\sqrt{h_1/Ih_3} - \sqrt{h_1/Ih_4}) \\ & +[(1-b)\mu_H^{-1}(1+\sqrt{Ih_1/h_4}) + b\mu_L^{-1}(\sqrt{h_1/h_2} + \sqrt{Ih_1/h_4})] \\ & \times[\Sigma\chi^{-1} - \mu_H h_{L1}(\mu_H - \mu_M) - \mu_L h_{L2}(\mu_L - \mu_M)]\}^{-1}, \end{aligned} \tag{27}$$

$$\begin{aligned} t_4 = {} & \tau\sqrt{h_1/(Ih_4)}\{[(1-b)\mu_H^{-1} + b\mu_L^{-1}] \\ & \times[\Sigma\chi^{-1} - \mu_H h_{L1}(\mu_H - \mu_M) - \mu_L h_{L2}(\mu_L - \mu_M)] \\ & -[\Sigma\mu_O^{-1} + h_{L3}(\mu_O - \mu_M)]\}\{[\Sigma\mu_O^{-1} + h_{L3}(\mu_O - \mu_M)] \\ & \times(\sqrt{Ih_1/h_3} - \sqrt{Ih_1/h_4}) + [(1-b)\mu_H^{-1}(1+\sqrt{Ih_1/h_4}) \\ & +b\mu_L^{-1}(\sqrt{h_1/h_2} + \sqrt{Ih_1/h_4})][\Sigma\chi^{-1} \\ & -\mu_H h_{L1}(\mu_H - \mu_M) - \mu_L h_{L2}(\mu_L - \mu_M)]\}^{-1}. \end{aligned} \tag{28}$$

$$\sqrt{h_1}t_1 + \sqrt{h_2}t_2 = \sqrt{h_3 I^{-1}}t_3 + \sqrt{h_4 I^{-1}}t_4. \tag{29}$$

Using the above results, one can also obtain the optimal chemical potentials of the four iso-chemical-potential processes in the cyclic working substance as follows:

$$\begin{aligned} \mu_1 = {} & \mu_H - \{[\Sigma\mu_O^{-1} + h_{L3}(\mu_O - \mu_M)] \\ & \times(\sqrt{Ih_1/h_3} - \sqrt{Ih_1/h_4}) + [(1-b)\mu_H^{-1}(1+\sqrt{Ih_1/h_4}) \\ & + b\mu_L^{-1}(\sqrt{h_1/h_2} + \sqrt{Ih_1/h_4})][\Sigma\chi^{-1} \\ & - \mu_H h_{L1}(\mu_H - \mu_M) - \mu_L h_{L2}(\mu_L - \mu_M)]\}/h_1, \end{aligned} \tag{30}$$

$$\begin{aligned} \mu_2 = {} & \mu_L - \{[\Sigma\mu_O^{-1} + h_{L3}(\mu_O - \mu_M)] \\ & \times(\sqrt{Ih_1/h_3} - \sqrt{Ih_1/h_4}) + [(1-b)\mu_H^{-1}(1+\sqrt{Ih_1/h_4}) \\ & + b\mu_L^{-1}(\sqrt{h_1/h_2} + \sqrt{Ih_1/h_4})][\Sigma\chi^{-1} \\ & - \mu_H h_{L1}(\mu_H - \mu_M) - \mu_L h_{L2}(\mu_L - \mu_M)]\}/\sqrt{h_1 h_2}, \end{aligned} \tag{31}$$

$$\begin{aligned} \mu_3 = {} & \mu_O + \{[\Sigma\mu_O^{-1} + h_{L3}(\mu_O - \mu_M)] \\ & \times(\sqrt{Ih_1/h_3} - \sqrt{Ih_1/h_4}) + [(1-b)\mu_H^{-1}(1+\sqrt{Ih_1/h_4}) \\ & + b\mu_L^{-1}(\sqrt{h_1/h_2} + \sqrt{Ih_1/h_4})][\Sigma\chi^{-1} \\ & - \mu_H h_{L1}(\mu_H - \mu_M) - \mu_L h_{L2}(\mu_L - \mu_M)]\}/\sqrt{Ih_1 h_3}, \end{aligned} \tag{32}$$

$$\begin{aligned} \mu_4 = {} & \mu_M + \{[\Sigma\mu_O^{-1} + h_{L3}(\mu_O - \mu_M)] \\ & \times(\sqrt{Ih_1/h_3} - \sqrt{Ih_1/h_4}) + [(1-b)\mu_H^{-1}(1+\sqrt{Ih_1/h_4}) \\ & + b\mu_L^{-1}(\sqrt{h_1/h_2} + \sqrt{Ih_1/h_4})][\Sigma\chi^{-1} \\ & - \mu_H h_{L1}(\mu_H - \mu_M) - \mu_L h_{L2}(\mu_L - \mu_M)]\}/\sqrt{Ih_1 h_4}. \end{aligned} \tag{33}$$

These results can play an instructive role for engineers when they design the mass exchangers of a real chemical potential transformer.

(3) The cyclic model established herein can be applied to the systems such as mass exchangers, electrochemical, photochemical and solid state devices, and the fuel pumps for solar energy conversion systems[31,32]. It should be pointed out that, in general, the related quantities here have different definition forms for different systems. For example, in solid-state devices, eq. (2) is referred to as the current-voltage relations, where d*N*/d*t* is the current, and $\Delta\mu$ is the voltage, while in electrochemical devices, $\Delta\mu$ represents the gradient of electrochemical potential and the conjugated flow is the

transport of ions. When the transferred working substance in a chemical pump is electrons or ions, ΔN is the transferred electric charge, $\Delta\mu$ is EMF and h^{-1} is the resistance. Generally, h^{-1} is the mass flow resistance. Moreover, the working substance in a chemical potential transformer may be gas or liquid molecules in mass exchangers in addition to a current of electrons in solid-state devices[13]. The results obtained herein can provide some new theoretical instructions for the optimal design of these devices.

6 Special cases

The results of this paper include the optimal performance of the irreversible four-reservoir chemical potential transformer cycle, the irreversible three-reservoir chemical potential transformer cycle, the irreversible two-reservoir chemical engine cycle, the endoreversible four-reservoir chemical potential transformer cycle, the endoreversible three-reservoir chemical potential transformer cycle and the endoreversible two-reservoir chemical engine cycle.

6.1 Case 1: $I=1$ and $h_{Li}=0$ $(i=1, 2, 3)$

If there only exists the mass transfer resistance loss, i.e., $I=1$, $h_{Li}=0$ $(i=1, 2, 3)$, the irreversible four-reservoir chemical potential transformer cycle becomes the endoreversible four-reservoir chemical potential transformer cycle, and eqs. (16), (17), (19), (20), (22) and (23) become

$$\Sigma^* = \frac{\begin{array}{l}\{1-\mu_M[(1-b)\mu_H^{-1}+b\mu_L^{-1}]-(1-\mu_M\mu_O{}^{-1})\chi\}\\ (\{1-\mu_M[(1-b)\mu_H^{-1}+b\mu_L^{-1}]\}(\sqrt{b_2}-\sqrt{b_3})\\ +[(1-b)\mu_H{}^{-1}(1+\sqrt{b_3})+b\mu_L^{-1}(\sqrt{b_1}+\sqrt{b_3})]\\ (\mu_O-\mu_M))\chi\mu_H\mu_O{}^{-1}\end{array}}{\begin{array}{l}[(1-b)(1+\sqrt{b_3})+b\mu_H\mu_L^{-1}(\sqrt{b_1}+\sqrt{b_3})\\ +(\sqrt{b_2}-\sqrt{b_3})\chi\mu_H\mu_O{}^{-1}]^2\{\sqrt{b_2}-\sqrt{b_3}\\ +(1-b)\mu_H^{-1}[(1+\sqrt{b_3})\mu_O-(1+\sqrt{b_2})\mu_M]\\ +b\mu_L^{-1}[(\sqrt{b_1}+\sqrt{b_3})\mu_O-(\sqrt{b_1}+\sqrt{b_2})\mu_M]\}\end{array}}, \quad (34)$$

$$\chi_{\max} = \chi_r = \frac{1-[(1-b)/\mu_H+b/\mu_L]\mu_M}{1-\mu_O/\mu_M}, \quad (35)$$

$$\Sigma_\chi^* = 0, \quad (36)$$

$$\begin{aligned}\Sigma_{\max}^* &= \frac{1}{4}\{1-\mu_M[(1-b)\mu_H^{-1}+b\mu_L^{-1}]\}^2\\ &\times[(1-b)(1+\sqrt{b_3})+b\mu_H\mu_L^{-1}(\sqrt{b_1}+\sqrt{b_3})]^{-1}\\ &\times\{\sqrt{b_2}-\sqrt{b_3}+(1-b)\mu_H^{-1}[(1+\sqrt{b_3})\mu_O-(1+\sqrt{b_2})\mu_M]\\ &+b\mu_L^{-1}[(\sqrt{b_1}+\sqrt{b_3})\mu_O-(\sqrt{b_1}+\sqrt{b_2})\mu_M]\}^{-1},\end{aligned} \quad (37)$$

$$\chi_{\Sigma^*} = \frac{1-\mu_M[(1-b)\mu_H^{-1}+b\mu_L^{-1}]}{\begin{array}{l}2(\mu_O-\mu_M)/\mu_O+\{1-\mu_M[(1-b)\mu_H^{-1}+b\mu_L^{-1}]\}\\ (\sqrt{b_2}-\sqrt{b_3})\{[(1-b)\mu_H{}^{-1}(1+\sqrt{b_3})+b\mu_L^{-1}\\ (\sqrt{b_1}+\sqrt{b_3})]\mu_O\}^{-1}\end{array}}. \quad (38)$$

6.2 Case 2: $\mu_H=\mu_L$ and $h_1=h_2$

If $\mu_H=\mu_L$ and $h_1=h_2$, the irreversible four-reservoir chemical potential transformer cycle becomes the irreversible three-reservoir chemical potential transformer cycle with mass transfer resistance, mass leakage and internal irreversibilities. In this case, $h_{L1}=h_{L2}=h_L/2$, $b_{L1}=b_{L2}=b_L/2$ and eqs. (16), (17), (19), (20), (22) and (23) become

$$\chi = \frac{\begin{array}{l}\mu_O/\mu_H((1-I\mu_M/\mu_H)-(1+\sqrt{Ib_3})k\\ -b_{L3}(\mu_O-\mu_M)/\mu_H\{\sqrt{Ib_2}-\sqrt{Ib_3}+[(1\\ +\sqrt{Ib_3})\mu_O-(1+\sqrt{Ib_2})\mu_M]/\mu_H\}/k)\end{array}}{\begin{array}{l}I(\mu_O-\mu_M)/\mu_H+(\sqrt{Ib_2}-\sqrt{Ib_3})k\\ +b_L(1-\mu_M/\mu_H)\{\sqrt{Ib_2}-\sqrt{Ib_3}\\ +[(1+\sqrt{Ib_3})\mu_O-(1+\sqrt{Ib_2})\mu_M]/\mu_H\}/k\end{array}}, \quad (39)$$

$$\begin{aligned}\Sigma^* &= k[(1-I\mu_M/\mu_H)-(1+\sqrt{Ib_3})k]\\ &\{\sqrt{Ib_2}-\sqrt{Ib_3}+[(1+\sqrt{Ib_3})\mu_O\\ &-(1+\sqrt{Ib_2})\mu_M]/\mu_H\}^{-1}-b_{L3}(\mu_O-\mu_M)/\mu_H,\end{aligned} \quad (40)$$

$$\chi_{\max} = \frac{\mu_O}{\mu_H}\frac{\begin{array}{l}(1-I\mu_M/\mu_H)-(1+\sqrt{Ib_3})\\ \{\sqrt{Ib_2}-\sqrt{Ib_3}+[(1+\sqrt{Ib_3})\mu_O-(1+\\ \sqrt{Ib_2})\mu_M]/\mu_H\}H-b_{L3}(\mu_O-\mu_M)\mu_H^{-1}H^{-1}\end{array}}{\begin{array}{l}(\sqrt{Ib_2}-\sqrt{Ib_3})\{\sqrt{Ib_2}-\sqrt{Ib_3}\\ +[(1+\sqrt{Ib_3})\mu_O-(1+\sqrt{Ib_2})\mu_M]/\mu_H\}H\\ +I(\mu_O-\mu_M)\mu_H^{-1}+b_L(1-\mu_M/\mu_H)H^{-1}\end{array}}, \quad (41)$$

$$\begin{aligned}\Sigma_\chi^* &= ((1-I\mu_M/\mu_H)-(1+\sqrt{Ib_3})H\{\sqrt{Ib_2}-\sqrt{Ib_3}\\ &+[(1+\sqrt{Ib_3})\mu_O-(1+\sqrt{Ib_2})\mu_M]/\mu_H\}[(1-I\mu_M/\mu_H)\\ &\times(\sqrt{Ib_2}-\sqrt{Ib_3})+(1+\sqrt{Ib_3})I(\mu_O-\mu_M)/\mu_H]^{-1})\\ &\times H-b_{L3}(\mu_O-\mu_M)/\mu_H,\end{aligned} \quad (42)$$

$$\Sigma^*_{max}=\frac{1}{4}(1-I\mu_M/\mu_H)^2(1+\sqrt{Ib_3})^{-1}\{\sqrt{Ib_2}-\sqrt{Ib_3}+[(1+\sqrt{Ib_3})\mu_O-(1+\sqrt{Ib_2})\mu_M]/\mu_H\}^{-1}-b_{L3}(\mu_O-\mu_M)/\mu_H, \quad (43)$$

$$\chi_{\Sigma^*}=\frac{(1-I\mu_M/\mu_H)/2-2\{\sqrt{Ib_2}-\sqrt{Ib_3}+[(1+\sqrt{Ib_3})\mu_O-(1+\sqrt{Ib_2})\mu_M]/\mu_H\}b_{L3}(\mu_O-\mu_M)/\mu_H(1+\sqrt{b_3})(1-\mu_M/\mu_H)^{-1}}{I(1-\mu_M/\mu_O)+(1-I\mu_M/\mu_H)(\sqrt{Ib_2}-\sqrt{Ib_3})(1+\sqrt{Ib_3})^{-1}+2\{\sqrt{Ib_2}-\sqrt{Ib_3}+[(1+\sqrt{Ib_3})\mu_O-(1+\sqrt{Ib_2})\mu_M]/\mu_H\}(b_{L1}+b_{L2})(1+\sqrt{Ib_3})}, \quad (44)$$

where

$$H=\Big((\sqrt{Ib_2}-\sqrt{Ib_3})b_{L3}(\mu_O-\mu_M)/\mu_H-(1+\sqrt{Ib_3})b_L(1-\mu_M/\mu_H)+\{[(\sqrt{Ib_2}-\sqrt{Ib_3})b_{L3}(\mu_O-\mu_M)/\mu_H-(1+\sqrt{Ib_3})b_L(1-\mu_M/\mu_H)]^2[(1-I\mu_M/\mu_H)(\sqrt{Ib_2}-\sqrt{Ib_3})+I(\mu_O-\mu_M)/\mu_H(1+\sqrt{Ib_3})][b_L(1-\mu_M/\mu_H)^2-b_{L3}I(\mu_O-\mu_M)^2/\mu_H^2][\sqrt{Ib_2}-\sqrt{Ib_3}+[(1+\sqrt{Ib_3})\mu_O-(1+\sqrt{Ib_2})\mu_M]/\mu_H]^{-1}\}^{1/2}\Big)[(1-I\mu_M/\mu_H)(\sqrt{Ib_2}-\sqrt{Ib_3})+I(\mu_O-\mu_M)/\mu_H(1+\sqrt{Ib_3})]^{-1}.$$

6.3 Case 3: $\mu_H=\mu_L$, $h_1=h_2$ and $\mu_O\to\infty$

If $\mu_O\to\infty$, the irreversible four-reservoir chemical potential transformer cycle becomes the two-reservoir irreversible chemical engine cycle with mass transfer resistance, mass leakage and internal irreversibility[13]. In this case, the rate of energy pumping Σ^* and the COP χ correspond to the power output P and the efficiency η of a chemical engine[18], and eqs. (16), (17), (19), (20), (22) and (23) become

$$P^2+\mu_H^2\eta[H_I(\eta_r-\eta_I)-2h_L\eta_r]P+\mu_H^2\eta^2[(h_L\eta_r+H_I\eta_I/2)^2-H_I^2\eta_I^2/4]=0, \quad (45)$$

$$P_{max}=\mu_H^2H_1\eta_I^2/4, \quad (46)$$

$$\eta_P=\frac{\eta_r}{2}\left(1+\frac{2h_L\eta_r}{H_I\eta_I}\right)^{-1}, \quad (47)$$

$$\eta_{max}=\{\eta_I+\eta_rh_LH_I^{-1}[1-\sqrt{1+(H_I\eta_r)/(h_L\eta_I)}]\}\times\{1-[1+(H_I\eta_r)/(h_L\eta_I)]^{-1/2}\}, \quad (48)$$

$$P_\eta=\mu_H^2h_L\eta_r\{\eta_I+h_L\eta_rH_I^{-1}[1-\sqrt{1+(H_I\eta_r)/(h_L\eta_I)}]\}\times[\sqrt{1+(H_I\eta_r)/(h_L\eta_I)}-1], \quad (49)$$

where $\eta_r=1-\mu_M/\mu_H$, $\eta_I=1-I\mu_M/\mu_H$ and $H_I=h_1/(1+\sqrt{Ib_3})$.

6.4 Case 4: $I=1$, $h_{Li}=0$ $(i=1,2,3)$, $\mu_H=\mu_L$ and $h_1=h_2$

If $I=1$, $h_{Li}=0$ $(i=1,2,3)$, $\mu_H=\mu_L$ and $h_1=h_2$, the irreversible four-reservoir chemical potential transformer cycle becomes the endoreversible three-reservoir chemical potential transformer cycle[25] and eqs. (16), (17), (19), (20), (22) and (23) become

$$\Sigma^*=\frac{[1-\mu_M/\mu_H-(1-\mu_M/\mu_O)\chi][(1-\mu_M/\mu_H)(\sqrt{b_2}-\sqrt{b_3})+(1+\sqrt{b_3})(\mu_O-\mu_M)/\mu_H]\chi\mu_H/\mu_O}{[(1+\sqrt{b_3})+(\sqrt{b_2}-\sqrt{b_3})\mu_H/\mu_O\chi]^2\{\sqrt{b_2}-\sqrt{b_3}+[(1+\sqrt{b_3})\mu_O-(1+\sqrt{b_2})\mu_M]/\mu_H\}}, \quad (50)$$

$$\chi_{max}=\chi_r=\frac{1-\mu_M/\mu_H}{1-\mu_O/\mu_M}, \quad (51)$$

$$\Sigma^*_\chi=0, \quad (52)$$

$$\Sigma^*_{max}=\frac{1}{4}(1-\mu_M/\mu_H)^2(1+\sqrt{b_3})^{-1}\{\sqrt{b_2}-\sqrt{b_3}+\mu_H^{-1}[(1+\sqrt{b_3})\mu_O-(1+\sqrt{b_2})\mu_M]\}^{-1}, \quad (53)$$

$$\chi_{\Sigma^*}=\frac{1-\mu_M/\mu_H}{2(\mu_O-\mu_M)/\mu_O+(1-\mu_M/\mu_H)(\sqrt{b_2}-\sqrt{b_3})(1+\sqrt{b_3})^{-1}\mu_H/\mu_O}. \quad (54)$$

6.5 Case 5: $I=1$, $h_{Li}=0$ $(i=1, 2, 3)$, $\mu_H=\mu_L$, $h_1=h_2$ and $\mu_O\to\infty$

If $\mu_O\to\infty$, the irreversible four-reservoir chemical potential transformer cycle becomes the endoreversible two-reservoir chemical engine cycle[13,14,19], and eqs. (16), (17), (19) and (20) become

$$P=\mu_H^2h_1\eta(\eta_r-\eta)/(1+\sqrt{b_3})^2, \quad (55)$$

$$P_{max}=\frac{\mu_H^2h_1\eta_r^2}{4(1+\sqrt{b_3})^2}, \quad (56)$$

$$\eta_P=\eta_r/2. \quad (57)$$

The second law efficiency of the chemical engine at maximum power output is 1/2[13,14].

7 Conclusion

A generalized irreversible four-reservoir isothermal chemical potential transformer with the irreversibility of finite-time mass transfer, mass leakage and internal dissipation has been modeled in this paper, and the performance has been analyzed and optimized by using finite-time thermodynamics. The optimal relation between the rate of energy pumping and the coefficient of performance (COP) of the generalized irreversible four-reservoir isothermal chemical potential transformer has been derived. The maximum COP and the corresponding rate of energy pumping, as well as the maximum rate of energy pumping and the corresponding COP have also been obtained. Moreover, the influences of finite-time mass transfer, mass leakage and internal dissipation on the COP and the rate of energy pumping of the four-reservoir irreversible chemical potential transformer have been studied by detailed numerical examples. It was found that the mass leakage affects the optimal performance both qualitatively and quantitatively, while the internal dissipation affects the optimal performance quantitatively. The results obtained herein are generalized, from which all the relevant conclusions in the recent literature can be deduced directly. These results may be used in the design of mass exchangers, electrochemical, photochemical and solid state devices, fuel pumps and so on. They can provide some new theoretical instructions for the optimal design of these devices.

This paper considers only one chemical species which may be appropriate to photovoltaic devices, but real chemical processes necessarily involve several reacting species. It will be necessary to complicate the analysis. This paper emphasizes on performance analysis and optimization of isothermal chemical potential transformers. It should be studied further for chemical potential transformer with different reservoir temperatures (see Figure 1). Besides, the effects of finite heat capacity and finite chemical potential capacity[11] of the heat/mass reservoirs should also be studied.

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