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Soft X-ray ptychography as a tool for in operando morphochemical studies of electrodeposition processes with nanometric lateral resolution

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ABSTRACT

Crucial for the advancement of electrochemical materials science is understanding the lateral variations in the elemental and chemical state of constituents induced by electrochemical reactions at nanoscales. This requires in situ studies to provide observables that contribute to both modeling beyond the phenomenological level and transducing exactly the functionally relevant quantities A range of X-ray coherent diffraction imaging (CDI) approaches has recently been proposed for imaging beyond the diffraction limit with potentially dramatic improvements of time resolution with chemical sensitivity. In this paper we report a selection of ptychography results obtained in situ after successive steps of electrochemically driven growth, complemented with absorption and phase spectroscopy at high lateral resolution. We demonstrate the onset of morphological instability feature formation and correlate the chemical state of Mn with local growth rate controlled by the current density distribution resulting from morphological evolution.

1. Introduction

The availability of green, safe and reliable energy storage devices is a key to the deployment of next-generation technologies such as fully electrical vehicles, electrical aircraft and grid-storage devices for the rational implementation of renewable energy sources. In this field, electrochemistry is universally recognized for its essential prospective role and appropriate batteries and fuel cells are enabling components. Efficient electrochemical energy storage and recharging as well as regeneration of fuels for fuel cells critically rely on bulk phase formation and transformation processes that are seriously affected by multiscale localization problems leading to growth instabilities [1,2]. Typically, such instabilities are controlled by morphochemical couplings [3–5], leading 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 challenge in device improvement is preventing irregular material distribution generally due to uncontrolled current density (c.d.) distribution and dendrite formation.

The phenomenology and mathematical modeling of unstable electrodeposition processes have been described in an immense corpus of scientific and technological literature, dating back to ca. one century, but neither conclusive understanding has been gained nor have satisfactory control protocols been devised.

Some classical references have systematically set the phenomenological framework of unstable morphology development by electrodeposition morphologies (e.g. [1,6]), while a steadily increasing number of recent reports (e.g. [7–9]) is pinpointing a still wider class of 3D features the evolution of which should depend on the growth rate, including bath chemistry and mass transport. As far as the physico-mathematical understanding of these processes is concerned, early work based on phenomenological kinetics proposed that dendrite growth is controlled by mere electrokinetic activation [10] while later on the interplay between activation and diffusion control was indicated as a key to unstable electrocrystallization [1]. This simple framework allows straightforward incorporation of more sophisticated mass-transport contributions

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based on molecular-level modeling [11]. Statistical mechanics approaches have also been considered, based on nanocluster aggregation [7], diffusion-limited aggregation [12] and Montecarlo [13]. PDE modeling of unstable electrodeposition set out from an extension of the Mullins-Sekerka instability theory [14] and was later expanded to a reaction-diffusion model for two chemicals [15] as well as for combined morphology and chemistry [3,5,16]. More recently, phase-field theories, that add a variable describing the electrode-electrolyte interface as a diffuse quantity, have also been considered [17,18]. Finally, morphological development has been correlated to the c.d. distribution, as evaluated by multiphysics modeling, incorporating ionic transport by diffusion, migration and convection, phenomenological charge-transfer kinetics and viscous fluid-dynamics [19]. The general conclusion from these studies is that conceptually possible, but practically unsatisfactory approaches to the mitigation of these instability problems are the implementation of poorly controlled and expensive pulse plating programs and/or the use of chemically unstable, toxic and costly additives, that impose demanding bath maintenance procedures.

All considerations above indicated that full understanding and improvement of 3D electrochemical growth processes of multicomponent and multiphase functional materials requires the control of dynamic events at relevant length scales. Getting structural and chemically specific information down to the nanoscale is prerequisite, that has stimulated the use of synchrotron-based X-ray microspectroscopy and a range of imaging and microspectroscopy approaches have been developed (e.g. [20–24]). The combination of in situ scanning X-ray microscopy, electrochemical measurements and mathematical modeling [4,5] has yielded novel results of technological interest shedding light on the effect of growth or operating conditions on morphology and composition. However, both the lateral resolution and the acquisition rate still remain limiting factors.

Recently proposed approaches such as ptychography and keyhole CDI, have proved to be very efficient for ex situ chemical imaging of nanostructured materials [25–29]. These methods are based on coherent diffractive imaging (CDI), also called lensless microscopy, that overcomes the resolution limits imposed by focusing optics used in classical X-ray Microscopy by replacing the image forming lens with an iterative algorithm to simultaneously recover a phase and absorption image of the object [30–35]. In classical CDI the object size must be smaller than the illumination, and this limitation is partially overcome in Fresnel CDI by placing the object downstream of the focus of a Fresnel Zone Plate (FZP) to obtain quantitative images over a larger field of view [36–38]. Fresnel CDI also permits keyhole imaging, by using the pre-characterized illumination to obtain quantitatively image portions of extended objects [24,39,40]. These methods have been used to successfully image a range of specimens from biology to materials, across a range of X-ray energies. However, the object size limitations are fully handled by ptychography overlapping multiple CDI images, demonstrated first in electron microscopy [41] and later-on in X-ray microscopy [42]. Essential requirements for ptychography are (i) coherent spatially-confined X-ray beam, delivered by using pinhole or X-ray focusing optics and (ii) partial overlap of the illuminated regions when scanning the sample. At each position the coherent diffraction pattern is recorded in the far field. Ptychography with soft X-rays is in a less advanced stage than with hard X-rays, but recently, thanks to the advances in detector development, it has achieved the spectacular resolution of 5 nm [29]. Ptychography can provide chemical information by recovering the phase and amplitude functions obtained by scanning the photon energy across appropriate resonances [25,43–45]. Similarly, Fresnel CDI can be extended in a technique known as Phase-Diverse CDI [46], where Fresnel CDI images are overlapped transversely or both transversely and longitudinally [47,48]. While the probe is simultaneously recovered in ptychography allowing reliable beam characterization [49], phase-diverse CDI measures the probe independently and reducing the measurement time [28,50]. Recent advances have pushed these techniques further in terms of sample environment [24,48,51] and resolution [29], while the directly quantitative nature of both ptychography and phase-diverse CDI allow them to be used spectroscopically to gain insights to the elemental composition of the sample [24,29,43,45,52,53].

This paper reports an in situ soft X-ray ptychography study following representative successive steps of electrochemical phase formation processes using a liquid electrolyte, in particular the onset and evolution of unstable growth. Summarizing the methods and results recently obtained in our group [24] and presenting a selection of original data we demonstrate the great potential of in situ electrochemistry with unprecedented space and time-resolution to provide information incommensurably superior than ex-situ approaches. However, employing soft X rays in transmission is a challenging experiment, because it requires a wet cell operated in vacuum allowing the electrolyte and working electrode to be crossed by the beam. The reported spectroscopic CDI experiments follow in time at nanometric scale changes in morphology and chemical state during the electrodeposition of Mn-Co/polypyrrole (PPy) nanocomposites and the in situ space information is obtained by applying a novel reconstruction methodology [24].

2. Materials and methods

2.1. Ptychography measurements

Electrodeposition was monitored in *situ* through Fresnel CDI ptychography at the SXRI beamline of the Australian Synchrotron [54]. A monochromatized microprobe beam was delivered by FZP diffractive optics (160 μm diameter and an outermost zone with a 30 nm thickness and 30 μm central stop). We chose a relatively large beam because it allows us to cover a larger area faster with a lower dose [28], enabling us to image the evolution of the system in real time. In principle, this choice can give rise to the formation of Fresnel-like rings around features with larger contrast, but these are straightforwardly recognizable and only impact cosmetic aspects. Thus, in the trade-off in the choice of beam size between appearance of ringing in the images and degradation of in situ capabilities, we judged the former cost more convenient.

The sample was placed ~500 μm downstream of the focus, resulting in an illuminated area of the sample ~35 μm in diameter. The images were monitored by a 2048 × 2048 pixel CCD camera located ~32 cm from the focal spot [28]. Ptychographic scans were acquired with a 6 μm step size over a raster scan of 3 × 5 positions, giving a minimum overlap fraction of 82% [24]. With this approach, the central areas of the overall imaged ROI were reconstructed with a better accuracy than most external ones, where the overlapping fraction was lower. The electrochemical microcell – whose configuration allows illumination with an X-ray microprobe crossing the electrode/electrolyte assembly normally to the optical window (see Section 2.2 below) – was mounted on customized SXRI sample holder and the three-electrode system was connected to a potentiostat outside the vacuum chamber by means of a suitable electrical feedthrough. The NADIA [55] software library has been used for image reconstruction while pre and post processing was carried out with purposely developed Python algorithms.

2.2. Wet cell fabrication

The fabrication of the electrochemical cell, illustrated schematically in Fig. 1, is described in detail in [56]. The cell consists of two

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