Corrosion of Ferrous Alloys by Organic Compounds in Simulated Bio-Oils

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ABSTRACT

Bio-oils derived from biomass contain organic species and acids that can be corrosive to steel-based structural materials used for pipelines and storage tanks. It is, therefore, important to assess corrosivity of organic constituents in bio-oils and identify ferrous alloys with sufficient corrosion resistance. In this work, lactobionic acid, formic acid and catechol were selected as corrosive constituents in bio-oils and used to formulate simulated bio-oils 4 ferrous alloys, including 2.25Cr-1Mo steel and type 410, 201 and 316L stainless steels, were tested by Electrochemical Impedance Spectroscopy (EIS) and potentiodynamic polarization. The corrosivity of each simulated bio-oils was assessed using R_2, a charge transfer limiting resistance fitted from EIS spectra. While 2.25Cr-1Mo steel exhibited active corrosion with low R_2 values, the stainless steels showed high R_2 values associated with passive state. The values of R_2, considered proportional to the protectiveness of the passive film, appeared lower in lactobionic acid than in the other simulated bio-oils for the stainless steels, suggesting that lactobionic acid could be more aggressive to passive film than the other constituents of bio-oils. The overall goal of this work is to systematically study the impact of selected bio-oil constituents on corrosion of candidate structural materials for bio-oil production, transport, and storage, as well as provide feedback for potential optimization of bio-oil chemistries to reduce the risk of corrosion.

Key words: Bio-oil corrosion, biomass, structural material, stainless steel, EIS

INTRODUCTION

Biomass-derived oils have gained considerable interest as a renewable energy source to decrease the use of fossil fuels. These bio-oils commonly contain water and organic acids which could cause corrosion of steel-based structural materials.[1-4] In a previous study, formic acid in raw bio-oils was reported to corrode low alloy steels and produce iron formate as a corrosion product.[5-7] Another lab study compared the corrosion of a plain steel and stainless steels in condensed formic and acetic acids at 60°C and showed that stainless steels were not attacked by the condensate.[8] This result suggests that stainless steels could provide sufficient corrosion resistance in bio-oils. However, it is also reported that raw bio-oils at 50°C caused corrosion mass loss in type 409 stainless steel, but not in 304L and 316L austenitic stainless steels, indicating that not all stainless steels are immune to corrosion in bio-oils.[7]

While the selection of adequate stainless steels is one way to mitigate corrosion risk in bio-oils, the removal of corrosive species from bio-oils is another way to achieve this goal. A recent chemical characterization has identified 16 organic constituents commonly contained in commercial bio-oils, and

the corrosivity of each constituent on type 410 stainless steel was assessed by electrochemical impedance spectroscopy (EIS).[9] The result of this work indicated that three constituents, lactobionic acid, formic acid and catechol, could be more detrimental to a passive film than the others.[9] In this work, EIS and potentiodynamic technique was used to assess the corrosion resistance of two austenitic stainless steels and a low alloy steel in comparison to type 410 in solutions containing lactobionic acid, formic acid and catechol. The goal of this work is to evaluate the corrosivity of selected constituents for the candidate structurally alloys, which would provide guidelines to remove/decrease corrosive constituent(s) from bio-oils and/or select proper structural alloys for corrosion resistance.

EXPERIMENTAL METHODS

The ferrous alloys studied were type 410, 201 and 316L stainless steels in sheet form, and 2.25Cr-1Mo steel in round bar form. The alloy compositions measured by inductively coupled plasma optical emission spectroscopy and combustion techniques are summarized in Table 1. The microstructures of the ferrous alloys were characterized with and without etching to identify any feature(s) possibly leading to corrosion susceptibility. The solution for etching was a mixture of 33% glycerol, 17% HNO_3 and 50% HCl in volume ratio, and all chemicals used were reagent grade. The etching was conducted for less than 30 s at room temperature. For electrochemical measurements, a teflon holder with rubber ring sealing was used to expose 0.97 cm^2 of alloy surface (i.e. working electrode) in the horizontal direction, and Ni-mesh and mercury surface electrode (MSE) were used for counter and reference electrodes, respectively. Simulated bio-oils to test the corrosivity of target organic constituents were composed of base solvent and 0.1 molal solute. The base solvent contained 85 wt% deionized (DI) water and 15 wt% methanol, and the solute was either lactobionic acid, formic acid or catechol. Simulated bio-oil with two constituents, containing both 0.1 molal formic acid and 0.1 molal catechol, were also used. In addition to the simulated bio-oils, the alloys were tested in 0.1 M NaCl to obtain the reference data of corrosion behaviors in the ferrous alloys. The frequency range and amplitude used for EIS measurements were 1 MHz to 1 mHz and ±5 mV, but in some measurements, a frequency range of 100 kHz to 10 mHz was used instead because the frequencies higher than 100 kHz rather depends mostly on solution alone and did not yield impedance data associated with electrochemical reaction at the alloy surface. Prior to EIS measurements, open circuit potential (OCP) was measured for 1 h or less than 5 min. EIS was repeated up to 12 times with and without ~1 h OCP delay between the measurements. The variations in initial and intermediate OCP delays, however, did not cause any significant effect on the EIS spectra of the same alloy immersed for a similar duration. For the fitting of EIS spectra, a commercial computer software was used. In some measurements, anodic scanning was conducted after EIS measurement and OCP delay. The scanning was initiated at OCP and finished at the potential that achieved 0.3 $mA \cdot cm^{-2}$ or 800 mV_{MSE} above OCP with the scan rate of 0.167 $mV \cdot s^{-1}$.

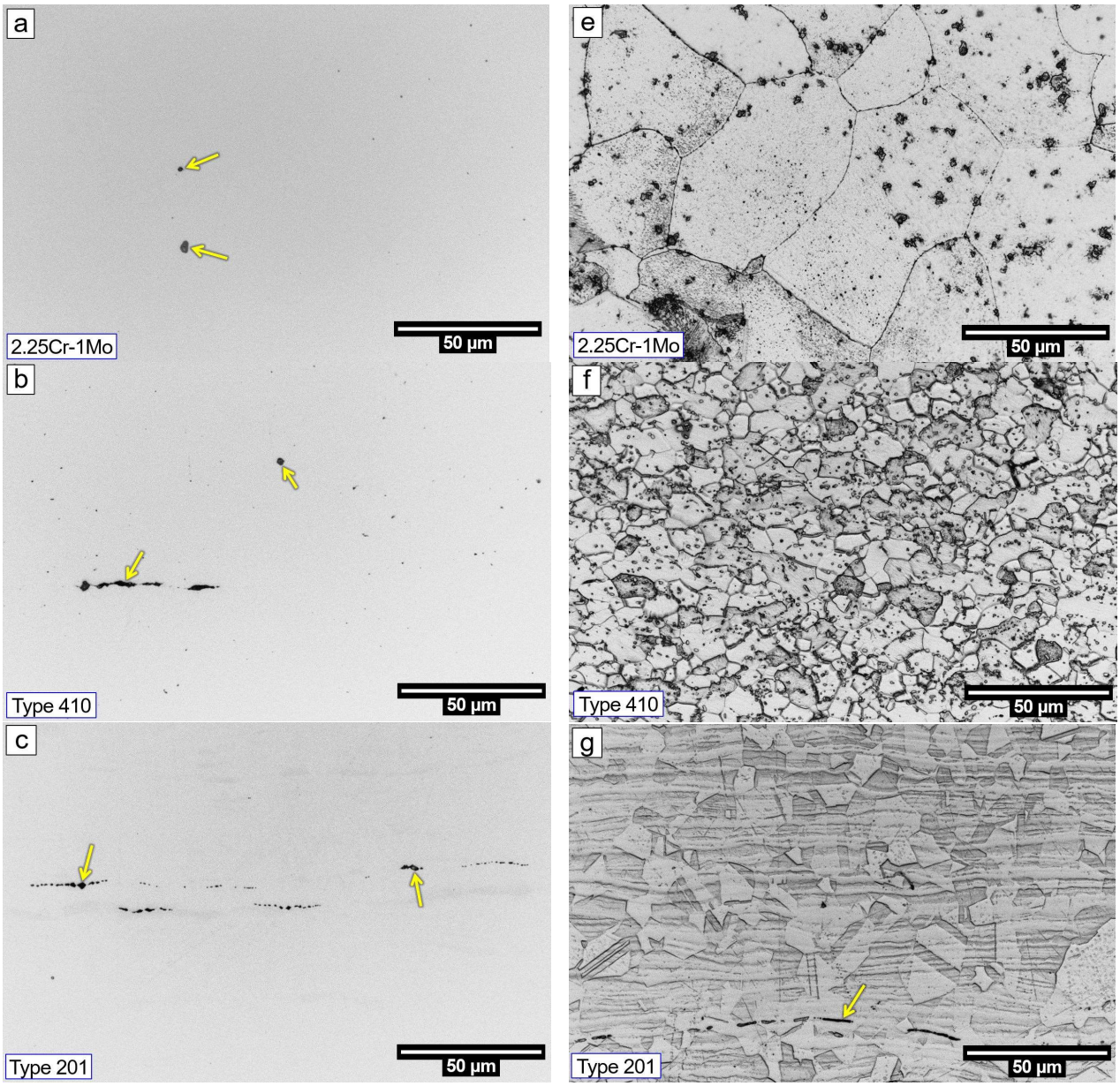
Table 1. Elemental composition of 4 ferrous alloys in mass percent, N, O and S contents are in ppm.

Ferrous alloy	UNS No.	Fe	Cr	Ni	Mn	Mo	Cu	Si	C	N	O	S	Other
2.25Cr-1Mo	K21590	95.69	2.22	0.14	0.51	1.01	0.09	0.17	0.092	45	9	50	0.01Co
Type 410	S41000	86.64	11.86	0.23	0.47	0.05	0.16	0.3	0.132	121	26	<10	0.06V, 0.02Co
Type 201	S20103	69.97	16.45	4.14	7.18	0.28	0.91	0.46	0.097	701	18	10	0.11V, 0.2Co
Type 316L	S31603	68.98	16.82	10.06	1.12	1.98	0.22	0.46	0.022	408	27	10	0.09V, 0.15Co

RESULTS

As-polished and etched cross-sections of the 4 ferrous alloys are shown in Fig. 1. On as-polished surfaces, 2.25Cr-1Mo showed rounded inclusions while the stainless steels had elongated inclusions

(Fig 1a-1d). In stainless steels, the breakdown of a passive film may be enhanced with increasing size of inclusions,[10,11] so the presence of any enlarged inclusion should be inspected. The sizes of elongated inclusions were not noticeably different in type 410, 201 and 316L, suggesting that there would be no differential size effect promoting passive film breakdown. The composition of inclusions, which has a more significant effect on passivity breakdown, is a matter of ongoing research and will not be discussed in this work. The grain size revealed by etching was significantly larger in 2.25Cr-1Mo steel than in the stainless steels (Fig 1e-1h). The microstructure of type 410 exhibited ferritic grains with particle-like second phases distributed uniformly. Both type 201 and 316L showed austenitic microstructures but a series of stripe-pattern was observed in type 201 only. This pattern is likely an indication of mechanical working during cold rolling. The preliminary observation of microstructures did not identify any unusual feature(s) that would render the alloy test samples more susceptible to corrosion.



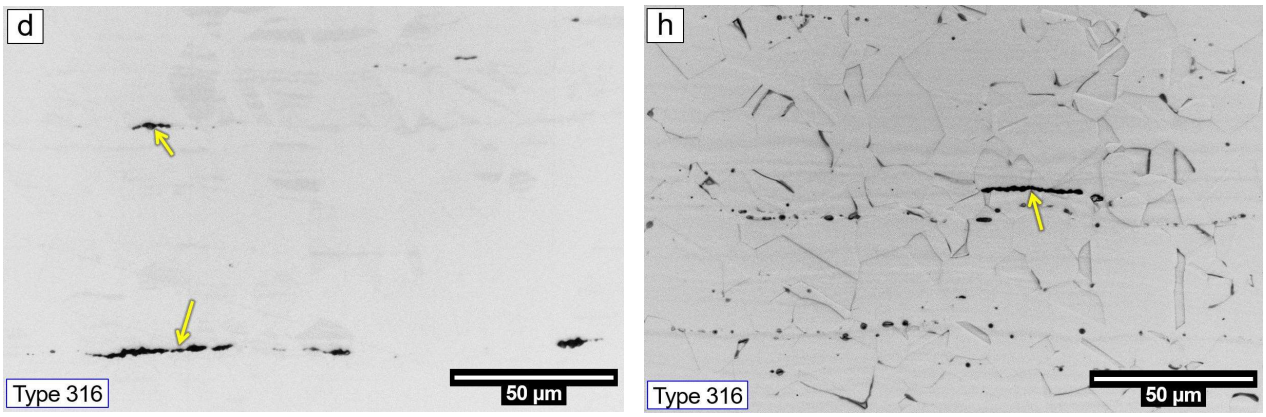


Figure 1. Cross-sectioned light microscopy images of 2.25Cr-1Mo, type 410, type 201 and type 316L with as-polished (a-d) and etched (e-h) conditions. Some Inclusions with few microns or larger in size are marked with arrows in the figures.

The impedance spectra of type 201 in 0.1 molal lactobionic acid and in 0.1 M NaCl are compared in Fig. 2a. The impedance values at 0.01 Hz were higher than 100 kohm or 97 kohm·cm^2 in both solutions. The current transients during subsequent anodic scanning are shown in Fig. 2b. In 0.1 M NaCl, spontaneous passive behavior followed by passivity breakdown (i.e. characterized by a sharp increase in current) was observed, which is typical for stainless steels in the NaCl concentration used in this work. In 0.1 molal lactobionic acid, the currents, measured from OCP to 0.1 V_{MSE}, were comparable to the passive current of type 201 in 0.1 M NaCl, suggesting that type 201 was in the passive state in lactobionic acid. Based on these results, the impedance values surpassing ~100 kohm are considered an indication of a passive state.

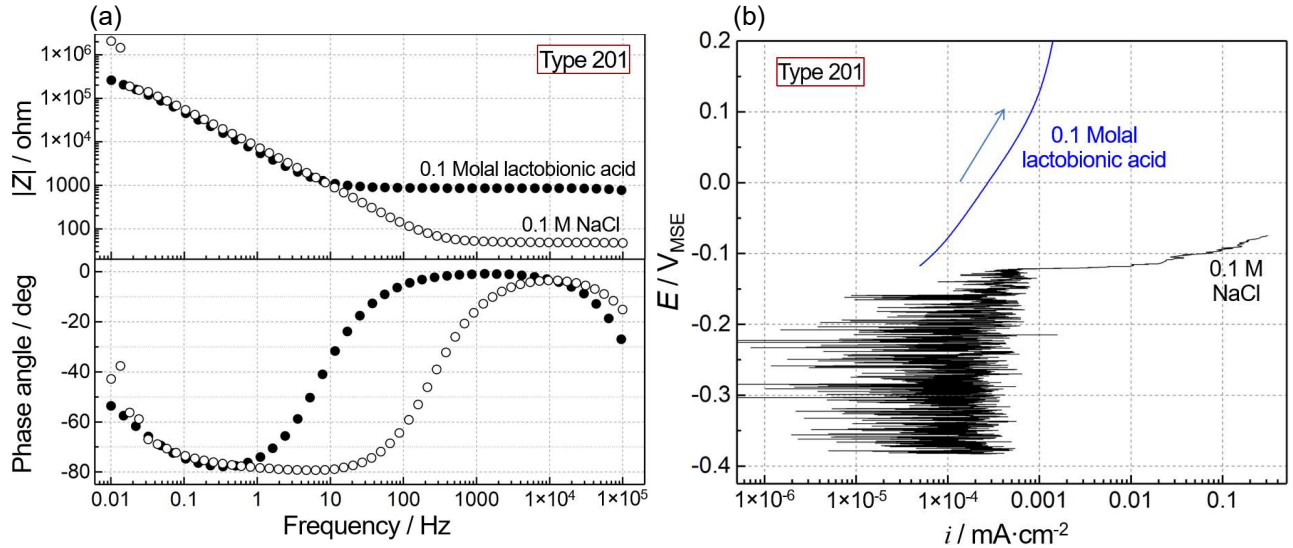


Figure 2. Results of (a) impedance spectra in bode plot and (b) current transients during anodic scan measured for type 201 in 0.1 molal lactobionic acid (in 85 wt% water and 15 wt% methanol solvent) and 0.1 M NaCl. The solution immersion time before the measurement of impedance spectra was ~24 h in lactobionic acid and ~1 h in 0.1 M NaCl. Anodic scans in (b) were conducted after the measurement of impedance spectra in (a). The source of the excess noise in the passive region data of type 201 is presumably associated with the sensitivity of reference electrode.

The impedance spectra of 2.25Cr-1Mo steel in 0.1 molal lactobionic acid and 0.1 M NaCl are presented in Fig 3a. The impedance value at 0.01 Hz was less than 2 kohm or 1.94 kohm·cm^2 in both solutions, which are significantly smaller than the impedance of type 201 at the same frequency (see Fig. 2a). In subsequent anodic scanning shown in Fig. 3b, the currents increased sharply with potential in both solutions, which is typical of actively corroding metals and alloys. These results indicate that 2.25Cr-1Mo steel experienced active corrosion, which resulted in much lower impedance values than that of type 201 during EIS measurement.

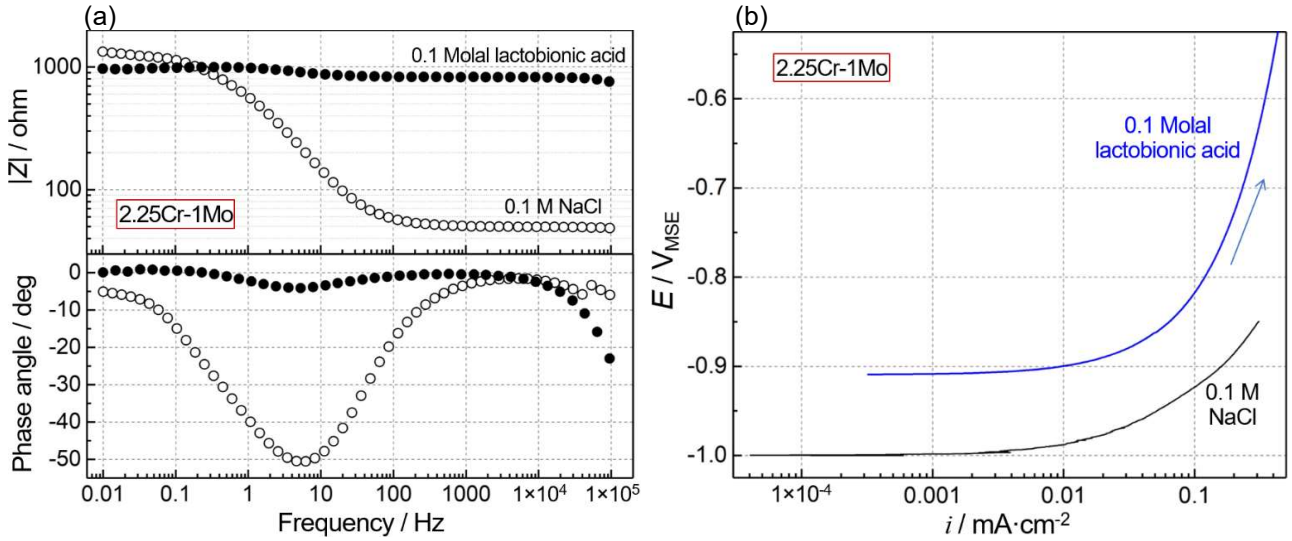


Figure 3. Results of (a) impedance spectra in bode plot and (b) current transients during anodic scan measured from 2.25Cr-1Mo steel in 0.1 molal lactobionic acid (in 85 wt% water and 15 wt% methanol solvent) and 0.1 M NaCl. The solution immersion time before the measurement of impedance spectra was ~1 h in both lactobionic acid and 0.1 M NaCl.

The impedance spectra of the 4 steels were fitted using the equivalent circuit model presented in Fig 4. This model contains R_1 corresponding to solution resistance and the parallel connection of R_2 and constant phase element (CPE) where R_2 and CPE account for the resistance limiting charge transfer process and non-ideal capacitive behavior at the solution-electrode interface, respectively. The fitted R_2 values measured in lactobionic acid, formic acid and catechol are presented in Fig. 5. The fitted R_2 values with shorter immersion time (< 15 h) were not significantly different from R_2 values with longer immersion time (> 15 h) in most cases, but the R_2 of type 410 and 201 in formic acid increased after 15 h. In all simulated bio-oils, the R_2 values of stainless steels were higher than 50 kohm·cm^2, indicating the stainless steels were in a passive state (no significant corrosion expected). The R_2 values of 2.25Cr-1Mo steel, on the other hand, were at least 2-3 orders of magnitude lower than the R_2 of stainless steels, suggesting active corrosion of this steel in the simulated bio-oils.

The average R_2 values of stainless steels are summarized in Table 2 for different simulated bio-oils including the mixture of catechol and formic acid. The R_2 data with shorter immersion time (< 15 h) was used for the average values to compare the initial resistances of the stainless steels in the simulated bio-oils. In most cases, the stainless steels exhibited an R_2 average higher than 200 kohm·cm^2, indicating that they are in the passive state and are highly resistant to uniform corrosion. Type 410 in lactobionic acid showed the lowest R_2 average although it is still much higher than the R_2 of non-passive 2.25Cr-1Mo steel. The variation of R_2, about 80 to 4000 kohm·cm^2, measured in the stainless steels could be associated with the stability of the passive film – the higher R_2 is, the more stable the passive film is.[12-14] Based on this idea, the stability of the passive film in each simulated bio-oil can be assessed using the

average R_2. In both type 201 and type 410, lactobionic acid resulted in the lowest R_2, suggesting that lactobionic acid may be more aggressive to passive film than the other bio-oil constituents. Such findings can help provide the basis both for materials selection and for recommended post-treatments of bio-oil chemistries. For example, according to this result for 201 and 410, it may be advisable that lactobionic acid be reduced, or if posible, removed from bio-oils for long-term storage. Further experimental work is in progress to assess R_2 of other ferrous alloys in the simulated bio-oils used in this work.

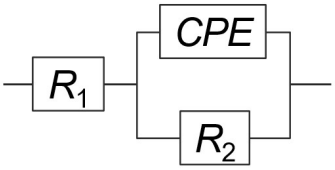


Figure. 4 Equivalent circuit model used to fit impedance spectra of 4 ferrous alloys.

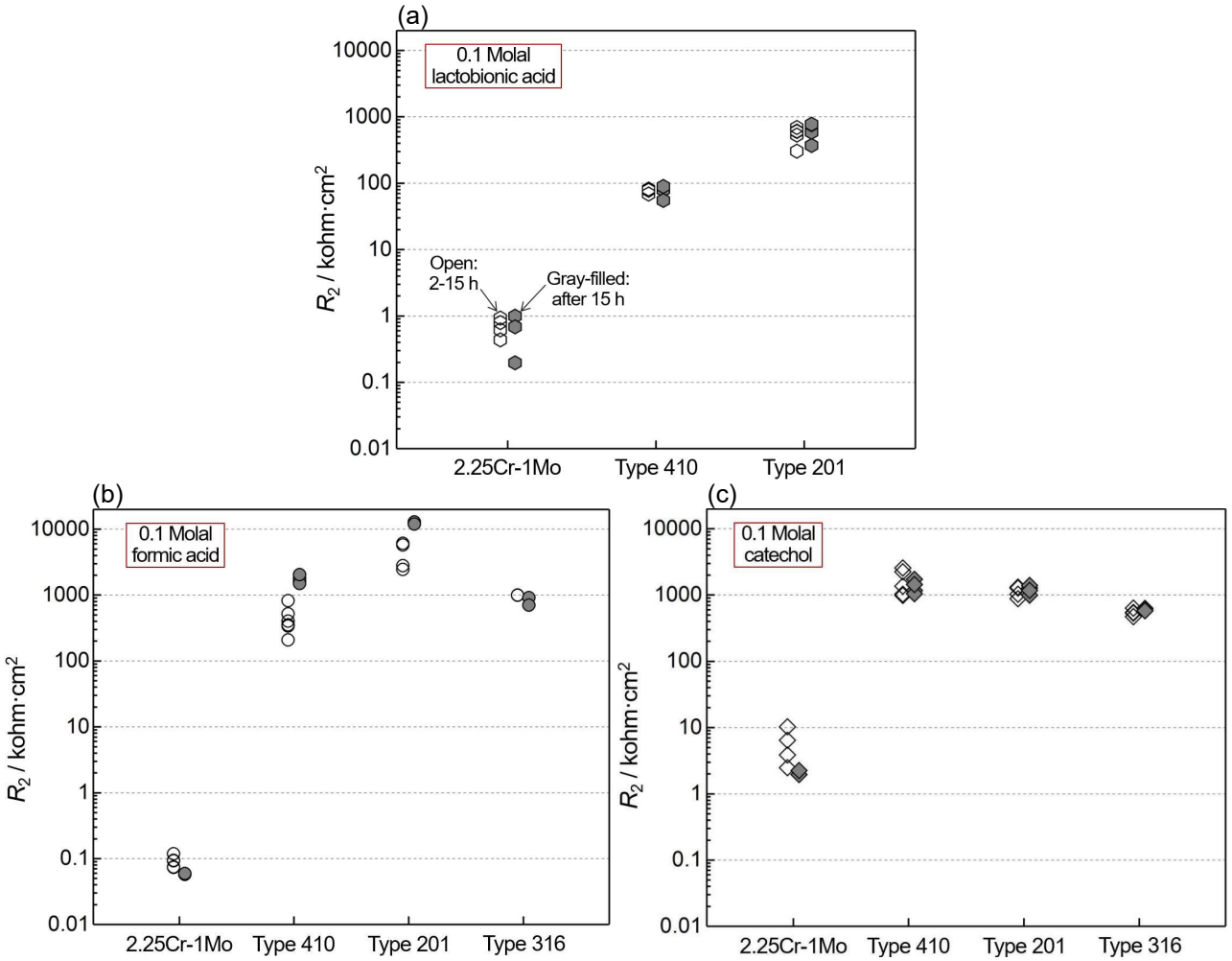


Figure 5. R_2 values from 3 ferrous alloys in (a) lactobionic acid, and 4 alloys in (b) formic acid and (c) catechol. The data is grouped in two variations of solution immersion time, 2-15 h (open symbols) and longer than 15 h (gray-filled symbols).

Table 2. The average R_2 of type 410, 201 and 316L stainless steels in different simulated bio-oils for the immersion time of 2-15 h. The standard deviations of R_2 are designated in the brackets.The R^2 values of type 316L in lactobionic acid and catechol + formic acid are being collected and will not be presented in this work.

	Average R_2 / kohm·cm^2		
	Type 410	Type 201	Type 316L
0.1 Molal lactobionic acid	76 (±6)	547 (±131)	-
0.1 Molal catechol	1637 (±647)	1126 (±179)	547 (±59)
0.1 Molal formic acid	441 (±194)	4268 (±1161)	996 (±3)
0.1 Molal catechol + 0.1 Molal formic acid	255 (±92)	2745 (±1347)	-

CONCLUSIONS

The corrosion resistance of 2.25Cr-1Mo steel and type 410, 201 and 316L stainless steels, in simulated bio-oils was assessed using R_2, the resistance limiting charge transfer, measured from EIS. In the simulated bio-oils containing lactobionic acid, formic acid, catechol and the mixture of formic acid and catechol, 2.25Cr-1Mo exhibited active corrosion with R_2 much lower than the stainless steels that are in the passive state. The variation in R_2 values of stainless steels in the bio-oil constituents, possibly associated with the stability of the passive film in each simulated bio-oil, suggested that lactobionic acid may be more aggressive to the passive film than the other simulated bio-oils.

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