Method of Manufactured Solutions for Poisson–Nernst–Planck Equations with Butler–Volmer Boundary Conditions

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Abstract

The Method of Manufactured Solutions (MMS) is a rigorous code verification technique that confirms a numerical implementation converges at the expected order of accuracy. An existing MMS formulation for the Poisson–Nernst–Planck (PNP) system imposes Dirichlet boundary conditions on the entire boundary, which tests the volumetric PDE discretization but completely avoids exercising the Butler–Volmer (BV) flux boundary condition. This document extends the MMS framework to include the nonlinear BV flux condition at the electrode boundary. The key idea is that the manufactured solution's normal flux at the electrode generically does *not* equal the BV rate evaluated at the manufactured concentrations and overpotential. We derive a boundary correction source term that accounts for this mismatch, incorporate it into the weak formulation, and specify the complete modified problem that the code must solve. Achieving the expected convergence rates on this modified problem simultaneously verifies the interior PDE discretization, the BV nonlinear flux implementation, and the coupling between them.

Contents

1 Introduction: Why BV BCs Need Special Treatment in MMS

The Method of Manufactured Solutions (MMS) is a widely-used code verification technique [1, 2, 3]. The procedure is:

1. Choose smooth, non-polynomial "manufactured" solutions for all unknowns.

2. Substitute them into the governing PDEs to compute volumetric source terms.

3. Solve the *modified* PDEs (with sources) numerically, using boundary and initial conditions evaluated from the manufactured solutions.

4. Compare the numerical solution to the known exact solution; verify that the error decreases at the expected rate under mesh refinement.

A standard MMS study for the PNP equations (as in the existing formulations document) chooses manufactured solutions that vanish on $\partial\Omega$ and imposes $c_i = c_i^{\text{exact}}$, $\phi = \phi^{\text{exact}}$ as Dirichlet conditions everywhere. This approach tests the volumetric discretization but *completely bypasses* the Butler–Volmer flux boundary condition—the most physically important and numerically challenging part of the electrochemical problem.

To verify the BV implementation, we must choose manufactured solutions that exercise the BV flux BC. The essential observation is that, for a generic manufactured solution, the diffusive/migratory flux at the electrode surface will *not* equal the BV reaction rate evaluated at the manufactured surface concentrations and overpotential. This mismatch requires an additional *boundary source term* in the weak form.

This document derives the complete MMS framework, including:

- The nondimensional PNP-BV strong form matching the `Forward/bv_solver.py` implementation.

- Choice of manufactured solutions with justification.

- Volumetric source terms $\hat{S}_i$ and $\hat{S}_\phi$.

- Boundary source terms $\hat{g}_i$ for each species at the electrode.

- The complete modified weak formulation.

- Pseudocode for the implementation.

- Expected convergence rates.

2 The PNP–BV System (Nondimensional)

We work entirely in nondimensional variables (hatted quantities), matching the solver conventions. The reference scales are: L (length), D_{ref} (diffusivity), c_{ref} (concentration), $V_T = RT/F$ (thermal voltage), $\tau = L^2/D_{\text{ref}}$ (time), $\kappa = D_{\text{ref}}/L$ (velocity / rate constant).

2.1 Domain and boundaries

The domain is the unit square $\Omega = [0,1]^2$ with boundary decomposition (see Figure 1):

$$\Gamma_{\text{elec}} = \{(x,0) : x \in [0,1]\} \qquad \text{(bottom, } y = 0 \text{: electrode)}, \tag{1}$$

$$\Gamma_{\text{bulk}} = \{(x,1) : x \in [0,1]\} \qquad \text{(top, } y = 1 \text{: bulk)}, \tag{2}$$

$$\Gamma_{\text{side}} = \{(0,y), (1,y) : y \in [0,1]\} \qquad \text{(left/right: insulating walls)}. \tag{3}$$
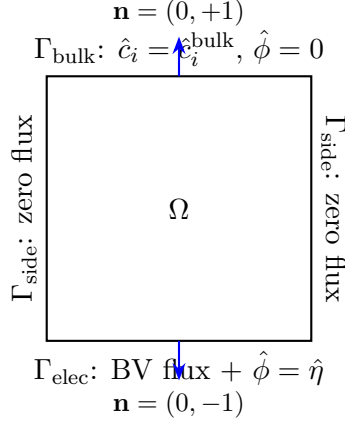
Figure 1: Domain $\Omega = [0,1]^2$ and boundary segments. The outward unit normal on the electrode Γ_{elec} is $\mathbf{n} = (0,-1)$.

2.2 Governing equations

Nernst–Planck equation   for species $i = 1, \dots, n$:

$$\frac{\partial \hat{c}_i}{\partial \hat{t}} = \nabla \cdot \left[\hat{D}_i (\nabla \hat{c}_i + z_i \hat{c}_i \nabla \hat{\phi}) \right] \quad \text{in } \Omega. \tag{4}$$

Here z_i is the valence, $\hat{D}_i$ the nondimensional diffusivity, and the electromigration prefactor (which is unity after nondimensionalization with V_T) has been absorbed.

Poisson equation:

$$-\hat{\varepsilon}\, \nabla^2 \hat{\phi} = \sum_{i=1}^{n} z_i \hat{c}_i \quad \text{in } \Omega, \tag{5}$$

where $\hat{\varepsilon} = (\lambda_D / L)^2$ is the squared Debye-length ratio.

2.3 Boundary conditions

Electrode (Γ_{elec}, $y = 0$):

- **Species:** Butler–Volmer flux condition. For each reaction j with stoichiometric coefficients s_{ij}:

$$-\hat{D}_i\big(\nabla \hat{c}_i + z_i \hat{c}_i \nabla \hat{\phi}\big) \cdot \mathbf{n} \;=\; \sum_j s_{ij}\, \hat{R}_j, \tag{6}$$

  where $\mathbf{n} = (0, -1)$ is the outward normal (pointing into the electrode).

- **Potential:** Dirichlet, $\hat{\phi} = \hat{\eta}$ (applied overpotential in thermal voltage units).

Bulk (Γ_{bulk}, $y = 1$):

- $\hat{c}_i = \hat{c}_i^{\mathrm{bulk}}$ (Dirichlet).

- $\hat{\phi} = 0$ (ground).

Sides (Γ_{side}):

- Zero-flux (homogeneous Neumann) for all species and potential.

2.4   Butler–Volmer reaction rates

For the O_2 reduction system, two reactions couple the species O_2 ($i = 0$) and H_2O_2 ($i = 1$):

$$\hat{R}_1 = \hat{k}_{0,1}\Big[\hat{c}_{O_2}\,\exp(-\alpha_1\hat{\eta}) - \hat{c}_{\mathrm{ref},1}\,\exp\big((1-\alpha_1)\hat{\eta}\big)\Big], \tag{7}$$

$$\hat{R}_2 = \hat{k}_{0,2}\,\hat{c}_{H_2O_2}\,\exp(-\alpha_2\hat{\eta}), \tag{8}$$

with stoichiometry matrix:

$$\mathbf{s} = \begin{pmatrix} s_{0,1} & s_{0,2} \\ s_{1,1} & s_{1,2} \end{pmatrix} = \begin{pmatrix} -1 & 0 \\ +1 & -1 \end{pmatrix}. \tag{9}$$

Species 0 (O_2) is consumed by $\hat{R}_1$; species 1 (H_2O_2) is produced by $\hat{R}_1$ and consumed by $\hat{R}_2$.

Remark 1 (General multi-reaction form). For a general system with n species and m reactions, the BV flux BC for species i at the electrode is:

$$-\hat{D}_i(\nabla \hat{c}_i + z_i \hat{c}_i \nabla \hat{\phi}) \cdot \mathbf{n} = \sum_{j=1}^m s_{ij}\, \hat{R}_j. \tag{10}$$

The MMS framework presented below holds for any number of species and reactions.

Remark 2 (Sign convention in the solver). In the solver (`bv_solver.py`), the BV flux enters the weak form as

$$F_{\mathrm{res}} \;-\!= s_{ij}\, \hat{R}_j\, v_i\, \mathrm{d}s(\mathrm{electrode}),$$

which arises from integration by parts: the boundary integral from IBP is $+ \int_\Gamma \hat{D}_i(\nabla \hat{c}_i + z_i \hat{c}_i \nabla \hat{\phi}) \cdot \mathbf{n}\, v_i\, \mathrm{d}s$, and substituting the BV condition (6) gives $-\sum_j s_{ij}\hat{R}_j\, v_i$ on the electrode.

3   Weak Formulation (No MMS Sources)

Before introducing manufactured solutions, we state the weak form that the solver implements. Let $v_i, w \in H^1(\Omega)$ be test functions with $v_i = 0$ on Γ_{bulk} (where Dirichlet BCs are imposed on $\hat{c}_i$) and $w = 0$ on $\Gamma_{\text{elec}} \cup \Gamma_{\text{bulk}}$ (Dirichlet BCs on $\hat{\phi}$).

Nernst–Planck:

$$\int_\Omega \frac{\partial \hat{c}_i}{\partial \hat{t}} \, v_i \, \mathrm{d}x + \int_\Omega \hat{D}_i\big(\nabla \hat{c}_i + z_i \hat{c}_i \nabla \hat{\phi}\big) \cdot \nabla v_i \, \mathrm{d}x$$

$$= -\sum_j \int_{\Gamma_{\text{elec}}} s_{ij} \, \hat{R}_j \, v_i \, \mathrm{d}s \quad \forall \, v_i. \quad (11)$$

The sign on the right-hand side is negative because the boundary integral from IBP gives $+\int_\Gamma \mathbf{J}_i \cdot \mathbf{n} \, v_i \, \mathrm{d}s$, and $\mathbf{J}_i \cdot \mathbf{n} = -\sum_j s_{ij}\hat{R}_j$ from the BV condition. Hence the boundary term is $-\sum_j s_{ij}\hat{R}_j \, v_i$. On Γ_{side}, the zero-flux condition makes the boundary integral vanish. On Γ_{bulk}, $v_i = 0$ by the Dirichlet lift.

Poisson:

$$\int_\Omega \hat{\varepsilon} \, \nabla \hat{\phi} \cdot \nabla w \, \mathrm{d}x = \int_\Omega \left(\sum_{i=1}^n z_i \hat{c}_i \right) w \, \mathrm{d}x \quad \forall \, w. \quad (12)$$

(The Neumann integral on Γ_{side} vanishes by the zero-flux condition, and $w = 0$ on the Dirichlet boundaries.)

4   Choice of Manufactured Solutions

4.1   Design requirements

The manufactured solutions must satisfy:

1. **Positivity:** $\hat{c}_i^{\text{ex}}(x, y) > 0$ everywhere (physical concentrations).

2. **Non-polynomial:** Cannot be exactly represented by the finite element basis, so that the discretization error is nonzero.

3. **Smoothness:** C^∞ to avoid polluting the convergence study with regularity issues.

4. **Nonzero normal flux at $y = 0$:** The manufactured flux at the electrode should be nonzero, to exercise the BV BC.

5. **Zero normal flux at $x = 0, 1$:** To be compatible with the zero-flux side walls (or else we would need side-wall correction sources too).

6. **Compatibility with Dirichlet BCs at $y = 1$:** The values $\hat{c}_i^{\text{ex}}(x, 1)$ and $\hat{\phi}^{\text{ex}}(x, 1)$ define the Dirichlet data on the bulk boundary.

4.2 Proposed manufactured solutions

We propose the following steady-state manufactured solutions (dropping the hat notation for brevity within this section; all quantities are nondimensional):

$$\boxed{c_i^{\text{ex}}(x,y) = c_{0,i} + A_i \cos(\pi x) \left(1 - e^{-\beta_i y}\right)} \tag{13}$$

$$\boxed{\phi^{\text{ex}}(x,y) = \eta_0 \left(1 - y\right) + B \cos(\pi x)\, y \left(1 - y\right)} \tag{14}$$

Parameters:

- $c_{0,i} > 0$: background (bulk) concentration for species i (e.g., $c_{0,0} = c_{0,1} = 1.0$).

- A_i: amplitude of the concentration perturbation (e.g., $A_i = 0.2$). Choose $|A_i| < c_{0,i}$ to ensure positivity.

- $\beta_i > 0$: controls the boundary-layer steepness (e.g., $\beta_i = 3$).

- η_0: the nominal electrode overpotential (matching the solver's $\hat{\eta}$).

- B: amplitude of the potential perturbation (e.g., $B = 0.1$).

4.3 Verification of design requirements

Positivity. At any (x,y):

$$c_i^{\text{ex}} \geq c_{0,i} - |A_i|\, |1 - e^{-\beta_i y}| \geq c_{0,i} - |A_i| > 0$$

provided $|A_i| < c_{0,i}$.

Non-polynomial. The $\cos(\pi x)$ and $e^{-\beta_i y}$ factors are transcendental.

Smoothness. Both expressions are $C^\infty(\bar{\Omega})$.

Nonzero flux at $y = 0$ (electrode). We compute:

$$\left. \frac{\partial c_i^{\text{ex}}}{\partial y} \right|_{y=0} = A_i\, \beta_i\, \cos(\pi x)\, e^{-\beta_i \cdot 0} = A_i\, \beta_i\, \cos(\pi x) \neq 0.$$

This is the key property: the manufactured solution has a nonzero diffusive flux at the electrode, which generically differs from the BV rate $\sum_j s_{ij} \hat{R}_j$.

Zero x-flux at $x = 0, 1$.

$$\frac{\partial c_i^{\text{ex}}}{\partial x} = -A_i \, \pi \, \sin(\pi x) \, (1 - e^{-\beta_i y}),$$

which vanishes at $x = 0$ and $x = 1$ since $\sin(0) = \sin(\pi) = 0$. Similarly,

$$\frac{\partial \phi^{\text{ex}}}{\partial x} = -B \, \pi \, \sin(\pi x) \, y(1 - y),$$

which also vanishes at $x = 0, 1$. Thus the zero-flux condition on Γ_{side} is automatically satisfied by both c_i^{ex} and ϕ^{ex}, and **no side-wall correction source is needed**.

Dirichlet values. At $y = 1$ (bulk):

$$c_i^{\text{ex}}(x, 1) = c_{0,i} + A_i \cos(\pi x) \, (1 - e^{-\beta_i}),$$

which is the Dirichlet BC value for $\hat{c}_i$ on Γ_{bulk}.

$$\phi^{\text{ex}}(x, 1) = 0,$$

which matches the ground condition $\hat{\phi} = 0$.

At $y = 0$ (electrode):

$$c_i^{\text{ex}}(x, 0) = c_{0,i} \qquad \text{(uniform, } x\text{-independent)},$$

$$\phi^{\text{ex}}(x, 0) = \eta_0,$$

which matches the electrode Dirichlet condition $\hat{\phi} = \hat{\eta}$ if we set $\hat{\eta} = \eta_0$.

5 Volume Source Terms

Substituting the manufactured solutions into the PDEs yields residuals that become the volumetric forcing functions. We work in steady state ($\partial \hat{c}_i / \partial \hat{t} = 0$) for simplicity; the time-dependent extension is straightforward.

5.1 Derivatives of the manufactured concentration

Let $f_i(y) = 1 - e^{-\beta_i y}$ so that $c_i^{\text{ex}} = c_{0,i} + A_i \cos(\pi x) f_i(y)$.

First-order derivatives:

$$\frac{\partial c_i^{\text{ex}}}{\partial x} = -A_i \, \pi \, \sin(\pi x) \, f_i(y), \tag{15}$$

$$\frac{\partial c_i^{\text{ex}}}{\partial y} = A_i \, \beta_i \, \cos(\pi x) \, e^{-\beta_i y}. \tag{16}$$

Second-order derivatives:

$$\frac{\partial^2 c_i^{\text{ex}}}{\partial x^2} = -A_i \, \pi^2 \, \cos(\pi x) \, f_i(y), \tag{17}$$

$$\frac{\partial^2 c_i^{\text{ex}}}{\partial y^2} = -A_i \, \beta_i^2 \, \cos(\pi x) \, e^{-\beta_i y}. \tag{18}$$

Laplacian:

$$\nabla^2 c_i^{\text{ex}} = -A_i \cos(\pi x) \left[\pi^2 f_i(y) + \beta_i^2 e^{-\beta_i y} \right]. \tag{19}$$

5.2 Derivatives of the manufactured potential

Let $\phi^{\text{ex}} = \eta_0(1 - y) + B \cos(\pi x)\, y(1 - y)$.

First-order derivatives:

$$\frac{\partial \phi^{\text{ex}}}{\partial x} = -B\,\pi\,\sin(\pi x)\, y(1 - y), \tag{20}$$

$$\frac{\partial \phi^{\text{ex}}}{\partial y} = -\eta_0 + B\,\cos(\pi x)\,(1 - 2y). \tag{21}$$

Second-order derivatives:

$$\frac{\partial^2 \phi^{\text{ex}}}{\partial x^2} = -B\,\pi^2\,\cos(\pi x)\, y(1 - y), \tag{22}$$

$$\frac{\partial^2 \phi^{\text{ex}}}{\partial y^2} = -2B\,\cos(\pi x). \tag{23}$$

Laplacian:

$$\nabla^2 \phi^{\text{ex}} = -B \cos(\pi x)\big[\pi^2 y(1 - y) + 2\big]. \tag{24}$$

5.3 Species source term $\hat{S}_i$

The strong-form residual of the Nernst–Planck equation at the manufactured solution is:

$$\hat{S}_i = \underbrace{\frac{\partial c_i^{\text{ex}}}{\partial \hat{t}}}_{=0 \text{ (steady state)}} - \nabla \cdot \left[\hat{D}_i\big(\nabla c_i^{\text{ex}} + z_i c_i^{\text{ex}} \nabla \phi^{\text{ex}}\big)\right]. \tag{25}$$

Expanding the divergence:

$$\nabla \cdot \left[\hat{D}_i(\nabla c_i^{\text{ex}} + z_i c_i^{\text{ex}} \nabla \phi^{\text{ex}})\right] = \hat{D}_i\left[\nabla^2 c_i^{\text{ex}} + z_i\big(\nabla c_i^{\text{ex}} \cdot \nabla \phi^{\text{ex}} + c_i^{\text{ex}}\, \nabla^2 \phi^{\text{ex}}\big)\right]. \tag{26}$$

The gradient inner product is:

$$\nabla c_i^{\text{ex}} \cdot \nabla \phi^{\text{ex}} = \frac{\partial c_i^{\text{ex}}}{\partial x}\frac{\partial \phi^{\text{ex}}}{\partial x} + \frac{\partial c_i^{\text{ex}}}{\partial y}\frac{\partial \phi^{\text{ex}}}{\partial y}. \tag{27}$$

Using (15)–(21):

$$\frac{\partial c_i^{\text{ex}}}{\partial x}\frac{\partial \phi^{\text{ex}}}{\partial x} = A_i B\,\pi^2\,\sin^2(\pi x)\, f_i(y)\, y(1 - y), \tag{28}$$

$$\frac{\partial c_i^{\text{ex}}}{\partial y}\frac{\partial \phi^{\text{ex}}}{\partial y} = A_i\,\beta_i\,\cos(\pi x)\, e^{-\beta_i y}\big[-\eta_0 + B \cos(\pi x)(1 - 2y)\big]. \tag{29}$$

Therefore:

$$\boxed{\hat{S}_i = -\hat{D}_i\left[\nabla^2 c_i^{\text{ex}} + z_i\big(\nabla c_i^{\text{ex}} \cdot \nabla \phi^{\text{ex}} + c_i^{\text{ex}}\, \nabla^2 \phi^{\text{ex}}\big)\right]} \tag{30}$$

where each term is given by the expressions above.

Remark 3 (Implementation). In practice, $\hat{S}_i$ is evaluated symbolically using SymPy (or by direct UFL differentiation in Firedrake) rather than by hand-coding (28)–(29). The analytic expressions above serve as a cross-check.

5.4 Poisson source term $\hat{S}_\phi$

From the Poisson equation (5):

$$\hat{S}_\phi = -\hat{\varepsilon}\,\nabla^2\phi^{\mathrm{ex}} - \sum_{i=1}^{n} z_i\, c_i^{\mathrm{ex}}. \tag{31}$$

Using (24):

$$\boxed{\hat{S}_\phi = \hat{\varepsilon}\,B\cos(\pi x)\big[\pi^2 y(1-y) + 2\big] - \sum_{i=1}^{n} z_i\, c_i^{\mathrm{ex}}(x,y)} \tag{32}$$

For a charge-neutral system (e.g., $z_0 = z_1 = 0$ for neutral O_2/H_2O_2), the summation vanishes and $\hat{S}_\phi$ depends only on ϕ^{ex}.

6 Boundary Source Terms for Butler–Volmer BCs

This is the central new contribution. On the electrode Γ_{elec} ($y = 0$), the physical BV boundary condition states:

$$\underbrace{-\hat{D}_i(\nabla\hat{c}_i + z_i\hat{c}_i\nabla\hat{\phi})\cdot\mathbf{n}}_{\text{total flux leaving domain}} = \sum_j s_{ij}\,\hat{R}_j(\hat{c}|_{\mathrm{surf}}, \hat{\eta}). \tag{33}$$

When $\hat{c}_i = c_i^{\mathrm{ex}}$ and $\hat{\phi} = \phi^{\mathrm{ex}}$, the left-hand side is the *manufactured flux*:

$$\mathcal{F}_i^{\mathrm{ex}}(x) = -\hat{D}_i\big(\nabla c_i^{\mathrm{ex}} + z_i c_i^{\mathrm{ex}}\nabla\phi^{\mathrm{ex}}\big)\cdot\mathbf{n}\bigg|_{y=0}, \tag{34}$$

and the right-hand side is the *manufactured BV rate*:

$$\mathcal{B}_i^{\mathrm{ex}}(x) = \sum_j s_{ij}\,\hat{R}_j\big(c^{\mathrm{ex}}(x,0), \phi^{\mathrm{ex}}(x,0)\big). \tag{35}$$

In general, $\mathcal{F}_i^{\mathrm{ex}} \neq \mathcal{B}_i^{\mathrm{ex}}$, so we define the **boundary source term**:

$$\boxed{\hat{g}_i(x) = \mathcal{F}_i^{\mathrm{ex}}(x) - \mathcal{B}_i^{\mathrm{ex}}(x)} \tag{36}$$

This is the mismatch between the flux that the manufactured solution actually has and the flux that the BV kinetics would demand. Adding $\hat{g}_i$ as an extra boundary source "absorbs" this mismatch, ensuring that c_i^{ex} and ϕ^{ex} satisfy the modified problem exactly.

6.1 Explicit computation of $\mathcal{F}_i^{\mathrm{ex}}$

On Γ_{elec}, $\mathbf{n} = (0, -1)$, so:

$$\mathcal{F}_i^{\mathrm{ex}}(x) = \hat{D}_i\left(\frac{\partial c_i^{\mathrm{ex}}}{\partial y} + z_i c_i^{\mathrm{ex}}\frac{\partial\phi^{\mathrm{ex}}}{\partial y}\right)\bigg|_{y=0}. \tag{37}$$

(The sign flip from $\mathbf{n} = (0, -1)$ cancels with the minus in (34).)

Evaluating at $y = 0$:

$$\frac{\partial c_i^{\text{ex}}}{\partial y}\bigg|_{y=0} = A_i\,\beta_i\,\cos(\pi x), \tag{38}$$

$$c_i^{\text{ex}}(x,0) = c_{0,i}, \tag{39}$$

$$\frac{\partial \phi^{\text{ex}}}{\partial y}\bigg|_{y=0} = -\eta_0 + B\,\cos(\pi x). \tag{40}$$

Therefore:

$$\boxed{\mathcal{F}_i^{\text{ex}}(x) = \hat{D}_i\big[A_i\,\beta_i\,\cos(\pi x) + z_i\,c_{0,i}\left(-\eta_0 + B\cos(\pi x)\right)\big]} \tag{41}$$

Neutral species ($z_i = 0$):

$$\mathcal{F}_i^{\text{ex}}(x) = \hat{D}_i\,A_i\,\beta_i\,\cos(\pi x) \qquad (z_i = 0).$$

This is purely diffusive and varies with x.

6.2   Explicit computation of $\mathcal{B}_i^{\text{ex}}$

The BV rates are evaluated at the manufactured surface values. From Section 2.4:

$$\hat{R}_1^{\text{ex}} = \hat{k}_{0,1}\big[c_{0,0}\,e^{-\alpha_1\eta_0} - \hat{c}_{\text{ref},1}\,e^{(1-\alpha_1)\eta_0}\big], \tag{42}$$

$$\hat{R}_2^{\text{ex}} = \hat{k}_{0,2}\,c_{0,1}\,e^{-\alpha_2\eta_0}. \tag{43}$$

Note that these are *constants* (independent of x) because $c_i^{\text{ex}}(x,0) = c_{0,i}$ and $\phi^{\text{ex}}(x,0) = \eta_0$ are both x-independent.

For the two-species, two-reaction system:

$$\mathcal{B}_0^{\text{ex}} = s_{0,1}\,\hat{R}_1^{\text{ex}} + s_{0,2}\,\hat{R}_2^{\text{ex}} = -\hat{R}_1^{\text{ex}}, \tag{44}$$

$$\mathcal{B}_1^{\text{ex}} = s_{1,1}\,\hat{R}_1^{\text{ex}} + s_{1,2}\,\hat{R}_2^{\text{ex}} = \hat{R}_1^{\text{ex}} - \hat{R}_2^{\text{ex}}. \tag{45}$$

6.3   Final boundary source terms

Combining (41) and (44)–(45):

$$\hat{g}_0(x) = \hat{D}_0\,A_0\,\beta_0\,\cos(\pi x) + z_0\,\hat{D}_0\,c_{0,0}\left(-\eta_0 + B\cos(\pi x)\right) + \hat{R}_1^{\text{ex}}, \tag{46}$$

$$\hat{g}_1(x) = \hat{D}_1\,A_1\,\beta_1\,\cos(\pi x) + z_1\,\hat{D}_1\,c_{0,1}\left(-\eta_0 + B\cos(\pi x)\right) - \hat{R}_1^{\text{ex}} + \hat{R}_2^{\text{ex}}. \tag{47}$$

Remark 4 (Neutral species simplification). For neutral species ($z_0 = z_1 = 0$), the electromigration terms vanish:

$$\hat{g}_0(x) = \hat{D}_0\,A_0\,\beta_0\,\cos(\pi x) + \hat{R}_1^{\text{ex}}, \tag{48}$$

$$\hat{g}_1(x) = \hat{D}_1\,A_1\,\beta_1\,\cos(\pi x) - \hat{R}_1^{\text{ex}} + \hat{R}_2^{\text{ex}}. \tag{49}$$

Note that $\hat{g}_i$ has both a spatially-varying part (from the manufactured flux) and a constant part (from the BV rates).

7 Complete Modified Weak Formulation

The MMS problem is: find $(\hat{c}_i, \hat{\phi}) \in V_h$ such that

Nernst–Planck (steady state):

$$\int_\Omega \hat{D}_i \big(\nabla \hat{c}_i + z_i \hat{c}_i \nabla \hat{\phi}\big) \cdot \nabla v_i \, \mathrm{d}x = \int_\Omega \hat{S}_i \, v_i \, \mathrm{d}x$$

$$- \sum_j \int_{\Gamma_{\mathrm{elec}}} s_{ij} \, \hat{R}_j(\hat{c}|_{\mathrm{surf}}, \hat{\phi}|_{\mathrm{surf}}) \, v_i \, \mathrm{d}s - \int_{\Gamma_{\mathrm{elec}}} \hat{g}_i \, v_i \, \mathrm{d}s \quad \forall\, v_i \in V_h^0, \quad (50)$$

where V_h^0 denotes the test space with functions vanishing on Γ_{bulk} (the Dirichlet boundary for $\hat{c}_i$).

Poisson:

$$\int_\Omega \hat{\varepsilon} \, \nabla \hat{\phi} \cdot \nabla w \, \mathrm{d}x = \int_\Omega \left(\sum_{i=1}^n z_i \, \hat{c}_i \right) w \, \mathrm{d}x + \int_\Omega \hat{S}_\phi \, w \, \mathrm{d}x \quad \forall\, w \in W_h^0. \quad (51)$$

Boundary conditions:

$$
\begin{aligned}
\hat{c}_i &= c_i^{\mathrm{ex}}(x, 1) & &\text{on } \Gamma_{\mathrm{bulk}}, & (52) \\
\hat{\phi} &= 0 & &\text{on } \Gamma_{\mathrm{bulk}}, & (53) \\
\hat{\phi} &= \eta_0 & &\text{on } \Gamma_{\mathrm{elec}}, & (54) \\
\text{BV flux} &+ \text{source } \hat{g}_i & &\text{on } \Gamma_{\mathrm{elec}} \text{ (natural BC, in weak form)}, & (55) \\
\text{zero flux} & & &\text{on } \Gamma_{\mathrm{side}}. & (56)
\end{aligned}
$$

7.1 Interpretation of each term

Equation (50) has three right-hand side contributions:

1. **Volume source $\hat{S}_i$:** Compensates for the fact that c_i^{ex} does not satisfy the PDE $\nabla \cdot \mathbf{J}_i = 0$ in the interior.

2. **BV flux $\hat{R}_j$:** The actual Butler–Volmer reaction rate, computed from the *numerical* solution's surface concentrations and the overpotential $\hat{\eta}$. This is the term that exercises the BV boundary condition implementation.

3. **Boundary correction source $\hat{g}_i$:** A *known, precomputed* function of x (since it depends only on the manufactured solution). It corrects for the mismatch between the manufactured flux and the BV rate. Crucially, $\hat{g}_i$ is *not* a function of the numerical unknowns — it is data, like $\hat{S}_i$.

7.2 Why this works

When $(\hat{c}_i, \hat{\phi}) = (c_i^{\mathrm{ex}}, \phi^{\mathrm{ex}})$, each term in (50) satisfies:

- LHS $= \int_\Omega \hat{D}_i(\nabla c_i^{\text{ex}} + z_i c_i^{\text{ex}} \nabla \phi^{\text{ex}}) \cdot \nabla v_i \, \mathrm{d}x.$

- RHS term 1: $\int_\Omega \hat{S}_i \, v_i \, \mathrm{d}x$, where $\hat{S}_i = -\nabla \cdot [\hat{D}_i(\nabla c_i^{\text{ex}} + z_i c_i^{\text{ex}} \nabla \phi^{\text{ex}})].$

- RHS terms 2+3: $-\sum_j s_{ij} \hat{R}_j^{\text{ex}} v_i - \hat{g}_i v_i = -\mathcal{B}_i^{\text{ex}} v_i - (\mathcal{F}_i^{\text{ex}} - \mathcal{B}_i^{\text{ex}}) v_i = -\mathcal{F}_i^{\text{ex}} v_i.$

Integrating by parts on the LHS:

$$\text{LHS} = -\int_\Omega \nabla \cdot [\hat{D}_i(\cdots)] \, v_i \, \mathrm{d}x + \int_{\Gamma_{\text{elec}}} \hat{D}_i(\cdots) \cdot \mathbf{n} \, v_i \, \mathrm{d}s$$
$$= \int_\Omega \hat{S}_i \, v_i \, \mathrm{d}x - \int_{\Gamma_{\text{elec}}} \mathcal{F}_i^{\text{ex}} \, v_i \, \mathrm{d}s. \tag{57}$$

This equals the RHS, confirming that c_i^{ex} is an exact solution of the modified problem.

7.3 Residual form for the solver

In the solver's residual-form convention ($F_{\text{res}} = 0$ at the solution), the MMS weak form is:

$$F_{\text{res}} = \sum_{i=1}^n \left[\int_\Omega \hat{D}_i(\nabla \hat{c}_i + z_i \hat{c}_i \nabla \hat{\phi}) \cdot \nabla v_i \, \mathrm{d}x - \int_\Omega \hat{S}_i \, v_i \, \mathrm{d}x \right.$$
$$\left. + \sum_j s_{ij} \int_{\Gamma_{\text{elec}}} \hat{R}_j \, v_i \, \mathrm{d}s + \int_{\Gamma_{\text{elec}}} \hat{g}_i \, v_i \, \mathrm{d}s \right]$$
$$+ \int_\Omega \hat{\varepsilon} \nabla \hat{\phi} \cdot \nabla w \, \mathrm{d}x - \int_\Omega \left(\sum_i z_i \hat{c}_i \right) w \, \mathrm{d}x - \int_\Omega \hat{S}_\phi \, w \, \mathrm{d}x = 0. \tag{58}$$

Note the signs:

- The BV term has $+s_{ij}$ (not $-s_{ij}$) because the solver convention is $F_{\text{res}} -= s_{ij} \hat{R}_j v_i \, \mathrm{d}s$, which corresponds to $F_{\text{res}} \mathrel{+}= (-s_{ij}) \hat{R}_j v_i \, \mathrm{d}s$. Wait — let us be precise. In the solver, the minus sign comes from: $F_{\text{res}} -= s_{ij} \hat{R}_j v_i \, \mathrm{d}s$. This means $F_{\text{res}} = \cdots + (-s_{ij} \hat{R}_j v_i) \, \mathrm{d}s$. In our notation above, the BV boundary integral on the RHS of (50) has $-s_{ij} \hat{R}_j v_i$, so moving it to the LHS (into F_{res}) gives $+s_{ij} \hat{R}_j v_i$ — which is *not* what the solver does.

  Let us reconcile: the solver has $F_{\text{res}} = [\text{diffusion}] - s_{ij} \hat{R}_j v_i \, \mathrm{d}s(\cdots)$. For MMS, we add: $F_{\text{res}} -= \hat{S}_i v_i \, \mathrm{d}x + \hat{g}_i v_i \, \mathrm{d}s$. This gives the correct sign.

To avoid sign confusion, we state the **implementation rule**:

$$\boxed{\begin{aligned} F_{\text{res}}^{\text{MMS}} = F_{\text{res}}^{\text{original}} &- \sum_{i=1}^n \int_\Omega \hat{S}_i \, v_i \, \mathrm{d}x \\ &- \sum_{i=1}^n \int_{\Gamma_{\text{elec}}} \hat{g}_i \, v_i \, \mathrm{d}s - \int_\Omega \hat{S}_\phi \, w \, \mathrm{d}x \end{aligned}} \tag{59}$$

That is: *subtract* the volume source terms and the boundary correction sources from the existing residual. The BV flux terms ($s_{ij} \hat{R}_j$) are *already* in $F_{\text{res}}^{\text{original}}$ and are left untouched.

8 Time-Dependent Extension

For a time-dependent MMS study (useful for testing the time-stepping scheme), replace the manufactured solutions with:

$$c_i^{\text{ex}}(x, y, t) = c_{0,i} + A_i \, \cos(\pi x) \, (1 - e^{-\beta_i y}) \, e^{-\gamma t}, \tag{60}$$

$$\phi^{\text{ex}}(x, y, t) = \eta_0 (1 - y) \, e^{-\gamma t} + B \cos(\pi x) \, y(1 - y) \, e^{-\gamma t}, \tag{61}$$

where $\gamma > 0$ controls the temporal decay rate.

The volume source term for the Nernst–Planck equation gains an additional time-derivative contribution:

$$\hat{S}_i^{(t)} = \frac{\partial c_i^{\text{ex}}}{\partial t} - \nabla \cdot \left[\hat{D}_i (\nabla c_i^{\text{ex}} + z_i c_i^{\text{ex}} \nabla \phi^{\text{ex}}) \right] = -\gamma \, A_i \, \cos(\pi x) \, (1 - e^{-\beta_i y}) \, e^{-\gamma t} + \cdots \tag{62}$$

The boundary source terms $\hat{g}_i(x, t)$ must also be re-evaluated at each time step, since both the manufactured flux and the manufactured BV rates now depend on t (through the surface concentrations and potential, which decay as $e^{-\gamma t}$).

For the time-stepping residual, the solver uses backward Euler:

$$F_{\text{res}}^{(t)} = \frac{\hat{c}_i^{n+1} - \hat{c}_i^n}{\Delta \hat{t}} \, v_i + \text{spatial terms}.$$

The MMS time derivative source is then discretized consistently:

$$\hat{S}_i^{(t,n+1)} = \frac{c_i^{\text{ex}}(t^{n+1}) - c_i^{\text{ex}}(t^n)}{\Delta \hat{t}} - \nabla \cdot [\cdots]^{n+1}.$$

This ensures that the temporal truncation error is tested as well.

9   Implementation Pseudocode

Algorithm 1 MMS verification with Butler–Volmer BCs

1: **Input:** mesh sizes $h_1 > h_2 > \cdots > h_K$; FE order p; MMS parameters $(c_{0,i}, A_i, \beta_i, \eta_0, B)$; BV parameters $(\hat{k}_{0,j}, \alpha_j, \hat{c}_{\mathrm{ref},j})$; PNP parameters $(\hat{D}_i, z_i, \hat{\varepsilon})$.

2: — **Precompute manufactured expressions (symbolic/UFL)** —
3: Define $c_i^{\mathrm{ex}}(x,y)$ via (13), $\phi^{\mathrm{ex}}(x,y)$ via (14).
4: Compute $\hat{S}_i(x,y)$ via (30) (UFL auto-differentiation).
5: Compute $\hat{S}_\phi(x,y)$ via (32).
6: Evaluate manufactured surface values: $c_i^{\mathrm{ex}}(x,0)$, $\phi^{\mathrm{ex}}(x,0)$.
7: Compute $\mathcal{F}_i^{\mathrm{ex}}(x)$ via (41) (or UFL gradient + dot with normal).
8: Compute $\hat{R}_j^{\mathrm{ex}}$ from (42)–(43) at surface values.
9: $\mathcal{B}_i^{\mathrm{ex}} \leftarrow \sum_j s_{ij}\, \hat{R}_j^{\mathrm{ex}}$.
10: $\hat{g}_i(x) \leftarrow \mathcal{F}_i^{\mathrm{ex}}(x) - \mathcal{B}_i^{\mathrm{ex}}$.

11: **for** $k = 1, \ldots, K$ **do**   ▷ Mesh refinement loop
12:     Build mesh with element size h_k.
13:     Build function spaces, mixed function, test functions.
14:     Build standard $F_{\mathrm{res}}^{\mathrm{original}}$ (diffusion + electromigration + BV flux + Poisson), as in `bv_solver.build_forms`.
15:     **Add MMS sources:**
16:         $F_{\mathrm{res}} \mathrel{-}= \sum_i \int_\Omega \hat{S}_i\, v_i\, \mathrm{d}x$
17:         $F_{\mathrm{res}} \mathrel{-}= \sum_i \int_{\Gamma_{\mathrm{elec}}} \hat{g}_i\, v_i\, \mathrm{d}s$
18:         $F_{\mathrm{res}} \mathrel{-}= \int_\Omega \hat{S}_\phi\, w\, \mathrm{d}x$
19:     Set Dirichlet BCs from manufactured solutions:
20:         $\hat{c}_i = c_i^{\mathrm{ex}}(x,1)$ on Γ_{bulk}
21:         $\hat{\phi} = \eta_0$ on Γ_{elec}; $\hat{\phi} = 0$ on Γ_{bulk}.
22:     Solve $F_{\mathrm{res}} = 0$ (Newton iteration).
23:     Compute errors: $e_{L^2}^{(k)} = \|c_i^h - c_i^{\mathrm{ex}}\|_{L^2(\Omega)}$, $e_{H^1}^{(k)} = \|c_i^h - c_i^{\mathrm{ex}}\|_{H^1(\Omega)}$.
24: **end for**

25: — **Convergence rate computation** —
26: **for** $k = 2, \ldots, K$ **do**
27:     $r_k = \log(e^{(k-1)}/e^{(k)}) / \log(h_{k-1}/h_k)$.
28: **end for**
29: **Verify:** $r_k \to p + 1$ (L^2) and $r_k \to p$ (H^1) as $k \to \infty$.

9.1   Firedrake-specific implementation notes

1. **UFL-based source terms.** The cleanest approach is to define c_i^{ex} and ϕ^{ex} as UFL expressions using `SpatialCoordinate(mesh)`, then let UFL's automatic differentiation compute ∇c_i^{ex}, $\nabla^2 c_i^{\mathrm{ex}}$, etc. Example:

    ```
    x, y = fd.SpatialCoordinate(mesh)
    c_ex = c0 + A * fd.cos(pi*x) * (1 - fd.exp(-beta*y))
    ```

```
phi_ex = eta0*(1-y) + B*fd.cos(pi*x)*y*(1-y)
```

2. **Volume source via `div` and `grad`.**

```
J_ex = D*(fd.grad(c_ex) + z*c_ex*fd.grad(phi_ex))
S_i = -fd.div(J_ex)
```

3. **Boundary source.** The manufactured flux at $y = 0$:

```
n_vec = fd.FacetNormal(mesh)
F_manuf = -D*fd.dot(fd.grad(c_ex) + z*c_ex*fd.grad(phi_ex), n_vec)
```

The manufactured BV rate at surface values:

```
R1_ex = k01*(c0_O2*fd.exp(-alpha1*eta0)
              - c_ref1*fd.exp((1-alpha1)*eta0))
B_i_ex = s_i1*R1_ex + s_i2*R2_ex
g_i = F_manuf - B_i_ex
```

Add to residual:

```
F_res -= g_i * v_i * ds(electrode_marker)
```

4. **Dirichlet BCs.** On Γ_{bulk}:

```
bc_ci = fd.DirichletBC(W.sub(i), c_ex, bulk_marker)
bc_phi = fd.DirichletBC(W.sub(n), phi_ex, bulk_marker)
```

Since $c_i^{\mathrm{ex}}(x, 1)$ depends on x, the Dirichlet value is a UFL expression, not a constant. Firedrake handles this correctly.

5. **Error computation.**

```
err_L2 = fd.errornorm(c_ex, c_h, norm_type="L2")
err_H1 = fd.errornorm(c_ex, c_h, norm_type="H1")
```

6. **Electrode BV term.** The BV terms in the residual use the *numerical* surface concentrations $\hat{c}_i|_{\Gamma_{\mathrm{elec}}}$, *not* the manufactured values. This is essential: the BV nonlinearity must operate on the unknowns so that the Newton linearization correctly tests the BV Jacobian contributions.

10 Expected Convergence Rates

For continuous Galerkin finite elements of polynomial degree p on a quasi-uniform mesh with element size h, the standard a priori error estimates give:

Error measure	Rate	CG1
$\|u - u_h\|_{L^2(\Omega)}$	$\mathcal{O}(h^{p+1})$	$\mathcal{O}(h^2)$
$\|u - u_h\|_{H^1(\Omega)}$	$\mathcal{O}(h^p)$	$\mathcal{O}(h^1)$

These rates apply to both the species concentrations and the potential. The convergence study should verify these rates for:

- Each species $\hat{c}_i$ individually.

- The potential $\hat{\phi}$.

- (Optionally) the BV reaction rates $\hat{R}_j$ evaluated at the numerical surface concentrations, compared to $\hat{R}_j^{\text{ex}}$.

Important considerations:

1. **Asymptotic regime.** The expected rates are asymptotic — they hold for sufficiently fine meshes. On coarse meshes, pre-asymptotic behavior may cause the observed rate to differ from the theoretical value.

2. **Nonlinear BCs.** The BV flux condition is a nonlinear Robin-type BC. Standard FE theory still predicts the same convergence rates because the BV term enters the weak form as a boundary integral evaluated at the numerical solution — it does not change the bilinear form's coercivity or approximation properties. However, if the BV implementation has a bug (wrong sign, wrong scaling, etc.), the convergence rate will be degraded or the method will fail to converge entirely.

3. **Boundary layer resolution.** If β_i is large (steep boundary layer), uniform meshes may require very fine resolution to enter the asymptotic regime. Choose moderate β_i values (e.g., $\beta_i = 3$) for the convergence study, or use graded meshes.

4. **Mesh refinement sequence.** A good sequence for the unit square is $N \times N$ with $N \in \{8, 16, 32, 64, 128\}$, giving $h = 1/N$. This provides 4 convergence rate estimates.

11 Alternative: Simplified Single-Species Test Case

For initial debugging, a minimal test case with a single neutral species ($n = 1$, $z = 0$) and a single irreversible reaction is recommended:

PDE: $-\hat{D}\,\nabla^2 \hat{c} = \hat{S}$ in Ω, with BV flux $-\hat{D}\,\partial\hat{c}/\partial y|_{y=0} = R(\hat{c}|_{y=0})$ at the electrode.

Manufactured solution: $c^{\text{ex}} = 1 + 0.2\cos(\pi x)(1 - e^{-3y})$.

BV rate: $R = \hat{k}_0\, c|_{y=0}\, e^{-\alpha\hat{\eta}}$ (irreversible reduction).

Source terms:

$$\hat{S} = -\hat{D}\,\nabla^2 c^{\text{ex}} = \hat{D}\cdot 0.2\cos(\pi x)[\pi^2(1 - e^{-3y}) + 9\,e^{-3y}], \tag{63}$$

$$\hat{g} = \hat{D}\cdot 0.2\cdot 3\cos(\pi x) - \hat{k}_0\cdot 1\cdot e^{-\alpha\hat{\eta}}. \tag{64}$$

This test case decouples the Poisson equation entirely and isolates the diffusion + BV flux interaction. If this case achieves the expected convergence rates, one can proceed to the full coupled PNP-BV system with confidence.

12   Summary and Checklist

12.1   What the MMS verifies

Component	How it is exercised
Diffusion operator	Volume source $\hat{S}_i$
Electromigration coupling	Volume source $\hat{S}_i$ (via $z_i c_i \nabla\phi$)
Poisson equation	Volume source $\hat{S}_\phi$
BV flux BC (nonlinear Robin)	BV terms + boundary source $\hat{g}_i$
BV sign convention	$\hat{g}_i$ depends on stoichiometric signs
BV exponent / scaling	$\hat{R}_j^{\text{ex}}$ involves $e^{\pm\alpha\eta}$
Dirichlet BCs	Manufactured values on Γ_{bulk}
Zero-flux (Neumann) BCs	Manufactured solution satisfies these exactly
Species–Poisson coupling	Cross-terms in $\hat{S}_i$ and $\hat{S}_\phi$

12.2   Implementation checklist

✓ Define manufactured solutions as UFL expressions.

✓ Compute $\hat{S}_i$ via UFL `div`/`grad` (not by hand).

✓ Compute $\hat{S}_\phi$ similarly.

✓ Compute $\hat{g}_i$ on the electrode: manufactured flux minus manufactured BV rate.

✓ Build F_{res} as usual, then subtract source terms (Eq. (59)).

✓ Set Dirichlet BCs from manufactured solution values.

✓ Solve on a sequence of refined meshes.

✓ Compute L^2 and H^1 errors; verify convergence rates.

✓ Start with the simplified single-species case (Section 11).

✓ Then test the full multi-species, multi-reaction system.

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