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Reaction-Transport Coupling in a Nanostructured Porous Electrode

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Abstract

The function of nanoporous electrodes involves chemical reactions coupled to transport of reactants and products into and out of the solid matrix. To understand how this coupling can depend on electrode structure and chemistry, a general multiscale, molecular-level computational framework is introduced and applied to a model system containing a nanoporous photoanode, the dye-sensitized solar cell. The pore structure and electrolyte composition are systematically varied to probe this coupling, revealing that in most cases the photocurrent density depends on dye coverage within the anode matrix, the specific architecture of an individual pore, and electrolyte gradients in between the anode and cathode. The large electrolyte gradients that develop in the anode are not kinetically controlling. The computational framework demonstrated is general, and can be applied to other

electrochemical, photochemical and thermally driven nanoporous systems to evaluate the fundamental characteristics of their function.

Introduction

Nanostructured porous solid environments offer the possibility of high reaction efficiencies for many types of heterogeneous chemical and energy conversion systems because they have very high internal surface areas relative to their geometric area.¹⁻² They are frequently used in electrochemical systems such as batteries and solar energy conversion devices. Two general architectures are described in the literature: a random network of pores permeating an inorganic solid, or an ordered structure-pore assembly, often with structural hierarchies. In all cases the electrochemical reactions of interest take place at specific locations inside the porous solid and at a counterelectrode, and involve a permeating fluid (gas or liquid), with reactants and products transported into and out of the material. Numerous articles have been published on the design and synthesis of these architectures, and performance data such as current densities and product yields are often supplied. Models have been developed to examine their electrochemical properties, treating the chemistry in an averaged way.³⁻⁵ An understanding of the connection between how nanoporous electrode systems work at the molecular level and their operating characteristics⁶⁻⁷ provides very valuable information for identifying which chemical and architectural features have the greatest influence on electrode efficiency, and pinpoints pathways for improvement. In particular, understanding how transport of reactants in the pores affect rates can provide insights to why

efficiency improvements may not be as substantial as hoped given the increase in surface area relative to planar electrodes.⁸⁻¹⁰

Herein, a multiscale computational framework is presented for analyzing reactions coupled to transport in an entire nanoporous electrode – planar counterelectrode – electrolyte system in order to identify kinetically controlling factors. Multiscale modeling is most often implemented by using multiple models to capture processes at different scales in a system. When chemical kinetics are involved, however, multiscale modeling refers to solving the chemical master equation, where the master equation includes all processes at all scales.¹¹ The framework incorporates a molecular level description of key reactions on both electrodes and in the electrolyte, and Fickian diffusion in the solid and liquid phases. Numerical simulations generate the full spatially resolved time history of the system including nanometer scale interfacial excitation and charge transfer phenomena, elementary reactions throughout, statistical effects and macroscale transport. To demonstrate how the framework is used, a model system has been selected for study: the photoanode and dark cathode couple in a dye-sensitized solar cell (DSC). This system comprises many features common to porous electrode-containing systems and enjoys a wealth of literature on detailed properties and performance.¹²⁻¹³

DSC anodes are most often random networks of TiO_2 nanoparticles 12-20 nm in size, impregnated with dye, with porosity in the range of 50%.¹² Some architectures have also been reported using TiO_2 nanotube or ZnO_2

nanorod structures instead of nanoparticles.² In a DSC system, the anode is integrated with a cathode, and electrolyte is added to fill the gap between the electrodes, and the anode pores. Electrons are generated by photoexcitations in the anode, transported externally to the cathode, and returned to the anode via a redox couple, most often the I^-/I_3^- couple.¹⁴ Simulations of this system over a range of initial conditions can reveal general principles for how reaction-transport coupling can affect function across broad length and timescales.

Because the chemical processes involving the dye in the anode and I_3^- reduction at the cathode are fast, it is reasonable to anticipate that the current generation efficiency of the DSC system would be governed by the balance of diffusion rates for electrons within the anode, I_3^- within the anode and toward the cathode, and for I^- toward and within the anode. This is illustrated in Figure 1, panel a. These transport processes are strongly affected by system geometry and electrolyte composition. Accordingly, systematic variation of these two characteristics will enable quantification of the connection between the current density and transport. Previous modeling studies have examined these points from a continuum, steady-state electrochemical perspective with a goal of finding system geometry and electrolyte compositions to optimize DSC efficiency.¹⁵⁻¹⁷ They focus on electron populations and consider in detail factors such as anode thickness and average porosity, but not specific details about pore aspect ratios, and

Figure 1. Schematic of the framework described in this work, as applied to the DSC model system. (a) Primary transport paths considered for the electrolyte components I₃⁻ and I⁻, and for electrons in TiO₂. (b) General architecture. The system thickness is 30 or 60 μm, with a 10 or 20 μm thick anode, typical of DSCs. The two cross sections examined are (i) 17% pore density, 42 nm x 32 nm with a 20 nm x 10 nm pore constructed from two adjacent 10 nm x 10 nm pore columns, or (ii) 59% pore density, 22 nm x 22 nm with two 10 nm x 10 nm pores and lateral periodic boundary conditions to interconnect the system. The 1 μm thick anode and cathode contacts at each end of the system are connected by a highly conducting wire. In all 4 cases the TiO₂ region is constructed using an assembly of columns with a 10 nm x 10 nm cross section. A straight column of contiguous TiO₂ material is referred to as a conduction path in this work.

predict the connection between I⁻ and I₃⁻ concentration gradients and overall photovoltage and current density. Here, the full interplay between

architecture, chemistry, charge generation and consumption, and transport is examined.

Framework and Model Construction

(a) Reaction scheme

Photogeneration of current by dye excitation is treated in this work as a purely chemical process. Molecular reaction stoichiometries, rate constants and diffusion coefficients are available for the basic steps involved in the reaction.^{12, 14, 18-19}

in the anode, and

at the cathode. The very fast electron injection step is treated implicitly in the R1 excitation rate constant. and charge carrier transport is dominated by diffusion, not drift.¹² Photovoltages are not required in this type of description of the kinetics, unlike the case for an electrochemical kinetic treatment.^{17, 20}

Table 1 presents the rate constants used in this study. Where possible rate constants are drawn from the literature, however this was challenging in the case of the anodic reduction reactions because the kinetics are fast and

captured as lifetimes or only indirectly measured.²¹⁻²² The cathodic reaction is complex²³ and rate constants for each of the steps are not available.

Table 1. List of kinetic parameters used in the simulations

Process	Step	Rate constant
Electrolyte reaction	R4	$3.8 \times 10^{-11} \text{ cm}^3/\text{mol-s}^{14}$
Anode-electrolyte interface reaction	R1	1 s^{-1}^{12}
	R2	$1 \times 10^{-10} \text{ cm}^3/\text{mol-s}^a$
	R3	$1 \times 10^{-10} \text{ cm}^3/\text{mol-s}^a$
Cathode-electrolyte interface reaction	R5	$1 \times 10^{-20} \text{ cm}^6/\text{mol}^2\text{-s}^a$
Electron diffusion	Electrolyte interface to anode TiO_2 matrix	$2 \times 10^{-4} \text{ cm}^2/\text{s}^{12 \text{ b}}$
	In TiO_2 matrix toward anode contact	$2 \times 10^{-4} \text{ cm}^2/\text{s}^{12 \text{ b}}$
	From anode contact to cathode contact	$1 \text{ cm}^2/\text{s}^a$
	From cathode to electrolyte interface	$2 \times 10^{-4} \text{ cm}^2/\text{s}^{12 \text{ b}}$
Iodide diffusion	I_3^- in electrolyte	$1 \times 10^{-5} \text{ cm}^2/\text{s}^{18-19 \text{ b}}$
	I_2^- in electrolyte	$1 \times 10^{-5} \text{ cm}^2/\text{s}^{18-19 \text{ b}}$
	I^- in electrolyte	$2 \times 10^{-5} \text{ cm}^2/\text{s}^{18-19 \text{ b}}$
	I_2^- from anode - electrolyte interface	$1 \times 10^{-5} \text{ cm}^2/\text{s}^{18-19 \text{ b}}$
	I^- to anode - electrolyte interface	$2 \times 10^{-5} \text{ cm}^2/\text{s}^{18-19 \text{ b}}$

^a assumed value for rate constant, selected to be very large

^b estimated from range in cited references

Accordingly the simple assumption is made that all events involving I_3^- reduction (cathode) or dye reduction (anode) are very fast, and an arbitrarily

large rate constant is assigned. The electrolyte is assumed to be an acetonitrile solution, which determines the I^-/I_3^- equilibrium and diffusion coefficients. Electron losses due to electrolyte-anode reactions are neglected because they are most likely to involve capture by I_2 in the pores,²⁴ which will have a low concentration due to the equilibrium favoring I_3^- formation when I^- is abundant.¹⁴

(b) Specific reaction conditions

The electrolyte composition is varied by specifying specific combinations of iodide ion concentrations. $[I_3^-]_0$ is set to 0.025M, 0.05M, 0.1M and 0.15M, with initial ($[I^-]$, $[I_3^-]$) of (3.16×10^{20} , 1.51×10^{19} mol/cm³), (3×10^{20} , 3×10^{19} mol/cm³), (2.71×10^{20} , 6.02×10^{19} mol/cm³) and (2.41×10^{20} , 9.03×10^{19} mol/cm³).¹⁹ $[I^-]_0 + [I_3^-]_0$ is maintained constant at 3.31×10^{20} mol/cm³. Counterions are not explicitly included. The dye concentration in the anode – electrolyte interfacial region is held constant at 4.4×10^{20} mol/cm³.¹² Conditions of (1) a light intensity of 1 sun, and uniform dye excitation in the anode, and (2) a zero initial electron concentration in the system (no dark current) are assumed. Simulations are run out to 0.8s, which is sufficient for an initial steady-state condition to be reached (or nearly so).

(c) System architecture

Anodes made of packed nanoparticles will incorporate a wide (and random) range of tortuous internal structures in one system. In this work

pore tortuosity is ignored, and single straight pores of well-defined length and cross section are used to identify how specific geometries influence the coupling between reaction and transport. As shown in Figure 1b, 4 separate architectures representing low density and high density pores, and thick and thin anodes are studied. A mnemonic is used to name them, Pore Density x% - pore length. As an example, the 59% pore density - 20 μm pore length case is referred to as PD59-20. Since Fickian diffusion rates depend on the magnitude of concentration gradients that develop during anode operation, for each architecture the initial I_3^- concentration, $[\text{I}_3^-]_0$, is varied from $1.51 - 9.03 \times 10^{19} \text{ mol/cm}^3$ (0.025-0.15M) as noted above.

The PD16 system is constructed as a 3-D grid of $63 \times 6 \times 5$ compartments, and the PD59 system's grid is $63 \times 4 \times 4$ compartments. In all 4 architectures, the solid body of the anode represented by a set of twenty $10\text{nm} \times 10\text{nm} \times 0.5 \mu\text{m}$ or $1 \mu\text{m}$ thick compartments stacked in columns between the anode contact and the bulk electrolyte. There is a 1 nm thick top dye layer at the anode-bulk electrolyte interface, and at the interior TiO_2 -pore interfaces. No photoactive dye is present at the bottom of the pores, on the anode contact material. 1nm thick interfacial compartments separate the cathode bulk from the electrolyte, defining the location of I_3^- reduction reactions. The PD-17 architecture has some additional thickness matching compartments in the TiO_2 regions in the same planes as the dye layers to accommodate insertion of these dye layers into the structure. The anode and cathode are constructed from a single layer of $1 \mu\text{m}$ thick compartments

matched in cross section to the anode compartments. A TiO_2 compartment therefore represents a stack of 50 or 100 10 nm nanoparticles in intimate contact, with no voids or interfacial resistance. A straight column of contiguous TiO_2 compartments is referred to as a conduction path in this work. The electrolyte-filled pore and the bulk electrolyte have the same compartment structure as the TiO_2 compartments.

The mechanistic steps R1-R5 are assigned to the appropriate compartments. R1-R3 take place in the 1 nm thick dye layers. R4 takes place in electrolyte compartments. R5 takes place in the 1 nm thick interfacial layer at the cathode. Electrons are assumed to be uniformly distributed within the TiO_2 , anode and cathode compartments and each electrolyte compartment is assumed to be well mixed at all times. Fickian diffusion paths for electrons are provided between all the TiO_2 , anode contact and cathode compartments, and for I^- , I_2^- and I_3^- between all electrolyte compartments. The PD-59 system utilizes ~~periodic boundary conditions~~ diffusion paths connecting top to bottom and side to side in the cross section direction to keep the computational expense of simulating a fully connected and dense system manageable, but the PD17 systems did not require them.

Values for key physical characteristics of the pore architectures used in the simulation data analysis are presented in Table 2. Fickian diffusion rates between two points in a volume depend on the magnitude of the diffusion coefficient and on the concentration gradient and the cross sectional area of the connecting volume. In these simulations, diffusion coefficients are the

same for each species in the four architectures and gradients are calculated for each architecture using a subvolume with constant cross section of 10^{-12} cm^2 , so the rates can readily be compared by comparing the steady state gradients that develop in each system.

Table 2. Anode characteristics

Architecture	TiO ₂ volume, 1 conduction path, cm^3	Total dye volume for 1 TiO ₂ conduction path, cm^3	Total dye molecules covering 1 TiO ₂ conduction path	Pore volume, cm^3	Interior pore area, cm^2	Surface / volume, cm^{-1}
PD17-20	2.0E-15	2.0E-16	2.4E+05	4.0E-15	1.2E-08	3.0E+06
PD17-10	1.0E-15	1.0E-16	1.2E+05	2.0E-15	6.0E-09	3.0E+06
PD59-20	2.0E-15	8.0E-16	9.6E+05	2.0E-15	8.0E-09	4.0E+06
PD59-10	1.0E-15	4.0E-16	4.8E+05	1.0E-15	4.0E-09	4.0E+06

Cumulative event counters (EC) can be embedded in reaction steps without affecting the simulation to allow the type and location of certain events to be tracked along with the chemical history, enabling a deeper mechanistic understanding to be developed from the simulation results. The chemical reactions used in the simulations are R1-R5. EC are introduced as product species (in italics) to count excitation events, dye reduction events, solution phase disproportionation events and cathodic I_3^- reduction events, generating the form of the steps actually used:

EC do not diffuse, and remain in their compartments of origin to provide a record of the compartment's detailed history for analysis when the simulation is complete. Supplementary Information (SI) sections S1 and S2 present some details of their use in this work.

(d) *Simulation method*

The simulations are performed using a stochastic algorithm to solve the master equation for the reaction-diffusion system. It is a type of kinetic Monte Carlo calculation that performs a random walk through event space, and is a natural technique for modeling processes that depend on sporadic events and random fluctuations. Stochastic algorithms were developed as a fully rigorous methodology for single well-mixed volumes in the 1970s by Bunker,²⁶ and later Gillespie,²⁷ and have been significantly extended by Hinsberg and Houle to support full 3-D²⁸ and other features important for materials systems. The capabilities are currently embodied in the open access simulation package *Kinetiscope*,²⁵ and details are given on the website about the available capabilities.

In the simulation loop, each step in the mechanism is probability-weighted using the instantaneous rate calculated from its rate law, and the next event to occur is selected randomly among all the steps. These sum of these probabilities is used to generate the time step corresponding to the

event; the time step is not predetermined. When physically accurate (or approximate but reasonably close) rate constants are used for the simulations, as is the case here, an absolute time scale is calculated, allowing the simulation outputs to be compared directly to experimental measurements. Because there is no differential equation integration, an exceptionally broad dynamic range of process rates and concurrent phenomena such as variable electric fields and volume changes can be incorporated into a single calculation, providing nanoscale to macroscale information in a natural way. Recent examples of how multiscale experimental-computational studies can be used for mechanism discovery in complex materials systems include reaction-diffusion processes in polymers and organic aerosol.²⁹⁻³⁰

Results and Discussion

(a) Spatial distributions of electrolyte components

Complete concentration vs time spatial maps are calculated for the 16 cases examined in this work. Electrolyte maps are of particular interest, and presented in Figure 2-5 for the PD17-20, PD59-20, PD17-10 and PD59-10 systems, respectively. They show that for all electrolyte compositions, the I^- and I_3^- spatial distributions in the pore and the bulk electrolyte above it become nonuniform, or polarized, with a notable dependence of the extent of polarization on initial pore architecture.

Figure 2. Maps of concentration vs time of electrolyte components for one 10 nm x 10 nm x 20 μm pore column in PD17-20 as a function of initial I_3^- concentration. The distance axis for each map ranges from the anode contact (1 μm) to the cathode contact (61 μm), with the anode-bulk electrolyte interface located at 21 μm . Residual I_2^- present after disproportionation is at low concentrations ($< 0.01\%$).

Figure 3. Maps of concentration vs time of electrolyte components for one 10 nm x 10 nm x 20 μm pore column in PD59-20 as a function of initial I_3^- concentration. The distance axis for each map ranges from the anode contact (1 μm) to the cathode contact (61 μm), with the anode-bulk electrolyte interface located at 21 μm . Residual I_2^- present after disproportionation is at low concentrations (< 0.01%).

Figure 4. Maps of concentration vs time of electrolyte components for one 10 nm x 10 nm x 10 μm pore column in PD17-10 as a function of initial I_3^- concentration. The distance axis for each map ranges from the anode contact (1 μm) to the cathode contact (31 μm), with the anode-bulk electrolyte interface located at 11 μm . Residual I_2^- present after disproportionation is at low concentrations ($< 0.01\%$).

Figure 5. Maps of concentration vs time of electrolyte components for one 10 nm x 10 nm x 10 μm pore column in PD59-10 as a function of initial I_3^- concentration. The distance axis for each map ranges from the anode contact (1 μm) to the cathode contact (31 μm), with the anode-bulk electrolyte interface located at 11 μm . Residual I_2^- present after disproportionation is at low concentrations ($< 0.01\%$).

The extent of concentration polarization is extracted from the maps and shown in Figure 6. The time dependence of the associated gradients is presented in Figures S1-S4 in SI Section 1. The gradients are responsible for transport of I_3^- , formed by I_2^- disproportionation (R4), out of the pore and into the bulk electrolyte toward the cathode, where it undergoes reaction R5 to

generate I^- . This reaction consumes 2 electrons, and is a key step in current flow in the system.

Figure 6. Polarization of electrolyte components at steady state, calculated by dividing the component concentration by its initial value. 0 is located at the bottom of the anode contact. The dotted lines mark the location of the anode-bulk electrolyte interface.

(b) Calculated current densities

Reaction R5 does not start until an average electron concentration of $2-7 \times 10^{18} \text{ cm}^{-3}$ is

established in the system, consistent with electron concentrations under open circuit and operating conditions measured in literature studies.^{13, 31-33}

Electron gradient maps similar to Figures 2-5 are produced in the simulations but are not relevant to this study. Event counters (EC) in the anode are used to compare the number of dye excitation (R1) to dye reduction (R2) events, (SI section 2, Table S1). They show that in all 16 cases the total numbers of R1 and R2 events per unit volume of the dye layer are identical, indicating there is no pore geometry dependence for the dye regeneration process.

Figure 7. Current densities calculated from the I_3^- reduction rate at the cathode as a function of pore architecture and electrolyte composition ($[I_3^-]_0$). (a) absolute current densities, where “all” means all 4 electrolyte composition cases. The current densities are constant in time and independent of electrolyte with 2 exceptions, PD59-20 with $[I_3^-]_0 = 0.025$ and $0.5M$; (b) current densities scaled by dye amount-per-TiO₂ conduction

path characteristic of each pore architecture. The PD59-20 with $[I_3^-]_0 = 0.025$ and 0.5M cases are represented by circled symbols.

EC at the cathode track the total number of I_3^- reduction reactions as a function of time, (SI Section 3, Figure S6). The EC is doubled to determine the number of electrons consumed, and differentiated to obtain an instantaneous current density (Figure 7). The current densities (Figure 7a) are strongly dependent on architecture, but not on electrolyte composition for all but 2 of the 16 cases. A 10 micron thick anode produces half the current of a 20 micron thick anode, and PD59 currents are 4x those of PD17. The 4x scaling can be understood from the characteristics of the four architectures in Figure 1b. The PD17 structure has one layer of dye on average per stack of TiO_2 nanoparticles, the TiO_2 conduction path, while the PD59 structure has 4 layers. Thus, the current scales with *amount* of dye per TiO_2 conduction path, not the dye concentration, which is constant for all systems, and the scaling factors for the systems PD59-20 : PD59-10 : PD17-20 : PD17:10 are 8 : 4 : 2 : 1. Figure 7b shows that the average current density after a scaling correction is $9.5 \times 10^{-3} \text{ A/cm}^2$. This value can be taken to be the contribution to the total current density of a 10 μm length of TiO_2 conduction path with 25% of the maximum dye amount. The 2 exception cases have reduced current, as expected from Figure 7a.

(c) Connection between current density and reactions

Both reactions R1 and R5 are directly connected to current density, with R1 being the electron source step, and R5 being the electron drain step. R1 is a (pseudo)first order step dependent only on the dyes available since

illumination is constant and uniform, and R5 is a step second order in electron concentration and first order in $[I_3^-]$. In order to evaluate which of these steps may control the kinetics, the dependences of current density on the amount of dye in the anode and on $[I_3^-]$ at the cathode are plotted in Figure 8. Figure 8a shows a linear dependence on

Figure 8. Dependence of current density on chemical reactions as a function of pore structure. (a) Dependence on the amount of dye excited on the TiO₂ conduction path in the anode where the line is a least squares fit with slope of 0.5 s⁻¹ calculated from the number of electrons consumed at the cathode per second per dye; (b) dependence on $[I_3^-]$ at the cathode. The circled symbols are for the 2 PD59-20 cases, $[I_3^-]_0 = 0.025$ and 0.05M, where the current undergoes transients as shown in Figure 7a.

dye amount per TiO_2 conduction path, with a slope of 0.5 sec^{-1} . This is an apparent first order rate constant. Since 2 dye excitations are required for each I_3^- reduction (and electron consumption) event, the apparent rate constant is $\frac{1}{2}$ the actual dye excitation rate constant of 1 sec^{-1} . Figure 8b shows the dependence of current on the local $[\text{I}_3^-]$. As can be seen in Figure 3, the I_3^- dependence only appears when $[\text{I}_3^-]$ becomes very small at $[\text{I}_3^-]_0$ values of 0.025 and 0.05 M for the PD59-20 case. Otherwise, the currents are not kinetically controlled by R5. They are, however, proportional to the source of the electrons: the dye excitation in the anode. This explains the current transients in Figure 7a: rapid depletion of I_3^- at the cathode limits current flow, and is predicted to result in significant buildup of electron density in the system.

(d) Connection between current density and transport

When current flow is not reaction-limited by the cathode, it must be transport limited. In these simulations, Fickian diffusion rates are readily compared using the steady state gradients that develop in each system. Figure 9 compares the dependence of current density on gradients for I^- and I_3^- in the pore electrolyte and the bulk electrolyte. Raw pore values are shown in Figure 9a. The scatter seen in the Figure is due to pore architecture. I_3^- is formed only in solution

Figure 9. Electrolyte ion gradient dependence of current density in (a) and (b) the anode pore and (c) the bulk region in between the anode and cathode, as a function of pore structure. (b) is derived from (a) by normalizing for the pore geometry scaling dependence of the disproportionation reaction that forms I_3^- and I^- in the electrolyte. The circled symbols are for the 2 PD59-20 cases, $[I_3^-]_0 = 0.025$ and $0.05M$, where the current undergoes transients as shown in Figure 7a.

(R4), and the relative rate of disproportionation depends on the surface to volume ratio of the pore (SI Section 2 and Figure S5), which is $PD17/PD59 = 0.75$, as well as the pore length. These geometric factors predict gradient scaling factors for the systems PD59-20 : PD59-10 : PD17-20 : PD17:10 of $2.67 : 1.33 : 2 : 1$. The scaled current densities are independent of pore gradients as shown in Figure 9b. The opposite is found in the bulk electrolyte, as seen in Figure 9c. A strong linear dependence between electrolyte gradients and current density shows R5 is solely under transport control.

No anode recombination electron loss processes are included, however a small electron loss occurs via escape of I_2^- into the bulk electrolyte as

shown in Figures 2-5. The simulation results (Table S1) are analyzed to compare net electron formation events (R1) to net disproportionation events (R4) to net $[I_2^-]$ in the bulk electrolyte. The difference is small at 0.8s, about 0.2% fewer disproportionations than excitations, and essentially all due to processes at the anode-bulk electrolyte interface. When $[I_2^-]$ is too small for disproportionation to occur, electrons carried by them cannot contribute to current flow and are thereby lost to the system.

Conclusions

The hypothesis tested in this study is that when very fast reactions occur in nanoporous electrodes, the chemistry is strongly influenced by transport limitations through very small spaces. The simulation results show clearly that for the model conditions investigated, this is not the case. The photocurrent is strongly dependent on system architecture, i.e. size, shape and density of the pores. In all but two cases the kinetics of electron flow are determined by a fast generation reaction in the anode, and transport of a disproportionation product through the bulk electrolyte to react at the cathode. Pore gradients are large but do not control the kinetics under any of the conditions examined here. Kinetic control is spatially distributed, with photocurrent simultaneously determined by reactions in one part of the system and by transport in another. This situation is counterintuitive, and reveals that transport limitations in nanoporous electrodes are not inevitable

and that the system is best understood as a whole rather than as the sum of components.

Because the simple computational framework used here is generic to many (photo)electrochemistries (and indeed photochemical and thermal chemical systems), it can be used to identify broader principles such as the conditions under which transport in an electrode's pores does dominate. These can then be used to find electrode architectures, chemistries and reactant loadings that ensure that factors that control function are present by design and not by accident. That porous electrode architecture is so important to function suggests that the highly heterogeneous environment of a porous anode fabricated from a thin film of sintered nanoparticles will be challenging to use for characterization of fundamental chemical and physical quantities. Use of highly uniform architectures such as nanowires on a grid may be a more useful experimental strategy.

ASSOCIATED CONTENT

Supporting information Time histories of gradients in the 4 architectures. Spatially resolved excitation, reduction and disproportionation events in the anode. I_3^- neutralization events at cathode. Excel file with data tables.

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