

CREVICER 1.1 Modeling and Computational Simulation Guide

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Introduction

In this new release, CREVICER 1.1 was extended from the occluded corrosion mass transport model CREVICER 1.0. in order to model the inhibitor release and transport from the organic coating with hydrotalcite pigment or the anodic protection from the aluminum clad in atmospheric corrosion condition. It is expected that CREVICER 1.1 may assist in evaluating the design parameters of the organic, inorganic, and hybrid organic-inorganic coatings. This release mainly works for the atmospheric corrosion. If users want to run the crevice corrosion modeling, they can either modify the source code of CREVICER 1.1 or directly use the source code of CREVICER 1.0. In the future, a better GUI will be designed to handle different modeling scenarios such as crevice corrosion modeling, anodic protection by aluminum clad, inhibitor release and inhibition from the hybrid organic/inorganic coatings, and etc.

What's new?

New functions in CREVICER 1.1 include Al^{3+} hydrolysis reaction equilibria, pH-dependent inhibitor release, Cl^- gettering by HT coating for the ion exchange mechanism, and inhibitor loading. Another significant improvement is to fix the memory leak, thus long time simulation become possible. Other functions, e.g. CO_2 corrosion, more accurate inhibitor release kinetics models, influence of mass boundary layer in the solution, and etc. will be included in the future release. There are many changes in this release including the GUI and source code, which are summarized below.

1) Nodes and elements Information

Table 1. Finite element and node files for different scratch sizes

Scratch size (μm)	Element file	Node file
50	ELIST50	NLIST50
150	ELIST150	NLIST150
500	ELIST500	NLIST500
1500	ELIST1500	NLIST1500
2500	ELIST2500	NLIST2500
3500	ELIST3500	NLIST3500
5000	ELIST5000	NLIST5000

Scratch size and water layer thickness selections have been added. Once user selects the scratch size, only the corresponding element and node files can be used. The corresponding files are listed in the Table 1.

2) Materials Information

Two materials selections have been added in the GUI. Although user can see all sorts of materials types in the GUI, users can only choose AA2024 and coated AA2024 for the current modeling of inhibitor release from the epoxy with hydrotalcite pigments or anodic protection by Al clad. When user wants to test the Al clad protection, modification on the kinetics of coated AA2024 is also required in order to get the meaningful results.

3) Species Information

In this work, totally 12 chemical species have been considered in the modeling. They are Na^+ , Cl^- , Al^{3+} , $\text{V}_{10}\text{O}_{28}^{6-}$, H^+ , O_2 , OH^- , AlOH_2^+ , $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})_3$, $\text{Al}(\text{OH})_4^-$, Zn^{2+} . These species involve in the following processes:

- Electrochemical reactions

$\text{Al} \rightarrow \text{Al}^{3+} + 3 \text{e}^-$	anodic reaction
$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$	cathodic reaction

- Chemical reactions:

$\text{Al}^{3+} + \text{H}_2\text{O} = \text{Al}(\text{OH})^{2+} + \text{H}^+$	aluminum hydrolysis
$\text{Al}^{3+} + 2\text{H}_2\text{O} = \text{Al}(\text{OH})_2^+ + 2\text{H}^+$	
$\text{Al}^{3+} + 3\text{H}_2\text{O} = \text{Al}(\text{OH})_3 + 3\text{H}^+$	
$\text{Al}^{3+} + 4\text{H}_2\text{O} = \text{Al}(\text{OH})_4^- + 4\text{H}^+$	

- Ion exchange or adsorption/desorption processes

$\text{V}_6\text{O}_{28}^{6-} (\text{HT pigment}) = \text{V}_6\text{O}_{28}^{6-} (\text{solution})$	vanadate inhibitor release
$\text{Zn}^{2+} (\text{HT pigment}) = \text{Zn}^{2+} (\text{solution})$	zinc inhibitor release
$\text{Cl}^- (\text{solution}) = \text{Cl}^- (\text{HT pigment})$	chloride gettering

Na^+ ion was used to maintain the electrical neutrality in the solution.

Currently, only a constant inhibitor release rate and certain inhibitor loading have been added to the model. It is open to add more inhibitor release kinetics and other design parameter of the hybrid organic/inorganic coatings in the future. In this release, the inhibitor release pH dependency has been added into the GUI, however, these parameters have not been linked to the calculation. Therefore, users have to change the vanadate and zinc inhibitor release kinetics manually in following function in the source code:

```
Tmateria.cpp code,
double TAl2024coated::GetChemicalFlux(TSpeciesName name, TChemistry *chemistry,
double E, double T, double P, double area_correct)
```

4) Fix the memory leak problems

This problem was solved by Jean - Louis Mousson(JLM) and Bob Cottis(RAC). They largely solved memory leak problems associated with the failure to delete some of the TBArrElm objects properly. This was achieved by using the TBAE Manager class to manage the elements, with the instance (TBAE) being declared as a global object to ensure that it remains persistent. All changes were indicated by "// (JLM/RAC)".

What you can test?

As shown in the Table 2, the CREVICER 1.1 can be used to study the influence of these parameters on the protection of scratch on the sample. At the same time, a critical inhibitor concentration was assumed by the user to inhibit the corrosion on the scratch. This assumption depends on the knowledge of user and their experimental effort, especially when they deal with new inhibitor encapsulated in the hybrid organic/inorganic coatings and their inhibition. In this work, 0.1 mM vanadate inhibitor was assumed. Obviously this value needs the validation by the experiments.

Table 2. The list of adjustable parameters of inhibitor release modeling

<i>Release models (a)</i>	<i>Scratch size (μm) (b)</i>	<i>NaCl concen. (M) (c)</i>	<i>Water layer thickness (μm) (d)</i>	<i>Corrosion kinetics (e)</i>	<i>Simulation time (s) (f)</i>
Low pH dependence	500	0.01	100		500
Medium pH dependence	1500	0.1	500		
Medium high pH dependence	2500	1.0	5000		
High pH dependence	3500				
	5000				

- (a) User can test other inhibitor release models developed from their experimental release data.
- (b) Currently user can only test these default scratch sizes. If new scratch size is needed to test, they have to generate new mesh for the specific scratch size.
- (c) and (e) User can change the concentration of NaCl and corrosion kinetics based on their experimental resources.
- (d) Users can test not only the listed water layer thickness, but also any other thickness.
- (e) If user wants to simulate for interest corrosion time, manual change of the time step in the chemtest.cpp in the source code is required.

How to run?

The following steps are summarized for a successful simulation using CREVICER 1.1.

- A. Run the GUI by the executable file name ALV2GUILin. Refer to Figure 1.
- B. Change setting. Refer to Figures 2, 3, 4, 5.
- C. Run the simulation. Refer to Figures 6, 7.

D. Analyze the simulation results in these output data files. Refer to Figure 8.
E. Repeat calculation in other conditions and summary.
The above steps are discussed below with the examples.

A. Run GUI

The result is shown in Figure 1:

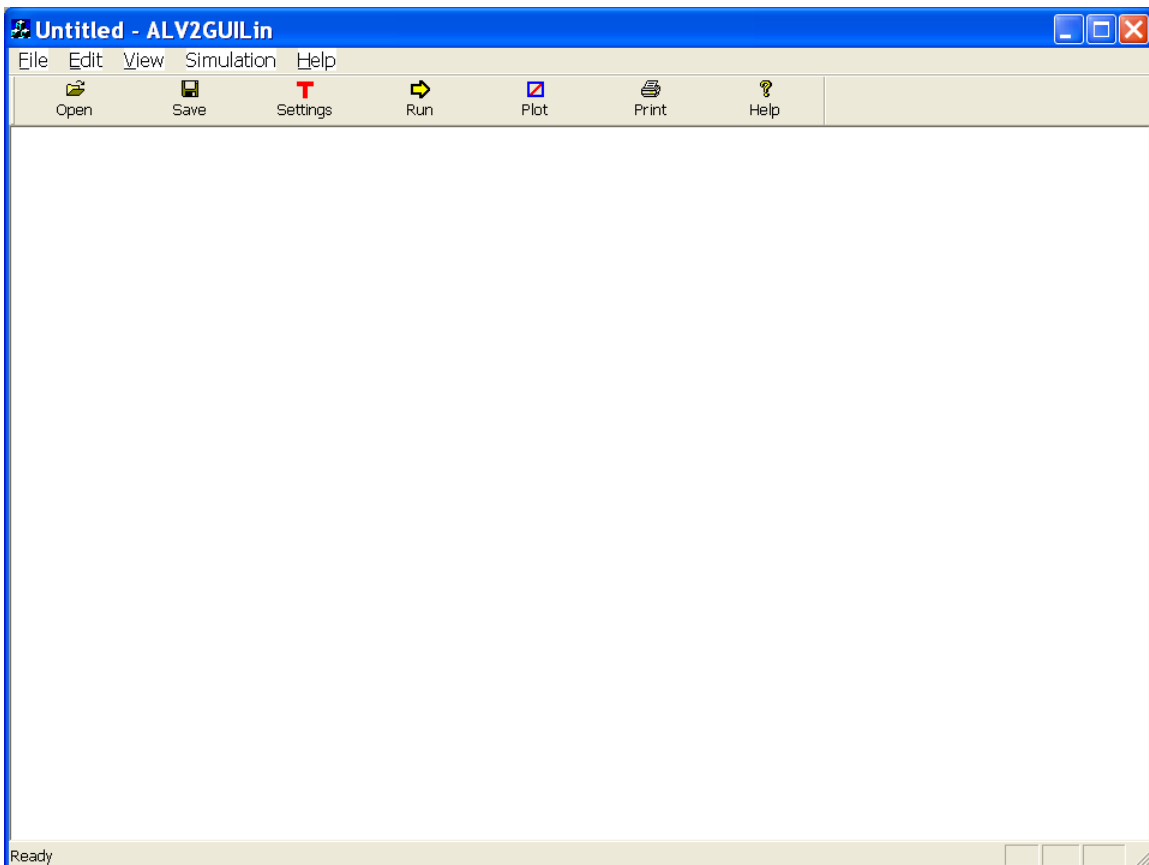


Figure 1 The window of CREVICER GUI

B. Change the setting

B1. Figure 2 shows how to select scratch size, nodes, elements, and water layer thickness.

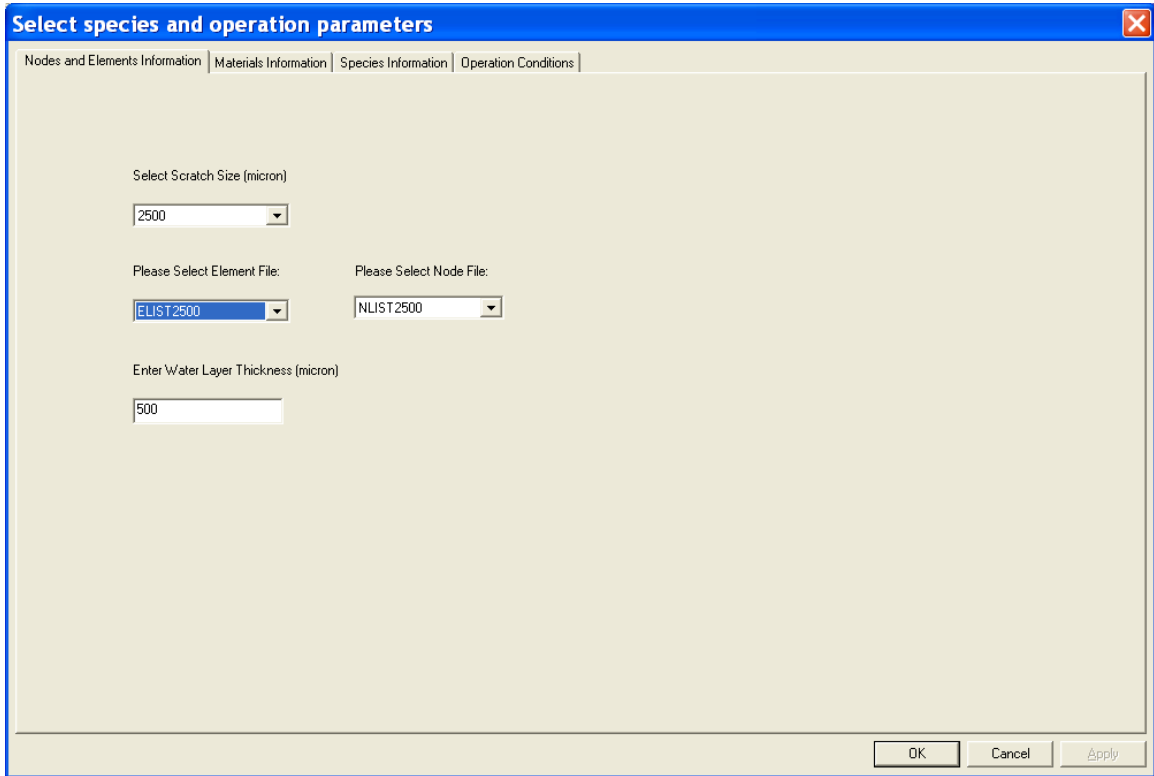


Figure 2 The window of CREVICER setting – scratch size, nodes, elements, and water layer thickness

B2. Figure 3 shows how to select materials. In the modeling of inhibitor release and transport from epoxy with hydrotalcite, only AA2024 and coatedAA2024 materials can be chosen. The chose of other materials will results in meaningless results although user can access other materials types in this moment. An advanced GUI will be built soon to automatically disable other materials if user wants to simulate the Al and coated aluminum corrosion system.

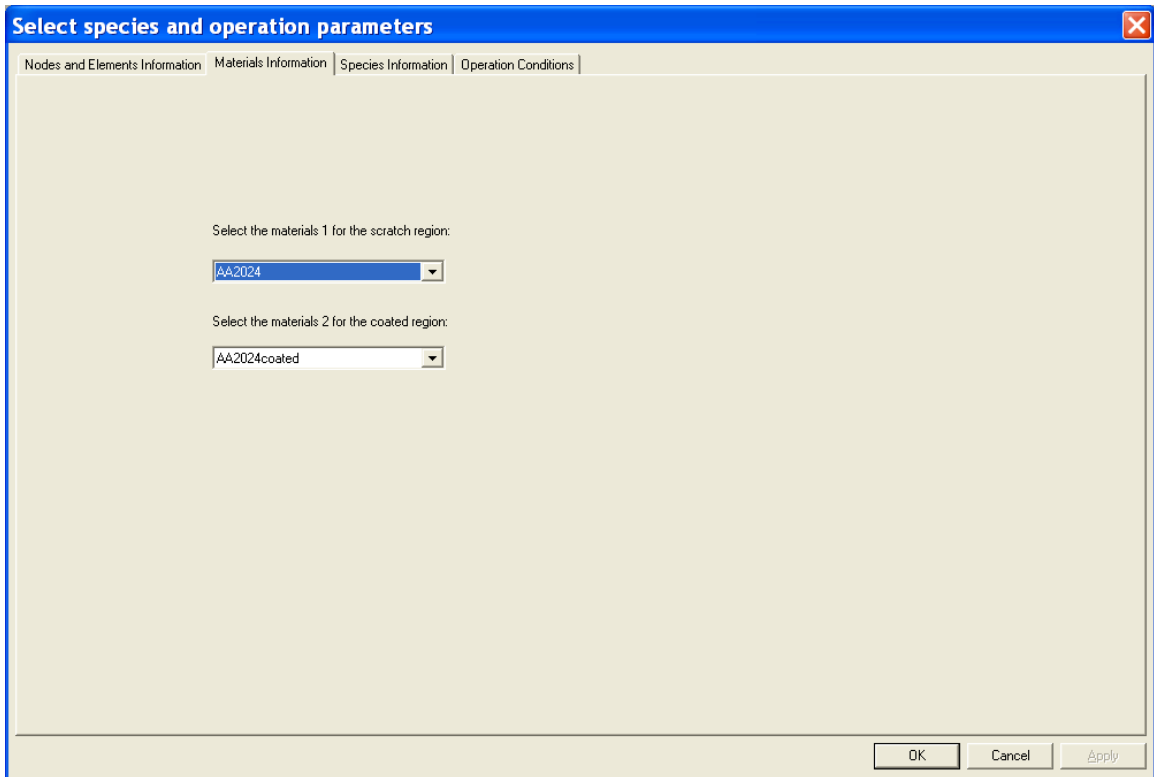


Figure 3 The window of CREVICER setting – select materials

B3. Add species

Select species and operation parameters

Nodes and Elements Information | Materials Information | Species Information | Operation Conditions

Species 1: Species 2: Species 3: Species 4: Species 5: Species 6: Species 7: Species 8: Species 9: Species 10: Species 11: Species 12:

Na+ Cl- Al+++ V10028- H+ O2 OH- AlOH++ AlOHOH- AlOHOH- AlOHOH- Zn++

Initial concentration at the crevice tip or scratch tip:

100 100 0 0 0.0001 0.6 0.0001 0 0 0 0 0

Is the initial concentration fixed or variable parameter?

Variable Variable Variable Variable Variable Fixed Variable Variable Variable Variable Variable Variable

Boundary concentration, e.g. the crevice mouth or coated edge.

100 100 0 0 0.0001 0.6 0.0001 0 0 0 0 0

Is the concentration at the boundary fixed or variable parameters?

Variable Variable Variable Variable Variable Fixed Variable Variable Variable Variable Variable Variable

Inhibitor Release Kinetics:

Vanadate release rate (mol/m²/s) = 2e-007 pH + 7e-011

Zinc release rate (mol/m²/s) = 0 pH + 0

OK Cancel Apply

Figure 4 The window of CREVICER setting – add 12 species

Figure 4 shows how to change the information for each chemical species. In the first line user can choose 12 species. The second line defines the initial concentrations of selected each species on the modeled sample (e.g. crevice, coated AA2024, or bare AA2024) while the third line defines these concentration as variable or fixed parameters. The fourth and fifth lines define the concentration at the crevice mouth or coated edge and define it fixed or variable parameters, respectively. The inhibitor release kinetics has been tentatively added to this page; however, it is actually not linked to the calculation. User has to modify inhibitor release pH dependency in the source code as mentioned early.

B4. Operation conditions

In the first line user can define the initial value for potential, temperature, and pressure in the crevice or coated surface as shown in Figure 5. The second line defines the above three parameters as fixed or varied one. The third line defines the fixed boundary condition for potential, temperature, and pressure at the crevice mouth or coated edge.

Parameter	Initial Value	Fixed or Varied	Boundary Condition
Potential	-0.95	Variable	-0.7
Temperature	298	Fixed	298
Pressure	100000	Fixed	100000

Figure 5 The window of CREVICER setting – operation conditions

Once you finish changing the setting, click OK to close the setting window. You return to the main window. Now you push the button “Run”. The GUI will run the ALLin.exe, which read the file <parameters.txt>, carry out the simulation. So far you have generated the following information in the parameters.txt

```

-----
Scratch:
4
2500          !scratch size
Node and Element:
4
NLIST2500    !File name for nodes,
4
ELIST2500    !File name for elements,
500          !Water layer thickness (um)
Material:
10
AA2024       !Behaving as anode
11
AA2024coated !Behaving as cathode
Operation Conditions:
-0.95        !Electrical potential (volt)
0            !Variable
-0.7         !BCs
298          !Temperature (K)
1            !Fixed
298          !BCs
100000       !Pressure (Pa)
1            !Fixed
100000       !BCs
Add Species:
:Species 1
14
Na+          !Species 1 name
100          !Concentration for species 1, (mol/m3)
0            !Fixed or variable, 0-variable, 1-fixed
100          !BC for species 1
0            !BC is fixed
:Species 2
2
Cl-          !Species 2 name
100          !Concentration for species 2, (mol/m3)
0            !Fixed or variable, 0-variable, 1-fixed
100          !BC for species 2
0            !BC is fixed-1, variable-0
:Species 3
1
Al+++        !Species 3 name
0            !Concentration for species 3, (mol/m3)
0            !Fixed or variable, 0-variable, 1-fixed
0            !BC for species 3
0            !BC is fixed-1, variable-0
:Species 4

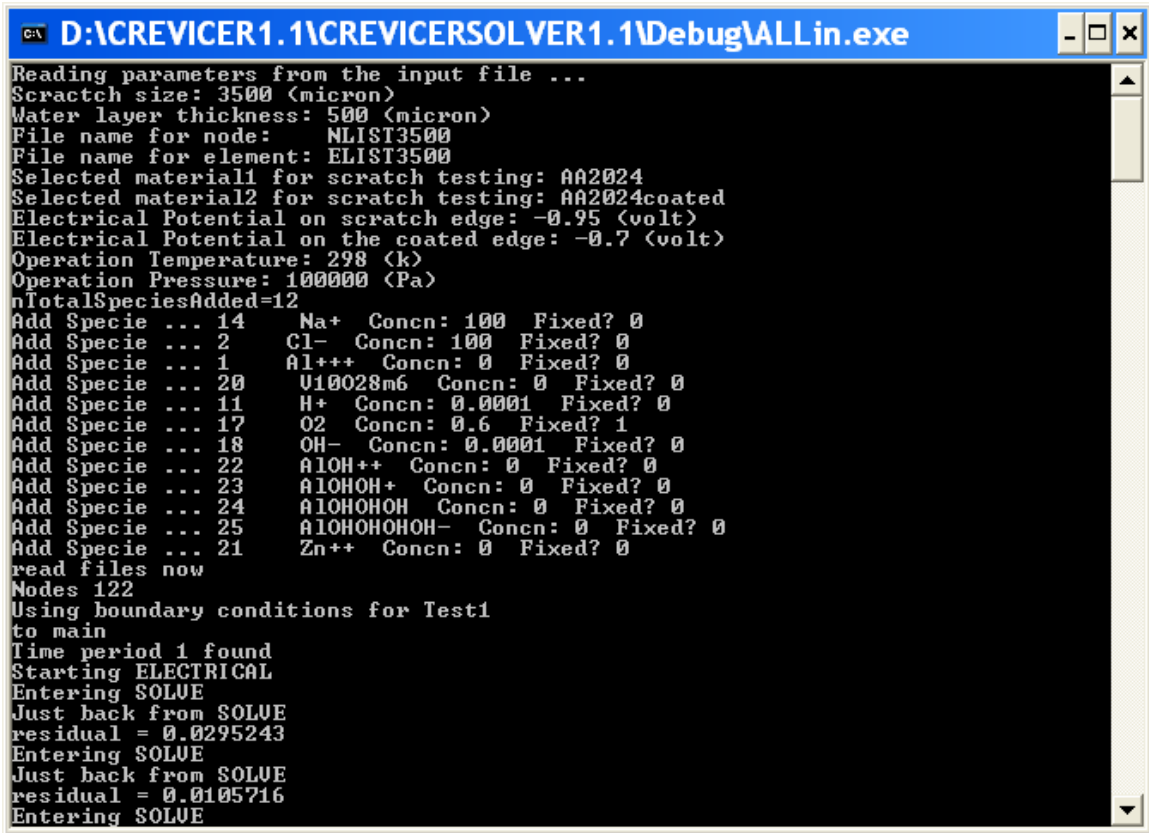
```

20
 V10O28m6 *!Species 4 name*
 0 *!Concentration for species 4, (mol/m3)*
 0 *!Fixed or variable, 0-variable, 1-fixed*
 0 *!BC for species 4*
 0 *!BC is fixed-1, variable-0*
 :Species 5
 11
 H+ *!Species 5 name*
 0.0001 *!Concentration for species 5, (mol/m3) (pH=7)*
 0 *!Fixed or variable, 0-variable, 1-fixed*
 0.0001 *!BC for species 5(pH=7)*
 0 *!BC is fixed-1, variable-0*
 :Species 6
 17
 O2 *!Species 6 name*
 0.6 *!Concentration for species 6, (mol/m3)*
 1 *!Fixed or variable, 0-variable, 1-fixed*
 0.6 *!BC for species 6*
 1 *!BC is fixed-1, variable-0*
 :Species 7
 18
 OH- *!Species 7 name*
 0.0001 *!Concentration for species 7, (mol/m3) (pH=7)*
 0 *!Fixed or variable, 0-variable, 1-fixed*
 0.0001 *!BC for species 7(pH=7)*
 0 *!BC is fixed-1, variable-0*
 :Species 8
 22
 ALOH++ *!Species 8 name*
 0 *!Concentration for species 8, (mol/m3)*
 0 *!Fixed or variable, 0-variable, 1-fixed*
 0 *!BC for species 8*
 0 *!BC is fixed-1, variable-0*
 :Species 9
 23
 ALOHOH+ *!Species 9 name*
 0 *!Concentration for species 9, (mol/m3)*
 0 *!Fixed or variable, 0-variable, 1-fixed*
 0 *!BC for species 9*
 0 *!BC is fixed-1, variable-0*
 :Species 10
 24
 ALOHOHOH *!Species 10 name*
 0 *!Concentration for species 10, (mol/m3)*
 0 *!Fixed or variable, 0-variable, 1-fixed*
 0 *!BC for species 10*
 0 *!BC is fixed-1, variable-0*
 :Species 11
 25
 ALOHOHOHOH- *!Species 11 name*
 0 *!Concentration for species 11, (mol/m3)*
 0 *!Fixed or variable, 0-variable, 1-fixed*
 0 *!BC for species 11*
 0 *!BC is fixed-1, variable-0*
 :Species 12

21
Zn++ !*Species 12 name*
0 !*Concentration for species 4, (mol/m3)*
0 !*Fixed or variable, 0-variable, 1-fixed*
0 !*BC for species 4*
0 !*BC is fixed-1, variable-0*
&
Inhibitor Release Kinetics
For Vanadate
2e-007 !*Release equation parameter A;*
7e-011 !*Release equation parameter A;*
For Zinc
0 !*Release equation parameter A;*
0 !*Release equation parameter A;*
&

C. Run the simulation.

C1. When the ALLin.exe starts, you will see Figure 6.



```
Reading parameters from the input file ...
Scratch size: 3500 (micron)
Water layer thickness: 500 (micron)
File name for node: NLIST3500
File name for element: ELIST3500
Selected material1 for scratch testing: AA2024
Selected material2 for scratch testing: AA2024coated
Electrical Potential on scratch edge: -0.95 (volt)
Electrical Potential on the coated edge: -0.7 (volt)
Operation Temperature: 298 (k)
Operation Pressure: 100000 (Pa)
nTotalSpeciesAdded=12
Add Specie ... 14 Na+ Concn: 100 Fixed? 0
Add Specie ... 2 Cl- Concn: 100 Fixed? 0
Add Specie ... 1 Al+++ Concn: 0 Fixed? 0
Add Specie ... 20 U10028m6 Concn: 0 Fixed? 0
Add Specie ... 11 H+ Concn: 0.0001 Fixed? 0
Add Specie ... 17 O2 Concn: 0.6 Fixed? 1
Add Specie ... 18 OH- Concn: 0.0001 Fixed? 0
Add Specie ... 22 AlOH++ Concn: 0 Fixed? 0
Add Specie ... 23 AlOHOH+ Concn: 0 Fixed? 0
Add Specie ... 24 AlOHOHOH Concn: 0 Fixed? 0
Add Specie ... 25 AlOHOHOHOH- Concn: 0 Fixed? 0
Add Specie ... 21 Zn++ Concn: 0 Fixed? 0
read files now
Nodes 122
Using boundary conditions for Test1
to main
Time period 1 found
Starting ELECTRICAL
Entering SOLVE
Just back from SOLVE
residual = 0.0295243
Entering SOLVE
Just back from SOLVE
residual = 0.0105716
Entering SOLVE
```

Figure 6 The computational process - beginning

C2. When the simulation is over, you will see a small window to indicate “Simulations Completed” as shown in Figure 7.



Figure 7. Finish the simulation

Now click the OK button in the small window. The simulation is over.

D. Analyze the simulation results in these output data files.

In the directory `c:/user/local/CREVICERBASE/`, you can find output files as shown in Figure 8. Detail specifications are provided below.

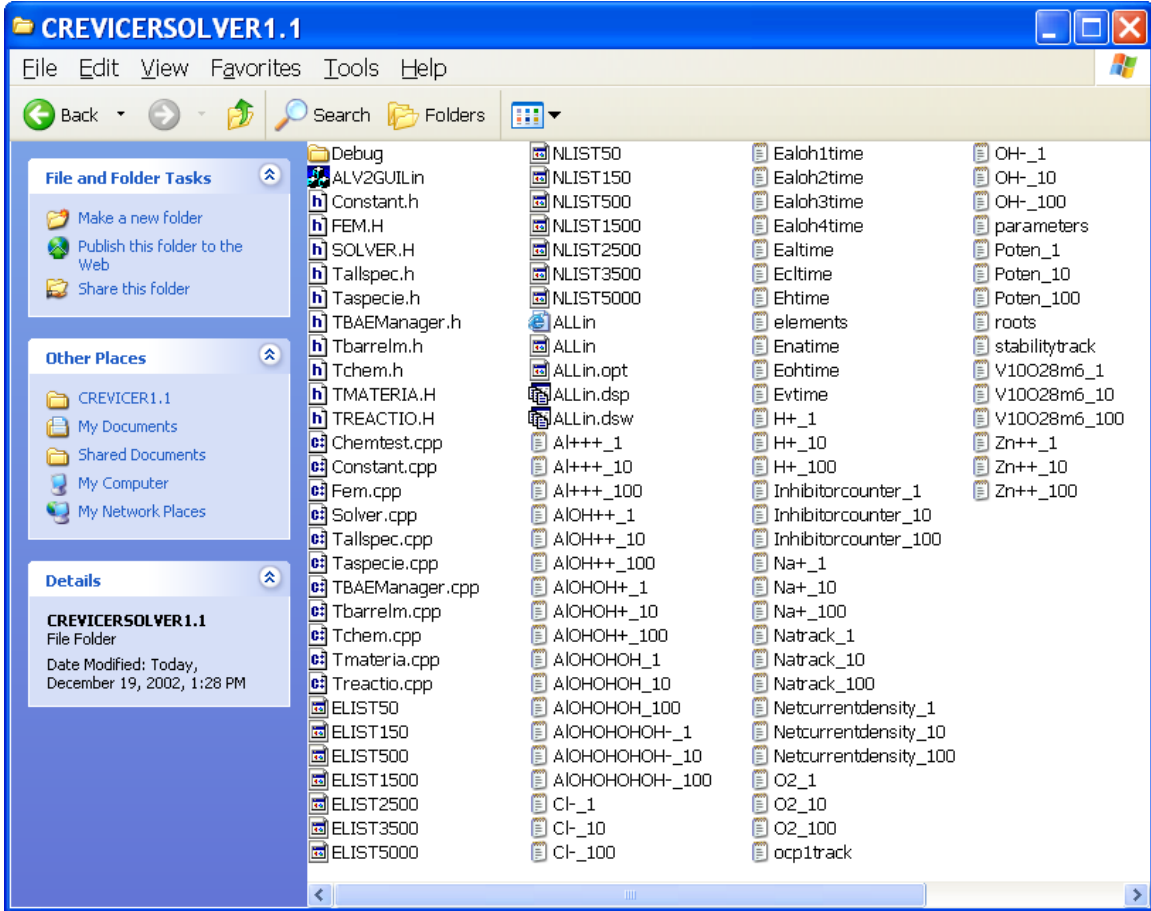


Figure 8 Output data files

`Al+++_1,....` The transient Al^{+++} concentration distribution on the sample surface at 0.1 seconds (assume the time step is 0.1 s). `Al+++_500` refers to the result at 50 seconds and so on. The similar output files are followed for other chemical species, such as, Na^+ , Cl^- , V10O28m6 , H^+ , O_2 , OH^- , AIOH^{++} , AIOHOH^+ , AIOHOHOH , AIOHOHOHOH^- , and Zn^{++} .

`Inhibitorcounter_1...` The transient inhibitor reservoir (mol/m^2) at 0.1 seconds.

In addition, potential and current distribution also uses the same format, such as,
Poten_1..... The transient potential distribution at 0.1 seconds.
Netcurrentdensity_1... The transient net current density and conductivity distribution at
0.1 seconds

Evertime.txt: The vanadate inhibitor concentration changes with time at a chosen location of the sample. The similar output files are for OH⁻, Na⁺, Cl⁻, Al³⁺, and Al³⁺ hydrolysis products as follows, Eohtime.txt, Enatime.txt, Ecltime.txt, Ealtime.txt, Ealoh1time.txt, Ealoh2time.txt, Ealoh3time.txt, Ealoh4time.txt. User need change the specific node number in the chemtest.cpp of the source code, which corresponds to the interested location on the sample surface.

E. Repeat calculation in other conditions and summary

User can repeat the test by changing other parameters as shown in the Table 2. For more information, please refer to the talk by Dr. Wang in ECS 2002 Fall Conference and the publication to be submitted to Journal of Electrochemical Society or the presentations on the coating research area on the CESE website.

December 20, 2002