

Technical Paper

Modeling of charge-mass transport in solid electrolyte-based electrochemical nanomanufacturing process

Keng Hsu^{a,*}, Nicholas Fang^b, Gautam Panikkar^a, Placid Ferreira^c^a The Polytechnic School, Fulton Schools of Engineering, Arizona State University, 7171 E. Sonoran Arroyo Mall, Mesa, AZ 85212, USA^b Department of Mechanical Engineering, Massachusetts Institute of Technology, 77 Massachusetts Ave., Cambridge, MA, 02139, USA^c Department of Mechanical Science and Engineering, University of Illinois at Urbana Champaign, 1206W. Green st., Urbana, IL, 61801, USA

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ABSTRACT

A numerical model was developed to capture the charge-mass transport in electrochemical nanomanufacturing processes based on mixed-conducting solid electrolyte material systems. This model was verified by the matching of numerical predictions and experimental measurements of process parameters. The model was also used to predict parameters affecting ionic current flow, and to study the temporal and spatial transport properties of solid electrolyte silver sulfide during an electrode dissolution process. Conditions in which phase separation could occur in silver sulfide were found. Enhanced transport properties due to confinement in lateral dimensions were also observed through the developed model.

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1. Introduction

1.1. Background

The unique nature of ionic transport is not only the origin of a number of physical and chemical phenomena but the core of a wide range of applications such as manufacturing, energy conversions, and sensing techniques. The materials in which ionic transport can take place include liquid electrolytes, polymers, amorphous glasses, as well as crystalline solids. Sharing the same coupled mass-charge transport properties with their liquid counterpart, solid-state ionic materials, such as silver sulfide and copper sulfide, have seen increasing research efforts in the area of understanding their transport physics, and developing their applications in memory devices, sensing, and actuation [1–6]. One unique application is the use of solid electrolytes as a tool for direct patterning of metals at the nano-scale [7–10]. First introduced by the authors, this method creates sub-50 nanometer resolution features using the solid contact-based anodic dissolution of a metal substrate in

contact with the pre-patterned solid electrolyte stamp as depicted in Fig. 1.

To fully exploit this process for development of a nanomanufacturing process, a complete understanding of the transport physics of the species involved is necessary in order to gain control of substrate quality, yield, and explore process capability. Silver sulfide is known to be a mixed-electronic-ionic conductor with an electronic conduction band gap of ~ 1.3 eV. The decoupling of such mixed conduction into its electronic and ionic component has historically been carried out by setting up the respective Nernst–Planck equations of the electronic and ionic species. These equations are set up under the relations between chemical potentials and electrochemical potentials only pertain to the silver sulfide compound. Under special end conditions such as fully-blocking and fully-reversible conditions for either electronic or ionic species, these equations can be solved analytically. In fully-blocking boundary conditions, either the ionic or electronic species is blocked from passing through an interface. However, none of these conditions are seen in practical applications that involves electrode reactions [11,12].

In this letter we introduce a numerical model to gain insight into the transient behavior of the ionic transport in solid electrolyte silver sulfide, Ag_2S , under these conditions: ionic transport in the electrolyte domain dominant and reaction on the metal-solid electrolyte interface dominant.

* Corresponding author. Tel.: +1 4807272720.

E-mail addresses: Keng.h.hsu@asu.edu, keng.h.hsu@gmail.com(K. Hsu), nicfang@mit.edu (N. Fang), Gautam.Panikkar@asu.edu (G. Panikkar), pferreir@illinois.edu (P. Ferreira).

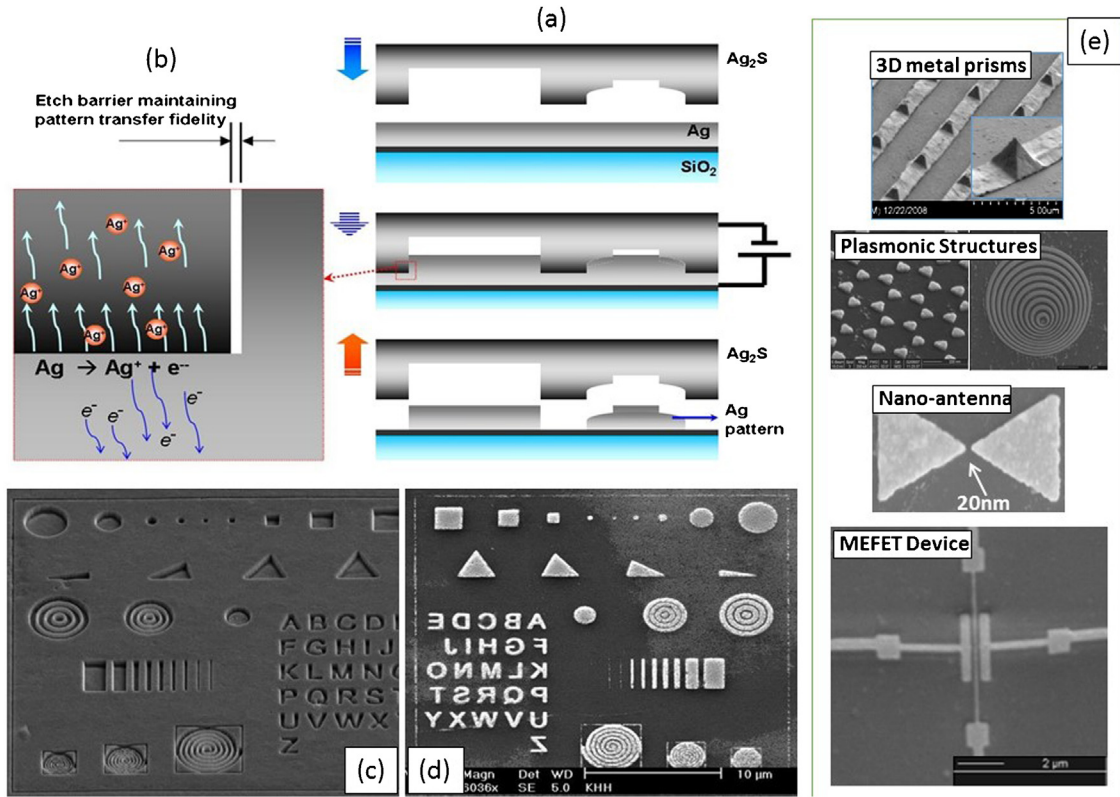


Fig. 1. Solid-state superionic stamping, S4, process and example results. (a), (b) Principle and process steps of S4 process. (c), (d) SEM micrographs of the solid electrolyte stamp and the resulting substrate. (e) Example nanostructures.

1.2. Model set up

1.2.1. Mixed electronic-ionic conduction in Ag_2S

In beta-silver sulfide, the conductivity of electrons is higher than that of silver ion in silver sulfide by about three orders of magnitude. This situation is realistically similar to that of an electrochemical environment where a supporting electrolyte with much higher conductivity is used. Under these conditions, the charge transport is mainly carried by the supporting electrolyte and the transport of the specie considered is mainly diffusive but with some migrative flow due to the finite conductivity of the supporting electrolyte. The transport of silver ions from silver dissolution in silver sulfide is similar to this picture. Most of the charge transport is carried by the electrons in the system, and the transport of silver ions is mainly diffusive but with some migrative contribution due to the finite conductance of electrons. This process can be modeled by setting up a Nernst–Planck equation for the silver ions and a DC conduction for the electrons to reflect the experimental conditions where a DC constant voltage is applied and the total current is measured. The two equations are then coupled by the relation unique to silver sulfide which describes the dependence of the electronic conductivity on the chemical potential of silver in silver sulfide.

$$\frac{\partial c_{Ag}}{\partial t} = \nabla \cdot \left\{ -D_{Ag} \nabla c_{Ag} + \mu_{Ag} F c_{Ag} \nabla V \right\} \quad (1)$$

$$-\nabla \cdot (\sigma_e \nabla V - J^{ext}) = 0 \quad (2)$$

and

$$\sigma_e = \sigma_e^0 \left(1 + \frac{c_{Ag}}{c_{Ag}^0} \right) \quad (3)$$

where c_{Ag} , c_{Ag}^0 , D_{Ag} , μ_{Ag} are the concentration, intrinsic concentration, diffusivity, and mobility of silver in silver sulfide respectively.

σ_e is the electronic conductivity of silver sulfide, F is Faraday's constant, and V the applied voltage to the system.

A simulation domain whose geometry and dimension resembles the “solid electrolyte Pellet” shown in Fig. 2 is constructed in COMSOL in which the governing transport equation (Eq. (1)), direct-electronic current (Eq. (2)), and dependence of the electronic conductivity of silver sulfide on silver ion concentration (Eq. (3)) are applied. In the domain the transport of species is set to be an ionic species (silver ions) whose transport is enabled by the finite

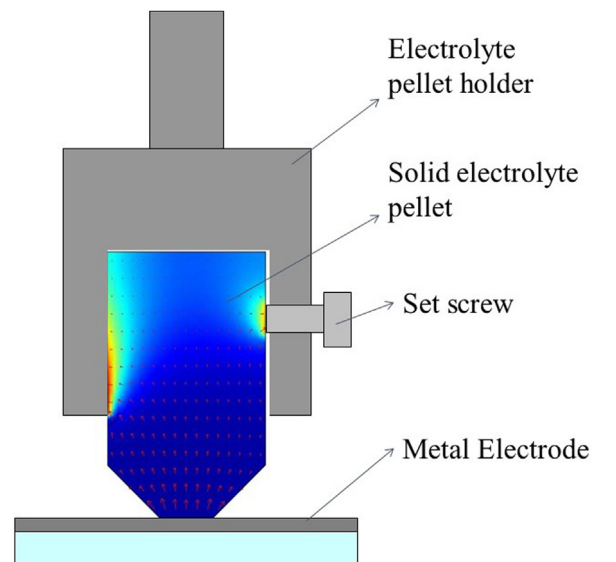


Fig. 2. Experimental solid electrolyte stamping tool configuration.

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