Electrochemical derusting in molten Na$_2$CO$_3$-K$_2$CO$_3$

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Abstract: The formation of a rust layer on the surface of iron and steels accelerates their degradation and eventually causes the failure of materials. In addition to fabricating a protective layer or using a sacrificial anode, repairing or removing the rust layer is another way to reduce the corrosion rate and extend the lifespan of iron and steels. Herein, an electrochemical deoxidation approach is employed to repair the rust layer in molten Na$_2$CO$_3$-K$_2$CO$_3$. The rust consists of oxides which can be electrochemically reduced to metals/alloys, releasing oxide ions into the molten salt. The electrochemical method uses electrons to convert oxide to metal rather than remove the entire rust layer away. Due to the fluidity of the molten salt electrolyte, the electrochemical derusting approach is not constrained by the shape of the objects. The rusty layer of iron rods and screws was electrochemically converted to iron by molten salt electrolysis. Thus, the high-temperature molten salt electrolysis may be an effective way to metalize iron rust and be used for repairing cultural relics and healing the rust layers on other metals.

Keywords: molten salt, electro-deoxidation, rust, stainless steel, derusting

1. Introduction
Iron and steel are the most widely used in our modern society [1]. Ideally, the formation of a dense oxide scale at the surface of metals is to gain the corrosion resistance. However, a rust layer often appears at the surface of iron and steels when they react with oxygen in natural or extremely corrosive environments, causing the degradation of iron and steels [2]. The general way to alleviate corrosion is to fabricate a protective layer, connect with a sacrificial anode, or engineer the surface, etc [3]. Although these approaches can slow down the rate of corrosion, the corrosion is still inevitable. Apart from corrosion protections, corrosion remediation could be an alternative way to mitigate the corrosion issues, thereby rehabilitating iron and steels. The derusting methods can be divided into two categories: Chemical and physical approaches [4-7]. The chemical way is to remove rust by dissolving the iron rust in acid solutions. This is a facile and low-cost approach, but will generate secondary wastes and cause the hydrogen embrittlement of iron and steels. The physical method is to remove the rust by external physical forces such as polishing, flame cleaning, grit blasting, sand blasting, ultrasonic cleaning, abrasive water jet, laser cleaning, etc. The physical methods are easy to deploy, but they are constrained by the thickness of the rust layer and the inevitable damage of the bulk metals.

Conventionally, the rust layer is usually removed by polishing or dissolving in acid solutions. However, the corrosion rate is different at different parts of the metal substrate, resulting in a rough metal surface underneath the rust layer. Moreover, the pitting corrosion could lead to a small hole in some local areas. In this case, the rust cannot be uniformly removed by a mechanical polishing or a deep hole will appear after the rust is dissolved by chemical etching. Rather than removing the rust away from the substrate, direct converting the rust to metals will be another way to rehabilitate the corrosion layer. In general, the rust mainly consists of oxides and hydroxides which can be reduced to metals by hydrogen, carbon, and reactive metals. However, hydrogen can
dissolve in steel and incur the hydrogen embrittlement, and carbothermic reduction needs a high
temperature and a sufficient contact between the rust and carbon. Moreover, the carbon or reactive
metals could change the composition of the metal substrate and thereby alter the physical
properties of the substrate. Electrochemical deoxidation employs electrons to reduce oxides under
a controlled potential, which has been used for extracting metals/alloys from the oxides and
sulfides [8-17]. In an electrochemical cell, the solid oxides in the form of a porous pellet act as the
cathode which is reduced to metals/alloys, releasing oxide ions into the electrolyte where the
released oxide ions transfer to the anode and are then oxidized to oxygen at an inert anode [18-
20]. Since the reduction of the solid oxide obeys the three-phase interline model [21-23], the
surface reduction is quite fast and the rate-determining step is the diffusion of oxide ions outwards
from the oxide core to the pre-metalized shell. Moreover, the electrochemical reduction is not
restricted by the shape of the cathode because the reduction happens where the liquid electrolyte
can reach. Therefore, the electrochemical process could be an effective method to convert the rust
layer back to metals/alloys, repairing the rust rather than damaging it.

Unlike the chemical and physical methods, the electrochemical method is to convert rust to
metals rather than remove away the rust layer. In other words, the electro-derusting method is a
conversion method. Taking advantage of the rapid reduction rate of thin oxide layer in molten salts
[24, 25], the electrochemical method was employed for converting the thin rust scale to metal, i.e.
the electrochemical metalization of the rust. The use of electrons does not introduce any
contaminations, and the electrolyte is flowable that the deoxidation is not limited by the shape of
the object. For example, the threaded-shape-like object can be easily healed. Moreover, oxygen
ions could be pulled out from the tiny pitting hole because the diffusion of oxide ions could be
enabled under cathodic polarization. In this paper, the electrochemical conversion of rust on the
surface of iron/steel was conducted in molten Na$_2$CO$_3$-K$_2$CO$_3$ using a cost-effective Ni-based inert anode, and the electrochemical reduction behaviors of rust were investigated by cyclic voltammetry (CV).

2. Experimental

2.1 Cyclic voltammetry

The electrochemical cell was contained in an alumina crucible (ID: 9.4 cm, Height: 12.3 cm, Shanghai Shuocun Co., Ltd.) which was housed in a one-end-closed stainless steel (SS) test vessel (ID: 12 cm, Height: 60 cm), and the test vessel was heated by a vertical tube furnace. The granule-like Na$_2$CO$_3$ and K$_2$CO$_3$ were mechanically mixed in a plastic bottle (Na$_2$CO$_3$ : K$_2$CO$_3$ = 59 : 41, molar ratio, AR grade, Kermel Co., Ltd.). Then, the mixture was transferred into the Al$_2$O$_3$ crucible and vacuum-dried at 300°C for 12 h. After that, the Al$_2$O$_3$ crucible was put into the SS test vessel while ramping the temperature and flowing Ar gas to maintain the inert atmosphere for all following electrochemical measurements. After the salt was melt, pre-electrolysis was conducted between a nickel sheet (2 × 2 cm) cathode and a Ni10Cu11Fe anode under a constant cell voltage of 1.8 V for 4 h. The cyclic voltammetry was performed with the three-electrode setup to investigate the electrochemical reduction behaviors of the iron rust. The working electrode was the rusty iron wire (ID: 0.5 mm), the counter electrode was the home-made Ni10Cu11Fe alloy (ID: 2 cm) [26-28], and the pseudo-reference electrode was a Ag wire (ID: 0.5 mm, > 99.99%). The CV measurements were controlled by an electrochemical workstation (CHI 1140, Shanghai Chenhua, Co., Ltd.).

2.2 Electrochemical derusting
The drying and pretreatment of the molten salt was the same as the above-mentioned process. The electrochemical derusting of the rust layer on the surface of an iron rod was performed in a two-electrode cell with the same Na$_2$CO$_3$-K$_2$CO$_3$ melt that was used for CV measurement. The electrochemical derusting process was conducted in a two-electrode electrolytic cell with the molten Na$_2$CO$_3$-K$_2$CO$_3$ electrolyte (Fig. 1). The rusty iron served as the cathode, and a Ni10Cu11Fe alloy served as an inert anode [26, 29, 30]. Constant cell voltages between the cathode and anode were supplied by a battery testing system (Shenzhen Neware Co., Ltd., the maximum supply current and voltage are 6 A and 5 V). Under a constant potential, the rust was electrochemically reduced to iron, releasing oxide ions into the electrolyte, subsequently the oxide ions diffuse towards the anode where the oxide ions were electrochemically oxidized to oxygen gas. As the Ni10Cu11Fe has been confirmed as a stable oxygen-evolution inert anode, the rust could be electrochemically converted to metal and oxygen, i.e., the rust is electrochemically converted to iron and oxygen in the molten salt.

![Fig. 1. Schematic of the electrochemical metalization of iron rust in molten Na$_2$CO$_3$-K$_2$CO$_3$.](image)

Fig. 1. Schematic of the electrochemical metalization of iron rust in molten Na$_2$CO$_3$-K$_2$CO$_3$. 
2.3 Characterization

All samples before and after electrolysis were characterized by scanning electron microscopy (SEM, FEI Sirion field emission), Energy Dispersive X-Ray Spectroscopy (EDS), and X-ray diffraction (XRD, Shimadzu X-ray 6000 with Cu Kα radiation at λ=1.5405 Å).

3. Results and discussion

To investigate the electrochemical reduction process, a fresh and a rusty iron wire were respectively used as the working electrode to conduct the cyclic voltammetry (CV) measurements. As shown in Fig. 2a, the deposition and stripping of Na was observed from the fresh-iron-wire working electrode. On the rusty iron wire working electrode, two more reduction peaks appear prior to the deposition of Na owing to the reduction of the iron rust. The reduction behaviors are similar to the electrochemical reduction of iron oxide in molten Na₂CO₃-K₂CO₃ [31], indicating that the rust formed on the iron mainly consists of iron oxide. Note that the rust could contain some hydroxides or oxyhydroxide which can be converted to oxide in the high-temperature conditions. The reduction behaviors of iron oxide in molten Na₂CO₃-K₂CO₃ have been studied by Wang et al [28, 31]. As shown in Fig. 2a, the redox peaks of c1’/a1’ are due to the deposition and stripping of Na, and the redox peaks of c1/a1, c2/a2 and c3/a3 are correlated to the reduction of Fe₂O₃. The reduction peak of c1 is the formation of NaFe₂O₃, c2/a2 refers to the reduction process from NaFe₂O₃ to NaFeO₂ and Fe, and the reduction peak c3 corresponds to the conversion of NaFeO₂ to Fe. On the reverse scan, the oxidation peaks could be due to the oxidation of Fe, NaFeO₂, and NaFe₂O₃. As shown in Fig. 2b, the reduction peaks remarkably decrease in the second scan because
most of the iron rust has been reduced at the first scan. In the third scan, no oxidation peak is observed due to the lack of oxide ion in the vicinity of the working electrode, indicating that the oxide ions released from the working electrode have entered into the electrolyte and oxidized at the counter electrode.

![Cyclic voltammograms of (a) a fresh iron wire (black line) and a rusty iron wire (red line) working electrodes, and (b) a rusty iron working electrode with multiple scans in molten Na$_2$CO$_3$-K$_2$CO$_3$ at 750°C, the scan rate is 100 mV/s.]

As shown in Fig. 3a, the iron rust is mainly comprised of Fe$_2$O$_3$. In addition to oxides, some undetected hydroxides or oxyhydroxide could exist in the form of the amorphous state. In molten Na$_2$CO$_3$-K$_2$CO$_3$, NiO [32] and Co$_3$O$_4$ [30] have been successfully reduced to Co and Ni, meaning that the electrochemical derusting method could be applied to various metal oxides. For the reactive metals, the molten salts of a much wider electrochemical window could be applied, i.e., the alkaline and alkaline-earth based hydroxide [33, 34], chlorides [35] and fluorides [36]. Moreover, engineering the component of molten salts and controlling the applied potentials could tailor the morphologies and carburization of the metal substrate [20].
Fig. 3. (a) XRD patterns of the rusty iron rod before and after electrolysis, (b) Current profile of the electrochemical derusting under a constant cell voltage of 2.3 V in molten Na$_2$CO$_3$-K$_2$CO$_3$ at 750°C.

Before electrolysis, the iron rust is yellowish. After electrolysis, the yellowish samples become grey with a metallic luster (Fig. 4). It is found that the yellowish rod turns grey within 5 min, indicating the reduction rate is quite fast. As shown in Fig. 4, the content of Fe reaches over 94% after 5 min of electrolysis. The content of Na is below 1% for all samples. Note that it is difficult to quantitatively measure the contents of C and O using EDS. From the current plot, the reduction current decreases to a plateau in 5 min (Fig. 3b).
Fig. 4. Digital photos and EDS analysis of (a) the rusty iron rods and the samples after being electrolyzed under a constant cell voltage of 2.3 V for (b) 5, (c) 15, (d) 30, (e) 45, and (f) 60 min.

Table 1. EDS analysis of the rusty iron rods and the samples after being electrolyzed under a constant cell voltage of 2.3 V for 5, 15, 30, 45, and 60 min

<table>
<thead>
<tr>
<th></th>
<th>C at.%</th>
<th>Na at.%</th>
<th>O at.%</th>
<th>Fe at.%</th>
<th>O%/Fe%</th>
</tr>
</thead>
<tbody>
<tr>
<td>rusty iron</td>
<td>--</td>
<td>--</td>
<td>65.5</td>
<td>34.5</td>
<td>190</td>
</tr>
<tr>
<td>2.3V – 5min</td>
<td>0.5</td>
<td>0.7</td>
<td>4.5</td>
<td>94.3</td>
<td>4.7</td>
</tr>
<tr>
<td>2.3V – 15min</td>
<td>0.8</td>
<td>0.6</td>
<td>3.6</td>
<td>95.0</td>
<td>3.7</td>
</tr>
<tr>
<td>Time (min)</td>
<td>Fe</td>
<td>Fe</td>
<td>Mn</td>
<td>P</td>
<td>Cu</td>
</tr>
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<td>-----------</td>
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</tr>
<tr>
<td>30</td>
<td>0.8</td>
<td>0.8</td>
<td>3.2</td>
<td>95.2</td>
<td>3.3</td>
</tr>
<tr>
<td>45</td>
<td>1.0</td>
<td>0.5</td>
<td>2.5</td>
<td>96.0</td>
<td>2.6</td>
</tr>
<tr>
<td>60</td>
<td>1.5</td>
<td>0.6</td>
<td>1.9</td>
<td>96.0</td>
<td>1.9</td>
</tr>
</tbody>
</table>

As shown in Fig. 5, the iron rust layer is converted to interconnected iron particles, which confirms that the electrochemical reduction of iron rust is complete. Since the activity of iron increases with decreasing the size of iron particle, the electrolytically metalized layer should be post-treated to form a perfect corrosion-resistant layer. In light of the improved chemical activity of the electro-metalized iron, this metalized layer could be used as a functional layer, such as the gas diffusion electrode [37, 38]. In addition, the iron rust has a rough surface with bract-shape particles of particle size ranging from 1 to 5 μm (Fig. 5a). After electrolysis, bract-shape particles turn to nodule-like particles which are the same as the electrolytic Fe obtained from the electrolysis of solid Fe₂O₃ [28].
Fig. 5. SEM images of the rusty iron (a) and the rusty iron after being electrolyzed under a constant cell voltage of 2.3 V for (b) 5, (c) 15, (d) 30, (e) 45, and (f) 60 min.

In general, the corrosion rate is different at different locations, resulting in the different depths of corrosion in different areas. Thus, the electrochemical approach is an effective way to heal the pitting point due to the electrolyte can reach the pitting area and the applied electric field can drive the oxide ions out from the deep pitting hole. As shown in Fig. 5b-e, the rough surfaces of the electrolytic iron rod are due to the different corrosion rates in different areas. From the cross-sectional SEM image (Fig. 6a), the thickness of the rust layer is ~100 µm. After electrolysis, the
oxide layer becomes porous owing to the deoxidation of the oxide layer (Fig. 6b). The thickness of the electrochemically metalized layer is almost the same as the original rust layer.

![Cross-sectional SEM images of (a) the rusty iron and (b) the rusty iron after being electrolyzed under a constant cell voltage of 2.3 V for 30 min.](image)

**Fig. 6.** Cross-sectional SEM images of (a) the rusty iron and (b) the rusty iron after being electrolyzed under a constant cell voltage of 2.3 V for 30 min.

The electrochemically metalized part is helpful for machining, heat treatment, electroplating, and coating an artificial corrosion-resistant layer. On the other hand, the reduction of the rust layer is a potential way to produce three-dimensional porous structures for other applications. Moreover, the metalization reaction takes place at the joint of metal electrode/oxide/electrolyte. Thus, the electrochemical metalization could be applied for machining the insulative oxide layer by the selective electrochemical reduction approach in molten salts.

In addition to the metalization of rusty iron rod, the rusty screw is electrochemically derusted in molten Na$_2$CO$_3$-K$_2$CO$_3$ (Fig. 7). It is obvious that the screw has a rough surface and depths of the thread (Fig. 7a) and slot (Fig. 7b) are ~1 mm and ~3 mm, respectively. After electrolysis, the rust on the screw disappears and, instead, the metallic luster appears, meaning that the rust layer formed on the surface of the screw is reduced back to metal (Fig. 7c-d). Note that the rust in the
slot is fully converted to metals, indicating that the electrochemical metalization is not limited by its shape. Hence, the electrochemical process is able to derust the rusty object with different shapes and structures where the electrolyte can reach. Although the electrochemical process is efficient, the repaired iron has a porous surface and could be reoxidized. For the object with irregular shape and roughness, the distribution of current at the electrode should be considered. Thus, the electrochemical derusting approach can be combined with some surface technologies to prevent further corrosion.

![Digital pictures of the rusty screws](image)

**Fig. 7.** Digital pictures of the rusty screws before (a, b) and after electrolysis (c, d) under a constant cell voltage of 2.3 V for 30 min in molten Na$_2$CO$_3$-K$_2$CO$_3$ at 750°C.

4. **Conclusions**

This paper demonstrates an electrochemical derusting route in molten Na$_2$CO$_3$-K$_2$CO$_3$. The iron rust primarily consisting of iron oxide can be electrochemically reduced to iron through a two-
step process. Under a constant cell voltage of 2.3 V, the rust can be electrochemically metalized in 5 min. The derusting process is applicable to the rusty objects of various shapes and structures. Moreover, the electrochemical derusting reaction can be tailored by adjusting the applied cell voltage and electrolyte. Note that the electrochemically metalized iron is porous that a post-treatment is needed to avoid being corroded again. This method could be an alternative way to repair specific metal objects to recover their original appearance rather than damaging the rust layer. Overall, the electrochemical metalization approach is a promising way to repair various rusty metals/alloys and cultural relics.

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References


