



Research paper

Turing pattern formation on the sphere for a morphochemical reaction-diffusion model for electrodeposition



Deborah Lacitignola^{a,*}, Benedetto Bozzini^b, Massimo Frittelli^c, Ivonne Sgura^c

^a Dipartimento di Ingegneria Elettrica e dell'Informazione, Università di Cassino e del Lazio Meridionale, via Di Biasio, I-03043 Cassino, Italy

^b Dipartimento di Ingegneria dell'Innovazione, Università del Salento, via Monteroni, I-73100 Lecce, Italy

^c Dipartimento di Matematica e Fisica "Ennio De Giorgi", Università del Salento, via per Arnesano, I-73100 Lecce, Italy

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ABSTRACT

The present paper deals with the pattern formation properties of a specific morpho-electrochemical reaction-diffusion model on a sphere. The physico-chemical background to this study is the morphological control of material electrodeposited onto spherical particles. The particular experimental case of interest refers to the optimization of novel metal-air flow batteries and addresses the electrodeposition of zinc onto inert spherical supports. Morphological control in this step of the high-energy battery operation is crucial to the energetic efficiency of the recharge process and to the durability of the whole energy-storage device. To rationalise this technological challenge within a mathematical modeling perspective, we consider the reaction-diffusion system for metal electrodeposition introduced in [Bozzini et al., *J. Solid State Electr.*17, 467–479 (2013)] and extend its study to spherical domains. Conditions are derived for the occurrence of the Turing instability phenomenon and the steady patterns emerging at the onset of Turing instability are investigated. The reaction-diffusion system on spherical domains is solved numerically by means of the Lumped Surface Finite Element Method (LSFEM) in space combined with the IMEX Euler method in time. The effect on pattern formation of variations in the domain size is investigated both qualitatively, by means of systematic numerical simulations, and quantitatively by introducing suitable indicators that allow to assign each pattern to a given morphological class. An experimental validation of the obtained results is finally presented for the case of zinc electrodeposition from alkaline zincate solutions onto copper spheres.

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1. Introduction and research motivation

Safe, reliable and durable electrochemical energy storage devices, such as batteries and metal-based fuel cells, are key to the real-scale deployment of renewable energy sources. Moreover, high-energy batteries are enabling components of a multiplicity of emerging technologies such as home- and grid-storage, electric aircraft, fully electrical vehicles and telemedicine. Efficient electrochemical energy storage in batteries and regeneration of metallic fuel for fuel cells with metallic anodes critically rely on recharging capabilities. Unfortunately, such recharging and regeneration processes - that imply bulk phase formation by electrochemical reactions, or 'electrodeposition' - are currently severely limited by growth instabilities. Such

* Corresponding author.

E-mail addresses: d.lacitignola@unicas.it (D. Lacitignola), benedetto.bozzini@unisalento.it (B. Bozzini), massimo.frittelli@unisalento.it (M. Frittelli), ivonne.sgura@unisalento.it (I. Sgura).

instabilities lead to progressive energy losses as a function of discharge-charge cycles, device lifetime limitation as well as, in some technologies such as lithium-based ones, to severe safety hazards. More specifically, the improvement of these devices demands to face the notable challenge represented by the development of metal growth processes that prevent irregular material distribution in general and the formation of outgrowth features, such as dendrites, in particular. Over the last 40 years, this problem has been attacked with a variety of experimental and theoretical approaches but - notwithstanding the recently revived interest in metal-air technologies, that is currently producing a systematically increasing corpus of high-level literature - no definitive solution has been found.

The focus of this paper is on mathematical modeling and it is worth briefly recalling here - without any claim of completeness - some of the most representative approaches to the modeling of electrochemical dendrite formation that have been described in the literature, apart from our reaction-diffusion based that has been detailed in [9,10,42] and that henceforth we shall refer to as the “DIB model”. Early work based on phenomenological kinetics proposed that dendrite growth was controlled by electrokinetic activation [24], but this view was later corrected by considering the interplay between activation and diffusion control [56] and references therein. This simple, but physically transparent framework allows to replace the description of mass-transport in terms of diffusion formalism with more insightful models, such as the joint density functional method, that has recently inspired physically novel approaches to the suppression of dendritic growth [44]. Moreover, instabilities related to nanocluster aggregation have been recently modeled on the basis of classical nucleation theories, combining diffusive mass transport and simple geometrical assumptions [23].

Among approaches based on a statistical description of phase formation, the diffusion-limited aggregation model was used to simulate the zinc electrodeposition process in 1D [18] and a kinetic Monte Carlo approach has been proposed, assigning position-dependent van der Waals and electrochemical energies to individually depositing zinc atoms [45]. On the differential modeling side, instead electrodeposition instabilities were investigated by extending the Mullins–Sekerka instabilities theory to the electrochemical case, considering the buildup of electrochemical potential gradients [40]. This approach has been expanded to a reaction-diffusion model for two chemicals, [17]. More recently, phase-field theories, that add a variable describing the electrode-electrolyte interface as a diffuse quantity, have been proposed for the modeling of Zinc (Zn) dendrite formation [19,71].

Finally, it is worth mentioning that Zn morphology has been correlated to, rather than modelled with, the current density distribution. This quantity has been evaluated by multiphysics PDE modeling, incorporating ionic transport by diffusion, migration and convection, phenomenological charge-transfer kinetics and Navier–Stokes equations [72]. Electrodeposition on spherical particles in a range of spouted- and fluidized-bed configurations has been described, chiefly in the field of metal recovery from wastewater streams, e.g. [11] and references therein. Research focus in the field is generally on the precise evaluation of the current density distribution as a function of the operating conditions and, apart from special research motivations [8], electrodeposit morphology is typically neglected owing to the limited thicknesses of the coatings of practical interest in the relevant technologies. Nevertheless, very recently, the technological importance of the recovery of Zn from discharge electrolytes for off-line recharging and energy storage, e.g. [14,60] and references therein, has attracted research attention to the option of electrodepositing Zn onto electrochemically inert metallic particles, such as e.g. Cu spheres. Since, in this specific case, high thicknesses (range of hundred micron) are of interest and one would like to minimize metal loss by the formation of loose dendrites, morphological control is of notable practical importance. This point is particularly crucial, because the relevant growth process is based on alkaline zincate solutions and it is well known that smooth zinc layers cannot be electrodeposited from these electrolytes. Possible, but practically unsatisfactory approaches to the mitigation of these instability problems are on the one hand the implementation of poorly controlled and expensive pulse plating programs or, on the other hand, the use of chemically unstable, toxic and costly additives, that impose demanding bath maintenance procedures. Moreover in Zinc-air fuel cells (ZAFC) with hopper-type anodes, the optimisation of the shape and dimensions of Zn particles is still an open question [20] and mathematical tools to rationalise this aspect are highly desirable.

Unstable growth of Zn during electrodeposition from alkaline solutions onto flat electrodes has been the object of extensive studies and the research has been recently further fuelled by the practical importance of rechargeable Zn-based batteries. The literature features some classical references, that have systematically set the phenomenological framework - reviewed, among others, in [49,56] - together with a steadily increasing number of recent contributions that is pointing out a range of new aspects of this widely investigated process, the details of which are beyond the scope of this paper [1,23]. In particular, electrodeposited Zn exhibits a wide class of morphologies that depend in a poorly understood way on the growth rate. These can be broadly classified - in order of progressive degree of instability - as ‘compact’, layered, dendritic, spongy and mossy: only the first type is generally regarded as desirable for battery anodes, while high-surface forms such as dendrites have been recently considered of potential interest for catalytic applications [59].

The aim of this paper is thus to analyze the problem of unstable metal electrodeposition in the framework of the DIB model extending it to the case of electrodeposition on spherical cathodes. We have shown that the DIB model is able to capture many essential aspects of electrochemical pattern formation and it is thus suitable to handle the case of Zn electrodeposition from zincate solutions in energy storage applications. More in general, our work fits in the reaction-diffusion modeling framework that is particularly compelling with regard to its ability to account for pattern formation in a variety of biological, chemical and physical situations [50], many of which can be better tackled by adopting spherical domains. In fact, a close-knit group of papers has been devoted to theoretically analyze and numerically solve reaction-diffusion models on the surface of a sphere, e.g. [16,33,36,43,46,48,58,67,69]. It is worth noting that, among these works, as we do in the present research, the following ones explicitly refer to concrete applications: [69] considered the Turing model introduced in [3]

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