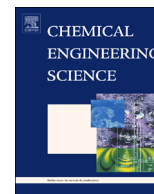




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# Modeling of flowable slurry electrodes with combined faradaic and nonfaradaic currents



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## HIGHLIGHTS

- Combined faradaic and nonfaradaic behavior of flowable slurry electrodes is modeled.
- A capacitive Damköhler number describing slurry electrode behavior is introduced.
- Scaling relationships for predicting current from slurry electrodes are created.
- Slurry electrodes are found to operate in four possible regimes.
- Length scales for asymmetric electroactive zone extension are determined.

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## ABSTRACT

Flowable slurry electrodes have received increased interest recently for use in electrochemical energy storage and water treatment systems. In an electrochemical cell these flowing electrodes can simultaneously support both faradaic currents (through reactions occurring at the slurry/solution interface) and nonfaradaic currents (through charging of the double layer capacitance of each slurry particle as it passes through the cell). In this paper, a model based on a three-dimensional set of macrohomogeneous equations that combines the effects of both types of current is developed. The model equations are applicable to flow battery, electrochemical flow capacitor, and flow-electrode capacitive deionization systems. Using this modeling approach, the performance of slurry electrodes in symmetric electrochemical cells is examined. Scaling techniques are applied to the equations in order to permit the prediction of the steady-state current that can be achieved from a slurry electrode as a function of cell dimensions, slurry properties, flow rate, reaction kinetics, and the potential applied across the cell. Depending on the values of four dimensionless combinations of the pertinent variables (the capacitive Graetz number, the nondimensional exchange current density, the conductivity ratio, and the flow behavior index) slurry electrodes are then shown to operate in one of four distinct operational regimes. Lastly, the variation of the physical extent of the reaction zone (i.e. electroactive zone extension) with respect to the relative magnitude of advection is characterized.

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## 1. Introduction

For several decades, slurry and fluidized bed electrodes have been extensively investigated for use in electrochemical systems (Heydecke and Beck, 1990). A variety of applications have been pursued, including water treatment and electrochemical energy storage (Appleb and Jacquier, 1976; Baria and Hulburt, 1973; Foller, 1986). Recent work with regard to slurry electrodes has mostly concerned three specific systems: flow batteries with flowable slurry electrodes (Duduta et al., 2011; Fan et al., 2014; Petek et al.,

2015), electrochemical flow capacitors (EFCs) (Presser et al., 2012), and flow-electrode capacitive deionization (FCDI) systems (Jeon et al., 2013).

Fluidized bed and slurry electrodes can support the conduction of charge through the creation of a dynamic percolation network. The current in this phase therefore acts just as it does in a porous electrode such as carbon felt or carbon paper (i.e. according to Ohm's law). The flowability of the slurry, though, offers advantages that are not present for stationary porous electrodes. For example, in FCDI systems the flowability of the slurry allows for continuous operations (as the electrodes can be charged in one cell and discharged in a separate cell) and allows for simple scale-up compared to standard porous electrode CDI approaches (Jeon et al., 2013). For hybrid flow battery systems where a plating reaction

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occurs on the negative electrode, the flowability of the slurry electrode allows for the energy density and power density to remain decoupled, which is not the case for porous electrodes (Petek et al., 2015). In EFC systems, the fact that the electrode is flowing (and thereby advecting both the particles and the double layers of charge that exist at the particle/solution interface) allows for the existence of a steady-state current that can be stored for subsequent discharge. The main disadvantage of slurry and fluidized bed electrodes relative to porous electrodes though is their generally low electronic conductivities.

Modeling efforts to account for the performance of electrochemical systems possessing fluidized bed and slurry electrodes have also been pursued in the past. Fleischmann and Oldfield (1971) began these efforts by studying fluidized bed electrodes that supported faradaic reactions. In that work, standard one-dimensional macrohomogeneous porous electrode equations were applied to the fluidized bed electrode and polarization relationships were derived. A three-dimensional model for a slurry supporting faradaic reactions along with coupled fluid flow and mass transfer was used by Brunini et al. (2012) in the context of the simulation of a semi-solid flow battery. This approach consisted of including the effects of slurry rheology in the Navier–Stokes equations (which, in turn, altered the advective velocity used by the mass transport equations). Examinations of rheological effects and the extension of the reaction zone due to the upstream and downstream continuation of the slurry electrode away from the current collector have also been reported (Smith et al., 2014a, 2014b). Combined faradaic and capacitive behavior in slurries and fluidized beds was first considered by Gabrielli et al. (1994) who used electrochemical impedance spectroscopy to study electroactive beds. Cyclic voltammetry of stationary slurry electrodes with accompanying modeling was recently performed by Hatzell et al. (2015).

However, advection of the surface charge (which is essential to account for the performance of EFCs and FCDI systems) was not included in any of these approaches. The work of Fleischmann and Oldfield did not do so because the fluidized bed electrode is completely contained within the cell, and so this advection is nonexistent. The work of Brunini, et al. did not do so because the flow rates they considered were very low, thereby making advection of surface charge negligible. The first attempt to model EFC performance was by Dennison et al. (2014) who included a hydraulic current in a one-dimensional equivalent circuit approach. The work of Hoyt et al. (2015a) added advection of the surface charge to three-dimensional macrohomogeneous equations through the inclusion of a total derivative of the overpotential. This led to concepts of overpotential boundary layers and various associated nondimensional numbers (Hoyt et al., 2015b). This previous work was directed toward the modeling of EFCs though, and, hence, it did not include Faradaic reactions.

Any model applicable to flowable slurry electrodes must include terms to account for both faradaic reactions and surface charge advection as any real slurry electrode can be expected to support both phenomena simultaneously, as has been observed experimentally. (Wu et al., 2015) This paper will unify the previous modeling efforts to include both phenomena and will show how their simultaneous presence in a flowing slurry electrode can result in behavior distinct from what occurs when either is present alone. Numerical and analytical approaches will then be applied to the model to determine the performance characteristics of flowable slurry electrodes in electrochemical cells.

## 2. Model development

The modeling approach applicable to a flowable slurry electrode will be developed based off of the unification of the existing

modeling approaches of Brunini et al. (2012) and Hoyt et al. (2015b), along with nomenclature from others (Wang et al., 1998; Gu et al., 2000; Devan et al., 2004). All of these approaches are macrohomogeneous models based off of the principals of Newman et al. (Newman and Tobias, 1962; Newman, 1991; Newman and Tiedemann, 1975). The combined model requires equations for fluid flow, ionic/electronic conduction, faradaic kinetics, overpotential advection, and mass transfer. After development of the general equations, a simplified set of nondimensional equations will be created in order to permit scaling analysis of slurry electrode performance in an electrochemical cell and discernment of the governing behavior.

### 2.1. Fluid flow model

The fluid flow of the slurry is assumed to be homogeneous (i.e. there is no velocity slip between the particulate and solution phases), and can hence be described by the continuity equation for an incompressible fluid and by laminar Navier–Stokes equations with associated equivalent fluid properties.

$$\nabla \cdot \vec{u} = 0 \quad (1)$$

$$\rho \left( \frac{\partial \vec{u}}{\partial t} + \vec{u} \cdot \nabla \vec{u} \right) = -\nabla p + \nabla \cdot \left( \mu_{eff} \left( \nabla \vec{u} + (\nabla \vec{u})^T \right) \right) \quad (2)$$

Here  $u$  is the shared velocity field of the respective particle and solution phases,  $p$  is the pressure,  $\rho$  is the mixture density, and  $\mu_{eff}$  is the effective viscosity of the slurry.

The slurries that are used as flowable electrodes typically exhibit shear-thinning behavior, and, as such, a non-Newtonian rheological model must be adopted, such as the Ostwald-de Waele power-law model used by Brunini et al. (2012). In this model, the effective viscosity is described as a function of the shear rate as

$$\mu_{eff} = K \dot{\gamma}^{m-1} \quad (3)$$

here  $K$  is the flow consistency index,  $m$  is the flow behavior index, and  $\dot{\gamma}$  is the magnitude of the rate-of-strain tensor (Macosko, 1994).

### 2.2. Electrochemical model

The electrochemical model for a flowable slurry electrode is based off of the macrohomogeneous approach where the slurry particles and the electrolyte are assumed to be interpenetrating homogeneous phases (Newman, 1991). For the model presented below, many of the assumptions from Devan et al. (2004) are adopted. These include the assumption that the diffusion coefficients, activity coefficients, transference numbers, double layer capacitance and electrolyte volume fraction are all uniform constants. Also, the solution phase is assumed to be a binary electrolyte that can be described by concentrated solution theory. Electrolytes with more complicated compositions (such as those with multiple reacting species) are not treated here, but can be modeled using extensions to this approach (Johnson and Newman, 1971).

A simple two-species charge transfer reaction of the canonical form (Newman, 1991) is assumed to occur at the particle/solution interface:



where  $s_k$  is the stoichiometric coefficient of the  $k$ th reactant species,  $M_k$  is the chemical symbol for the  $k$ th reactant species,  $z_k$  is the charge number of the  $k$ th species, and  $n$  is the number of electrons involved in the charge transfer reaction.

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