Online supplementary material to: Pretorius R, Crouse PL, Hattingh CJ. A multiphysics simulation of a fluorine electrolysis cell. S Afr J Sci. 2015;111(7/8), Art. #2014-0082, 5 pages. http://dx.doi.org/10.17159/sajs.2015/20140082

List of symbols

C_i	Concentration of chemical species i (mol/m^3)
$C_{0,i}$	Initial concentration of species i (mol/m^3)
C_P	Heat capacity at constant pressure $(\mathrm{J}\cdot/(kg\cdot K)$
C_{P0}	Heat capacity at constant pressure at 25 $°C(\mathrm{J}\cdot(kg\cdot K))$
d_b	Average bubble diameter (m)
D_i	Isotropic diffusion coefficient for chemical species i (m^2/s)
$\vec{F}$	Volume force vector $(\mathrm{kg}/(\mathrm{m}^2\cdot\mathrm{s}^2))$
F	Faraday constant $(\mathrm{A}\cdot s/mol)$
g	Gravitational acceleration (m/s^2)
i	Current density in electrolysis reactor (A/m^2)
i_n	Current density for electrode n (A/m^2)
i_0	Exchange current density (A/m^2)
k_n	Electrode n rate constants (m/s^1)
k_t	Thermal conductivity of electrolyte $(W\cdot(m\cdot K)$
n	Stoichiometric factor coefficient $(-)$
P	Pressure (kPa)
Q	Internal heat source (W/m^3)
R_i	Electrode surface molar flux for species i $(\mathrm{mol}/(m^2\cdot s^1))$
R_g	Ideal gas constant i $(\mathrm{J}\cdot(K^1\cdot mol^1))$
r_i	Reaction rate of species i in the electrolyte $(\mathrm{mol}\cdot(m^3\cdot s^1))$
T	Temperature of electrolyte (K)
t	Time (s)
T_0	Initial electrolyte temperature (K)
T_W	Temperature of cooling surface s (K)
$\vec{u}$	Velocity vector (m/s)

List of Greek symbols

α_i	Electron transfer coefficient $(-)$
β	Thermal expansion coefficient $(1/°C)$
ε_r	Relative permittivity $(-)$
Φ	Cell electric potential (V)
$\Phi_{0,i}$	Reference potential of electrode i (V)
φ_i	Volume fraction of phase i (V)
Φ_{RV}	Reversible cell voltage (V)
η_n	Surface overpotential of electrode n (V)
μ_i	Viscosity of fluid phase i $(Pa.s)$
$\mu_{m,i}$	Ionic mobility of species i $(m^2\cdot mol/(J\cdot s))$
ρ_i	Density of phase i (kg/m^3)
ρ_0	Electrolyte density at 25 $°C$ (kg/m^3)
σ	Electrical conductivity $(S\cdot/m)$

Electron transfer

The chemical reaction (electrolytic decomposition of the electrolyte into F_2 and H_2) is induced by electric potential as prescribed by Equation 1 (Laplace's equation) which models the primary current distribution and adheres to the assumption of Equation 2[8]:

$$-\nabla d(\sigma \nabla \Phi) = 0 \qquad \text{Equation 1}$$

$$\nabla \Phi^2 = 0 \qquad \text{Equation 2}$$

Current density distribution is modelled using Equation 3 (the Butler–Volmer equation) and Equation 4[9]:

$$\mathrm{i} = \mathrm{i}_0 \left[exp\left(\frac{\alpha_A F}{R_g T}\eta_s\right) - exp\left(\frac{\alpha_C F}{R_g T}\eta_s\right)\right] \qquad \text{Equation 3}$$

$$\mathrm{i}_0 = \mathrm{F}\sqrt{\mathrm{k}_a \mathrm{k}_c \mathrm{C}_{HF_2^-} \mathrm{C}_{HF}} \qquad \text{Equation 4}$$

Electrical conductivity was in turn modelled using the empirical relation shown in Equation 5. This equation assumes a linear relationship between electrical conductivity and gas fraction. Low gas fractions result in maximum conductivity, and vice versa.

$$\sigma = 1 + 5.67 \cdot \varphi_l \qquad \text{Equation 5}$$

Heat transfer

Heat transfer as a result of convection and conduction inside the reactor is modelled using Equation 6[3]:

$$\rho \mathrm{C}_p \, {\partial T}/{\partial t} + \nabla \cdot (-k_t \cdot \nabla T) = Q - \rho C_p \vec{u} \nabla T \qquad \text{Equation 6}$$

Heat generation in turn is modelled using Equation 7[3]:

$$\mathrm{Q} = \mathrm{i} \cdot (\Phi - \Phi_{RV}) \qquad \text{Equation 7}$$

Mass transfer

Reactant and product species movement is modelled using Equation 8[11]. This correlation incorporates convection, conduction, ion migration due to electric field and chemical reaction:

$$ {\partial C_i}/{\partial t} + \nabla \cdot (-D_i \nabla \mathrm{C}_i - z_i \mu_{m.i} F C_i \nabla \Phi + \mathrm{C}_i \vec{u}) = r_i \qquad \text{Equation 8}$$

Table 1 shows the three species assumed to comprise the system.

Table 1: Chemical species assumed to be present during the electrolytic process

Species	Charge number (z_i)
K	+1
HF	0
HF_2	-1

The dissociation reactions are given by Equation 9:

$$KF \cdot 2HF \rightarrow K^{+} + HF + HF_2^{-}$$ Equation 9

Relevant electrode half reactions are given by Equation 10 (anode) and Equation 11 (cathode) as supplied by Groult et al.[2]:

$$HF_2^{-} \rightarrow HF + \frac{1}{2}F_2 + e^{-}$$ Equation 10

$$2HF + e^{-} \rightarrow HF_2^{-} + \frac{1}{2}H_2$$ Equation 11

Dilute species flux at the electrodes was further modified to include the effect of bubbles on the electrode surface. This was implemented by coupling the calculated dilute species flux and liquid fraction (through multiplication) at the electrode boundary.

Momentum transfer

Flow induced inside the reactor was modelled by Equation 12, Equation 13 and Equation 14, representing the momentum transport, continuity and laminar bubbly flow equations, respectively. Subscripts 'l' and 'g' denote the liquid and gas phases, respectively[4,8]:

$$\varphi_l \rho_l \,{}^{\partial \vec{u}}/_{\partial t} + \varphi_l \rho_l (\vec{u} \cdot \nabla)\vec{u} = \nabla \cdot \left[-P\vec{I} + \varphi_l \vec{u}\left(\nabla \vec{u}_l + \nabla \vec{u}_l^{T}\right)\right] + \varphi_l \rho_l \vec{g} + \vec{F}$$ Equation 12

$$\nabla \cdot \vec{u} = 0$$ Equation 13

$$^{\partial \varphi_g \rho_g}/_{\partial t} + \nabla\left(\varphi_g \rho_g \vec{u}_g\right) = 0$$ Equation 14

The following assumptions allow for a simplified modelling procedure:

- The gas density is negligible compared to the liquid density.
- The motion of the gas bubbles relative to the liquid is determined by a balance between viscous drag and pressure forces.
- The two phases share the same pressure field.
- Gas volume fraction is less than 0.1.

Starting and boundary conditions

The starting conditions for the reactor are given in Table 2.

Table 2: Starting conditions used in the model

Transfer process	**Description**
Electron transfer	Cell voltage: 0 V
Heat transfer	Reactor temperature: 88 °C
Mass transfer	Reactive species concentration $C_{0,i}$:2000 mol/m^3
Momentum transfer	Velocity: zero

Boundary conditions used in the model are given in Table 3; representing electron, heat, mass and momentum transfer boundary conditions, respectively.

Table 3: List of parameters and expressions used during the simulation

Boundary	**Condition**
Anode surface	Gas flux specified. Thermal insulation. Specified current density.
Cathode surface	No slip for liquid flow. Gas flux specified. Thermal insulation. Specified current density.
Cooling walls	No slip for liquid. Temperature specified as T_W. Electrical insulation.
Electrolyte level	No electron or heat flow permitted (insulation). Slip condition for liquid flow.
Other boundaries	Thermal and electrical insulation. Liquid no slip condition.

Empirical equations used in the modelling procedure are given in Table 4.

Table 4: Modelling equations

Symbol	**Expression**
C_P	$C_P = C_{P0} + 0.00284 \cdot T$
R_A	$R_A = -\frac{i_A}{F}$
R_C	$R_C = -\frac{2 \cdot i_C}{F}$
i_A	$\mathrm{i}_A = \mathrm{i}_0 \left[exp\left(\frac{\alpha_A F}{R_g T}\eta_{s,A}\right) - exp\left(\frac{\alpha_C F}{R_g T}\eta_{s,A}\right)\right]$
i_C	$\mathrm{i}_C = \mathrm{i}_0 \left[exp\left(-\frac{\alpha_A F}{R_g T}\eta_{s,C}\right) - exp\left(-\frac{\alpha_C F}{R_g T}\eta_{s,C}\right)\right]$
$\eta_{s,A}$	$\eta_{s,A} = \Phi - \Phi_{0,A}$
$\eta_{s,C}$	$\eta_{s,C} = -\Phi - \Phi_{0,C}$
ρ	$\rho = {\rho_0}/{e^{(\beta \cdot (T - 25°C))}}$

A list of constants used during modelling is given in Table 5.

Table 5: Model constants

Symbol	**Value**	**Symbol**	**Value**
C_{P0}	$10.8\ \mathrm{J/(kg \cdot} K)$	ε_r	9
d_B	1 mm	Φ	12 V
D_{HF}	$2.8 \times 10^{-5} \mathrm{m}^2/s$	Φ_{RV}	1.9 V
$D_{HF_2^-}$	$3 \times 10^{-5} \mathrm{m}^2/s$	$\Phi_{0,A}$	2.9 V
k_t	$1.25\ \mathrm{W/(m \cdot} K)$	$\Phi_{0,C}$	0 V
k_A, k_C	$10\ m/s$	μ_l	$0.0113\ \mathrm{Pa \cdot s}$
T_0, T_W	$353.15\ K$	μ_g	$0.001\ \mathrm{Pa \cdot s}$
α_A, α_C	0.5	ρ_0	$2000 \cdot \mathrm{kg}/m^3$
β	$7.11 \times 10^{-4}/°C$	σ	$6.67 \cdot \mathrm{S}/m$

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