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Dynamic modelling of an oxygen mixed conducting membrane and model reduction for control

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ABSTRACT

In the first part of this paper we present a detailed model of an oxygen mixed conducting membrane (OMCM) monolith for air separation. In addition to the oxygen separation, the OMCM operates as a heat exchanger at elevated temperature and pressure. The model is based on energy and species conservation balances. It is shown that the oxygen permeation through perovskite-related materials is strongly dependent on the oxygen partial pressure difference across the membrane and on the temperature of the solid wall. The numerical results obtained from steady state as well as transient simulations agree well with the available data. In the second part, linear model reduction is applied to the OMCM model. The method for model reduction used here, balanced residualisation, reduces states while preserving steady-state behaviour. The comparison of two reduced-order models (19 states and 5 states, respectively) with the full-order model (>2000 states), reveals good agreement for frequencies lower than 1 Hz. The reduced models simulate faster, and can be used for controllability analysis and control design.

1. Introduction

In recent years the interest in efficient air separation has steadily increased. Existing technologies are, among others, cryogenic distillation and pressure swing adsorption. Another option is oxygen production by polymeric membranes. Whereas the former ones suffer from high capital and operation costs, polymeric membranes have a low separation factor for producing oxygen with purity not higher than 50% [1]. In contrast, air separation by means of perovskite-related oxygen mixed conducting membranes (OMCMs) is one of the most promising technologies combining high oxygen production and process simplicity [2,3,5]. In absence of leaks or cracks OMCMs exhibit 100% selectivity towards oxygen.

OMCMs can be incorporated in power cycles, where for example natural gas reacts with the separated oxygen in a nitrogen-free atmosphere[1] [6]. In the majority of research studies dealing with the design and operation of OMCMs in power cycles, lumped models have been applied in order to investigate the steady-state behaviour of both the OMCM and the whole power cycle [8,30].

In the present work, an oxygen mixed conducting membrane monolith model, based on the perovskite-related material $La_2NiO_{4+\delta}$ is studied, selected due to its good transport properties [3,5,9–13]. This compound belongs to the Ruddlesden–Popper series with the general composition $A_{n+1}B_nO_{3n+1}$, with A of group 1, 2, or 3 elements and B as a transition metal [3,5]. The crystal structure shows close proximity to the perovskite structure. Rocksalt-type AO sheets are inserted between blocks consisting of n ABO_3 perovskite-related layers [3,15,16]. $La_2NiO_{4+\delta}$ can accommodate considerable amounts of excess oxygen which is hosted in the form of oxygen interstitial defects in the La_2O_2 rock-salt layers. With increasing temperature this material undergoes a transition from semiconducting to pseudometallic behaviour. In this connection, the material loses its interstitial oxygen, and as a consequence thereof the concentration of electron holes decreases.

Monoliths for gas-phase applications have been extensively studied, in particular within the automobile industry [17]. The fabrication of OMCMs as monolith for power cycles is an interesting alternative to techniques such as the shell-and-tube configuration. Monoliths are characterised by low-pressure drop, high area-to-volume ratio, and ease of scale-up [14,18].

The transient monolith model is spatially distributed in one dimension with respect to energy and species conservation balances of gas and solid phase in the monolith. A two-dimensional model has been adopted for the insulation. Oxygen permeation of the OMCM incorporates bulk diffusion and surface reactions.

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[1] It is assumed that natural gas does not contain any impurities such as nitrogen and sulphur.

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The initial transient process of oxygen permeation over perovskite-related membranes has been experimentally analysed by several authors [20–22]. As the oxygen-defect zone spreads towards the oxygen-rich surface, the bulk-controlled oxygen permeation gradually increases until a steady-state oxygen-defect gradient is established. Transition times between 3 and 100 h have been reported, depending on material and thickness of the membrane as well as oxygen permeation control by surface reactions. However, once the steady-state oxygen permeation is established at high temperatures, it remains stable during relatively fast process conditions [21,22]. Therefore, a steady-state solution for the oxygen permeation is assumed.

With increasing computing power, process modelling could meet a higher standard with respect to complexity and accuracy. However, when dealing with large processes, including several highly complex models, the computational effort to obtain numerical solutions is still too large for process control. Whereas for process engineers accurate process results of material and energy flows are usually of interest, control engineers have to cope with the inherent dynamics of all process units. Information about exact energy and material flows are of second-order importance. Nonetheless, simple lumping of complex process models for control may lead to large errors. In order to address both, process models which accurately predict the material and energy flows, and models simple enough for control applications, model reduction can be used.

In the literature there is a large variety of model reduction methods for simulation and control purposes. Model reduction for simulation attempts to retain process model states, i.e. system behaviour for a particular set of inputs. For control purposes model reduction should retain the input–output behaviour. Whereas model reduction for linear process models is well established, model reduction for non-linear models is still an on-going research topic. For an overview of model reduction methods, the interested reader is referred to Refs. [23,24].

Several new approaches emerged in the past three decades. In particular, the proper orthogonal decomposition[2] (POD) gained much attention for model reduction of large dynamical systems [25–27]. In POD, a singular value decomposition is applied in order to obtain an orthogonal basis for snapshots, where the most dominant singular vectors are retained. This method does not incorporate the state-to-output behaviour and does not always give satisfactory results for control purposes. In addition to POD, there appeared several contributions on system identification where the input–output behaviour is obtained by neural networks [28]. Neural networks, however, need to be trained for certain scenarios and give rather poor approximations when applying to operation regimes out of the training range. In addition, the system behaviour cannot be traced back to certain causes. Model reduction based on linearization and balancing still seems to be the most suitable model reduction method for control purposes. Several methods including a balanced realisation have been developed, such as balanced truncation, optimal Hankel norm approximation and balanced residualisation. Compared to the former two model reduction methods, balanced residualisation preserves the linearized system's behaviour in steady state. Merely scaling reduced-order models to recover steady-state behaviour may lead to large errors.

In this contribution, balanced residualisation is applied to the OMCM model. The input–output behaviour is retained in conjunction with good model approximations with respect to key process variables such as sweep gas temperature and oxygen mole fraction. Reduced-order models incorporating 19 and 5 states, respectively are compared to the full-order model. Whereas the model with 19 states contains 99% of the system's energy (measured in Hankel singular values), the model with 5 retains 95 of the system's energy.

2. Oxygen mixed conducting membrane model

The oxygen mixed conductive membrane model is based on conservation balances, spatially distributed with respect to the monolith length (z coordinate), shown in Fig. 1. The OMCM is assumed to be fabricated as a two-fluid monolith which results in a high area-to-volume ratio [29]. This in turn leads to high heat and mass transfer rates. The gas-phase is treated as an incompressible fluid. The two counter-current stream compositions differ in temperature, massflow and oxygen partial pressure. Oxygen permeation occurs from the high oxygen partial pressure air stream to the low oxygen partial pressure sweep gas. Heat transfer proceeds in the opposite direction. Each air stream is connected to four sweep gas streams and vice versa, resulting in a checkerboard pattern. The solid wall, separating the two gas streams, is composed of the OMCM layer and a porous support layer of similar material. On one hand this support should be sufficiently porous to retard oxygen permeation and on the other hand provide high mechanical strength in order to prevent fracture under varying process conditions. In addition, the porous support should have a similar thermal expansion coefficient to keep thermal stresses during load changes at a low level when there is no other possibility for the OMCM to relax the strains by either extension or bending [14,31–34]. The membrane layer and porous support are combined with respect to heat transfer for reason of model simplification. Oxygen residence times in the solid wall are not considered because of the fast exchange of oxygen through the membrane layer. Therefore, species conservation balances are only given for the gas phases. In order to keep the modelling effort to a reasonable level, a repeating element is defined, which represents the entire number of gas channels and solid walls in the monolith. This repeating element,

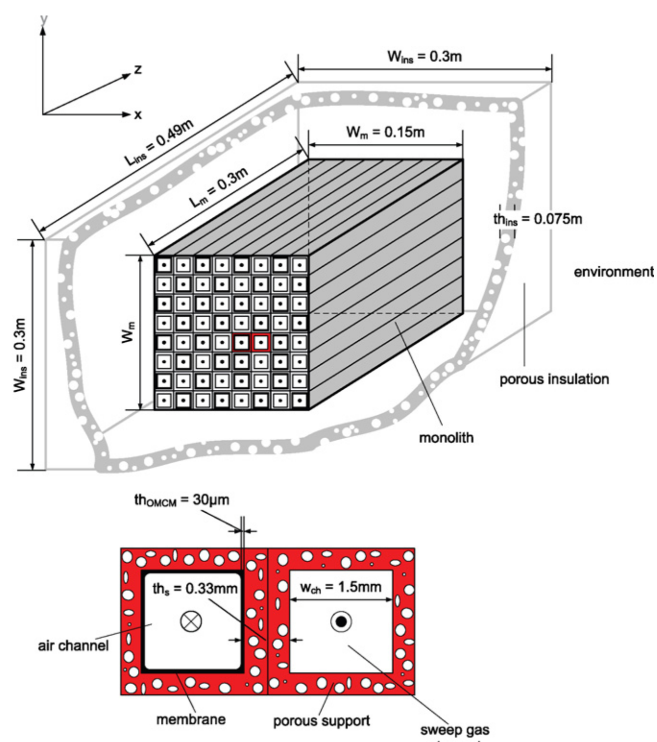

Fig. 1. Oxygen mixed conducting membrane: manifold (above), repeating element (below).

[2] POD is also known as the method of empirical orthogonal eigenfunctions, and Karhunen–Loève expansion.