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Nonequilibrium Thermodynamics of Porous Electrodes

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We reformulate and extend porous electrode theory for non-ideal active materials, including those capable of phase transformations. Using principles of non-equilibrium thermodynamics, we relate the cell voltage, ionic fluxes, and Faradaic charge-transfer kinetics to the variational electrochemical potentials of ions and electrons. The Butler-Volmer exchange current is consistently expressed in terms of the activities of the reduced, oxidized and transition states, and the activation overpotential is defined relative to the local Nernst potential. We also apply mathematical bounds on effective diffusivity to estimate porosity and tortuosity corrections. The theory is illustrated for a Li-ion battery with active solid particles described by a Cahn-Hilliard phase-field model. Depending on the applied current and porous electrode properties, the dynamics can be limited by electrolyte transport, solid diffusion and phase separation, or intercalation kinetics. In phase-separating porous electrodes, the model predicts narrow reaction fronts, mosaic instabilities and voltage fluctuations at low current, consistent with recent experiments, which could not be described by existing porous electrode models.

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