Postprint: Meso-Structure-Based Numerical Analysis and Experimental Study of Sodium Diffusion in Aluminum Electrolysis Cathode Carbon Blocks

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Abstract

Based on the heterogeneous nature of aluminum electrolysis cathode carbon block structures, they are treated as multiphase composite materials consisting of carbon aggregates and pitch binder, and the sodium diffusion process is investigated from a mesostructural perspective. Programs for random placement models of circular, elliptical, and polygonal aggregates with different particle size distributions and contents were developed using Matlab, generating seven mesostructural model images of cathode carbon blocks, which were imported into ANSYS as iges model files to establish two-dimensional finite element numerical models. Leveraging the analogy between the diffusion equation and the heat conduction equation, ANSYS thermal analysis elements were utilized to simulate and solve the sodium diffusion process, analyzing the effects of carbon aggregate particle size distribution, content, and morphology on sodium diffusion. The results demonstrate that carbon aggregates impose a more significant barrier to sodium diffusion within the carbon block compared to pitch; smaller aggregate particle roundness, finer particle size distribution, and higher content all lead to lower sodium diffusion rates. The circular carbon aggregate model with a particle size distribution of 0.003~0.006 m and a content of 80% exhibits the lowest sodium diffusion velocity. The simulation results show good agreement with experimental data, validating the accuracy and reliability of the simulation.

Full Text

Numerical Analysis and Experimental Research of Sodium Diffusion Process Based on Microstructure of Electrolytic Cathode Carbon Block

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Abstract

Based on the heterogeneous characteristics of aluminum electrolytic cathode carbon block structure, this study investigates the sodium diffusion process from a mesoscopic perspective by treating the carbon block as a multi-phase composite material composed of carbon aggregate and asphalt binder. A Matlab program was developed to generate random placement models of circular, elliptical, and polygonal aggregates with different particle size distributions and contents, yielding seven mesoscopic structural model images of cathode carbon blocks. These models were imported into ANSYS as igs files to establish two-dimensional finite element numerical models. Leveraging the similarity between the diffusion equation and heat conduction equation, ANSYS thermal analysis elements were employed to simulate the sodium diffusion process and analyze the influence of carbon aggregate size distribution, content, and morphology on sodium diffusion. The results demonstrate that carbon aggregate exhibits a greater hindrance effect on sodium diffusion compared to asphalt binder in carbon blocks. Sodium diffusion rate decreases with decreasing aggregate particle roundness, smaller aggregate size distribution, and higher aggregate content. The lowest sodium diffusion velocity occurs in the circular aggregate model with a size distribution of 0.003~0.006 m and content of 80%. The simulation results show good agreement with experimental data, proving the accuracy and reliability of the simulation.

KEY WORDS inorganic non-metallic materials, sodium diffusion, finite element simulation, cathode carbon block, aggregate

Modern aluminum electrolysis cells are the core equipment for industrial aluminum production. Although cathode carbon materials are theoretically not consumed during aluminum electrolysis, they suffer severe damage and even cracking under high-temperature and highly corrosive electrolyte conditions, particularly due to combined stress loading and chemical corrosion. Extending the service life of cathode carbon blocks represents a critical challenge. In aluminum reduction cells, cathode carbon blocks undergo chemical penetration corrosion by high-temperature molten salt electrolyte, especially metallic sodium. After cell operation, metallic sodium and high-temperature molten salt diffuse and penetrate into carbon blocks through defects and pores. Sodium enters the carbon crystal lattice to form intercalation compounds NaxC with larger volume, increasing the interlayer spacing of carbon crystals, altering the microstructure, reducing cohesion and internal friction angle, decreasing the effective peak strength and elastic modulus, and causing continuous deterioration of mechanical properties that leads to swelling and cracking of carbon block structures. Sodium and electrolyte infiltration also increase cathode voltage drop, with sodium penetration corrosion being particularly destructive. Consequently, sodium diffusion performance serves as a primary indicator for evaluating cathode carbon block performance.

Previous studies by Wu et al. simulated sodium diffusion in cathode carbon blocks using homogenization theory, abstracting the carbon block as a homogeneous model. However, mesoscopic-scale simulation of sodium diffusion has not been reported. In reality, cathode carbon blocks are heterogeneous particulate composites composed of carbon aggregate and asphalt binder. Research indicates that the random spatial distribution of constituent phases and their interactions result in extremely complex physicochemical properties. Current simulation studies on sodium diffusion in cathode carbon blocks contain non-negligible errors. This work establishes a mesoscopic two-dimensional random aggregate model based on the actual structure of cathode carbon blocks and uses ANSYS finite element analysis software to simulate sodium diffusion in heterogeneous carbon blocks, investigating the effects of aggregate size distribution, content, and morphology on the diffusion process.

1.1 Mathematical Model

Sodium transport into cathode carbon blocks involves diffusion, permeation, convection, capillary action, and electromigration, as well as their combined effects. The primary mechanism of sodium erosion is diffusion, which is generally described by Fick's second law. Assuming the cathode carbon block is in contact with a sodium environment with no initial sodium inside the block and uniform, isotropic diffusion coefficient, the two-dimensional sodium diffusion model can be expressed. By substituting initial and boundary conditions into the equation and solving this partial differential equation, the sodium concentration at any time and location can be obtained.

Due to mathematical similarities between the unsteady-state mass diffusion

equation and the transient heat conduction equation, this study employs the solution method for transient heat conduction to solve the unsteady-state sodium diffusion problem, utilizing thermal analysis elements in finite element software for numerical simulation. Table 1 provides a dimensional comparison between physical quantities in the heat conduction equation and those in the sodium diffusion model equation.

1.2 Mesoscopic Random Aggregate Model

A Matlab program was developed to generate random placement models of circular, elliptical, and polygonal aggregates with different size distributions and contents, producing seven aggregate model images. Using Illustrator software, these images were traced and converted into vector graphics, then imported into ANSYS as igs model files.

1.2.1 Random Placement Assumptions for Aggregates Aggregates were assumed to be placed within a circular region of 0.05 m diameter, following a uniform distribution pattern, with no overlapping, intersecting, or containing relationships between aggregate particles.

1.2.2 Aggregate Placement Algorithm Referencing literature [9], an aggregate shape generation algorithm was developed with model parameters listed in Table 2. The placement region morphology and size were determined based on the diameter of cylindrical cathode carbon block specimens, establishing an aggregate placement region diameter of 0.05 m. Carbon block aggregate particle sizes were composed of aggregates with different value ranges of r (0.003~0.006 m). The area percentage of aggregates in the placement region was determined based on the volume percentage of different types of cathode carbon block aggregate content ratios.

Seven geometric models of aggregates with different size distributions, contents, and morphologies were obtained, as shown in Figure 1.

[Figure 1: see original paper]

1.3 Model Establishment

This study employs a two-dimensional finite element model of a cylindrical carbon block circular cross-section with a diameter of 0.05 m for numerical simulation, as shown in Figure 2. Material parameters used in the finite element numerical simulation are listed in Table 3. The simulation assumes an initial boundary concentration of 3% at surrounding nodes and zero concentration at all interior nodes for transient calculation.

[Figure 2: see original paper]

2 Numerical Simulation

Sodium diffusion and swelling in cathode carbon blocks is an extremely complex multiphase physicochemical process. Sodium and other electrolytes from molten salt continuously diffuse into the carbon block interior, penetrating the carbon crystal lattice to form compounds with larger volume, causing carbon block swelling and cracking. The sodium swelling process in cathode carbon blocks is controlled by sodium diffusion in the carbon block. Since aggregates have lower diffusion coefficients than asphalt binder, aggregate properties significantly influence sodium diffusion velocity in carbon blocks. Using ANSYS, mass percentage concentration versus time curves (c-t curves) for sodium in different types of carbon blocks were obtained.

2.1 Effect of Aggregate Morphology on Sodium Diffusion Under conditions of aggregate particle size 0.003~0.009 m and content 70%, the sodium concentration distributions at 1800 s for different morphology models are shown in Figure 3. The results differ significantly from literature [10] simulations based on homogeneous cathode carbon block structure. Diffusion paths become complex, exhibiting heterogeneous and anisotropic characteristics, with obvious bypass diffusion phenomena on aggregate surfaces, causing sodium concentration contours to become distorted rather than smooth curves. This demonstrates that the mesoscopic network model can reflect differences in sodium diffusion performance among different constituent materials in cathode carbon blocks and more realistically simulate sodium diffusion.

Assuming the actual cross-sectional area of an aggregate particle in a two-dimensional plane is Sa and the area of its tightly circumscribed circle is Sb, the ratio Sa/Sb is defined as the roundness of the aggregate particle, as illustrated in Figure 4. The roundness value ranges between 0 and 1, with larger values indicating shapes closer to circular and smaller values indicating shapes closer to elliptical or flaky.

Analysis of Figure 5 reveals that sodium diffusion capacity differs among circular, elliptical, and polygonal aggregate models within the same diffusion time. Sodium diffusion rate is highest in the circular aggregate model and lowest in the elliptical aggregate model, indicating that aggregate morphology (roundness) affects sodium diffusion rate—smaller roundness leads to lower diffusion capacity.

Compared with homogeneous models, aggregates with lower sodium diffusion coefficients than asphalt binder increase diffusion path length and tortuosity, reducing the effective diffusion coefficient of sodium in carbon blocks. Both path length and tortuosity vary with geometric parameters, thereby altering diffusion rates. With identical size distribution and content, aggregates with smaller roundness have larger surface areas and longer boundaries in cross-section, creating longer diffusion paths and lower diffusion rates.

2.2 Effect of Aggregate Size Distribution on Sodium Diffusion Under identical morphology and content conditions, sodium concentration distributions at 1800 s for aggregate models with diameter size distributions of 0.003~0.006 m, 0.003~0.009 m, and 0.003~0.015 m are shown in Figure 6. Aggregate size distribution in carbon blocks determines particle size distribution, which can be described by the Fuller aggregate gradation curve [13].

As shown in Figure 7, sodium diffusion velocity is highest in the 0.003~0.015 m aggregate model and lowest in the 0.003~0.006 m model, indicating minimal diffusion resistance in the former. With identical morphology and content, when aggregates tend toward medium-large size distribution, the total number of aggregate particles decreases, sodium diffusion path length shortens, pore tortuosity reduces, diffusion resistance decreases, and diffusion coefficient increases, thereby enhancing sodium diffusion velocity. Conversely, more small-sized aggregate particles in carbon blocks result in higher sodium diffusion velocity.

[Figure 6: see original paper]
[Figure 7: see original paper]

2.3 Effect of Aggregate Content on Sodium Diffusion Under identical morphology and size distribution conditions, sodium concentration distributions at 1800 s for aggregate models with contents of 60%, 70%, and 80% are shown in Figure 8.

Figure 9 demonstrates that sodium diffusion rate is lowest in carbon blocks with 80% aggregate content. This occurs because carbon aggregates have higher graphitization degrees and smaller sodium diffusion coefficients than asphalt, creating greater hindrance to sodium diffusion. Higher aggregate percentages in carbon blocks result in lower effective diffusion coefficients and reduced diffusion rates. During the initial 3600 s of diffusion, each 10% increase in aggregate content reduces the average sodium diffusion velocity.

[Figure 8: see original paper]
[Figure 9: see original paper]

3.1 Experimental Validation

To verify the rationality of the finite element numerical simulation and parameters regarding the effect of cathode carbon block mesoscopic structure on electrolyte penetration, experiments employed cathode carbon blocks with circular aggregate roundness of 0.95, particle size range of 0.003~0.006 m, and asphalt content of 20%. The experimental setup for testing radial penetration in aluminum electrolysis is shown in Figure 10. The aluminum electrolysis cell was placed in a vertical tube furnace at 965°C with argon protection. The electrolyte height was 0.05 m with composition of 80% Na AlF , 10% Al O , and 10% NaF (molecular ratio 2.29). Cathode specimens were vertically placed on boron nitride 垫片 surfaces with a cathode current density of 0.65 A · cm ^{2} and electrolysis times of 1800 s and 3600 s. After electrolysis, specimens were lifted

to the upper furnace section and cooled to room temperature with the furnace before removal.

Specimens were scanned using a nanoVoxel-2000 micro-CT device. Samples were then taken at 0.002 m intervals along the radial direction, and sodium penetration in carbon cathodes was quantitatively analyzed using chemical neutralization titration [14] to obtain sodium concentration distributions along the radial direction at different electrolysis times. The initial sodium concentration at the specimen surface was 3%.

[Figure 10: see original paper]

3.2 Results and Discussion

CT images of specimen cross-sections after aluminum electrolysis are shown in Figure 11, where bright white substances represent metallic sodium and electrolyte melt that penetrated into the cathode carbon block interior. The color gradually lightens with increasing penetration depth, indicating decreasing concentrations of metallic sodium and electrolyte melt from outside to inside [15]. This concentration distribution profile matches the numerical simulation results of sodium concentration distribution in carbon blocks after 1800 s and 3600 s of aluminum electrolysis (Figure 12), demonstrating that this finite element numerical method can describe sodium diffusion in aluminum electrolysis cathode carbon blocks.

[Figure 11: see original paper]
[Figure 12: see original paper]

Figure 13 compares numerical simulation and experimental results of radial sodium concentration versus electrolysis time for circular aggregate cathode carbon blocks. Although some point deviations exist at certain radial distances (due to differences between circular aggregate geometric models and actual cathode carbon block aggregate shapes), the numerical simulation curves generally match the experimental curves well, verifying the accuracy and reliability of the mesoscopic structure-based sodium diffusion numerical method.

[Figure 13: see original paper]

4 Conclusions

(1) From a mesoscopic perspective, the two-dimensional random aggregate model treating cathode carbon blocks as two-phase heterogeneous composites of aggregate and asphalt matrix can realistically reflect the internal structure of cathode carbon blocks.

(2) Compared with asphalt in carbon blocks, carbon aggregate provides greater hindrance to sodium diffusion. Sodium diffusion rate decreases with decreasing aggregate particle roundness, smaller aggregate size distribution, and higher aggregate content. The lowest sodium diffusion

velocity occurs in the circular aggregate model with size distribution of 0.003~0.006 m and content of 80%.

(3) The sodium concentration diffusion curves obtained from numerical calculation and experiments show good agreement, proving the accuracy and reliability of the mesoscopic structure-based numerical simulation of sodium diffusion in aluminum electrolysis cathode carbon blocks.

References

[1] Wang Y, Tie J, Sun S, et al. Simulation method based on equivalent circuit to investigate the circuit characteristics in aluminum reduction cell [J]. Trans. Indian Inst. Met., 2015, 68(3): 443
[2] Tschöpe K, Schøning C, Rutlin J, et al. Chemical degradation of cathode linings in Hall-Héroult cells - an autopsy study of three spent pot linings[J]. Metall. Mater. Trans., 2012, 43B: 290
[3] Vasshaug K, Foosnæs T, Haarberg G M, et al. Formation and dissolution of aluminium carbide in cathode blocks[A]. Light Metals 2009[M]. The Minerals, Metals & Materials Society (TMS), 2009:
[4] Allard F, Soucy G, Rivoaland L. Formation of deposits on the cathode surface of aluminum electrolysis cells[J]. Metall. Mater. Trans., 2014, 45B: 2475
[5] Lossius L P, Øye H A. Melt penetration and chemical reactions in 16 industrial aluminum carbon cathodes[J]. Metall. Mater. Trans., 2000, 31B: 1213
[6] Kunihiro, Hideki etc. First-principles study of alkali metal-graphite intercalation compounds[J]. Journal of Power Sources, 2013, 243:
[7] Brissona P Y, Darmstadtb H, Fafardc M, et al. X-ray photoelectron spectroscopy study of sodium reactions in carbon cathode blocks of aluminium oxide reduction cells[J]. Carbon, 2006, 44(8): 1438
[8] Lorentz Petter Lossius, Harald A. Øye. Melt penetration and chemical reactions in 16 industrial aluminum carbon cathodes[J]. Metallurgical and Materials Transactions B, 2000, 31(6): 1213
[9] Zhou X G, Li K F. Simulation analysis of chloride penetration in concrete with finite volume method[J]. Engineering mechanics, 2013, 7: 34
[10] Zolochevsky A, Hop J G, Foosnaes T, Øye H A. Rapoport-Samoilenko test for cathode materials- II swelling with external pressure and effect of creep[J]. Carbon2005, 43: 1222
[11] Wang L C, Bao J W. Meso scale model of moisture transfer in cracking concrete[J]. Journal of Building Materials, 2014, 17(6):
[12] Xiao J Z, Lu D, Ma Z M. Mesoscopic numerical simulation on chloride diffusion in concrete considering random distribution of recycled coarse aggregate[J]. Journal of Southeast University, 2014, 44(6)
[13] Xiao J Z, Lu D, Ma Z M. Meso scale numerical simulation of chloride diffusion in concrete with random distributed recycled coarse aggregate[J]. J. Southeast Univ. (Nat. Sci. Ed.), 2014, 44:
[14] Sørlie M, Øye H A. Cathodes in aluminium electrolysis, 2nd. Dusseldorf: Aluminium-Verlag, 1994.

[15] Chauke1 L, Garbers- Craig A M. Reactivity between carbon cathode materials and electrolyte based on industrial and laboratory data [J]. Carbon, 2013, 58: 40

Note: Figure translations are in progress. See original paper for figures.